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1 **Polar Aromatic Compounds (PAC) in Soot from Premixed Flames of Kerosene, Paraffinic**
2 **Synthetic Kerosene, and Kerosene-Synthetic Biofuels**

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8 **KEYWORDS:** Biofuels, Polar Aromatic Hydrocarbons (PAHs), nitro-PAHs, oxy-PAHs, kerosene, 1-
9 butanol, 2, dimethylfuran, methyloctanoate, diethylcarbonate.

10
11 **ABSTRACT**

12 Polar Aromatic Compounds (PAC) adsorbed on soot produced in laboratory premixed flames of
13 fossil kerosene (Jet A-1), Synthetic Paraffinic Kerosene (SPK), and Jet A-1 - synthetic biofuels
14 (2,5-dimethylfuran, methyloctanoate, diethylcarbonate and 1-butanol) were characterized for
15 the first time in the aim of shedding light on the combustion mechanisms and evaluating the
16 environmental impact of these synthetic biofuels.

17 The following families of compounds were fractionated from the soot extracts and further their
18 relative abundances estimated: (a) oxa-AHs (xanthenes, benzoxanthene, alcoxy-AHs, furan...);
19 (b) aldehydes-AHs, (c) ketones-AHs; (d) quinones-AHs; (e) aromatic monocarboxylic acids; (f)
20 aromatic hydroxy-acids; (g) aromatic dicarboxylic acids; (h) nitrated-AHs (including amines,
21 acridines, cinnoline derivatives, carbazoles...); (i) nitro-AHs.

22 The results obtained point out that overall, soot from Jet A-1 - biofuels premixed flames are
23 richer in PAC than soot from pure Jet A-1 and SPK. Out of the fuels studied, Jet A-1 - 1-butanol
24 produces the highest concentrations of nitro-AHs (namely nitro-benzaldehydes), of aldehydes-
25 AH and hydroxy-AHs (including two isomers of hydroxy-benzaldehyde); whereas Jet A-1 -
26 diethylcarbonate produces the highest concentrations of quinone-AHs (especially
27 phenanthrene-quinones) and large concentrations of nitrated-AHs. On the other hand, soot
28 from Jet A-1 - methyloctanoate is the richest one in mono aromatic and dicarboxylic acids,
29 aromatic hydroxyacids, nitrated-AHs, and esters. Combustion of the Jet A-1 - 2,5-dimethylfuran
30 mixture emits the highest concentrations of ketone-AHs, and oxa-AHs (namely, furan
31 derivatives).

32 We should remark that although the soot samples were obtained from pre-mixed flames, the
33 lab conditions being far from the industrial conditions, particularly in terms of pressure; the
34 chemistry going on should not be so different that our findings could not be extrapolated to
35 industrial conditions.

36 **1. INTRODUCTION**

37 Kerosene is an oil distillate commonly used as solvent and aviation fuel for commercial and
38 military air transportation. Jet fuel are produced by distillation of crude oil (205  C to 260  C)¹.
39 They are mainly composed of hydrocarbons (C₈ to C₁₆). The chemical components of jet fuel
40 are: alkanes, iso-alkanes, naphthenes, and aromatics². Jet A-1 is the most frequently used jet
41 fuel in aviation industry.

42 The IATA as reported that in 2016, over 3.8 billion passengers and 54.9 Mt of goods were
43 transported, which corresponds to ca. 35% of world trade by value. Also, it is forecasted a
44 doubling of the number of air passenger over the next 20 years³.

45 In this context, for ensuring a sustainable development of aviation industry, it is not enough
46 relying only on increasing fuels efficiency, but one needs to develop alternative renewable
47 fuels to meet the increasing fuel demand and reduce dependency on oil-derived fuel, and cut
48 off CO₂ emissions as demanded by International Civil Aviation Organization (ICAO). In fact, this
49 organization, adopted in 2016 a global carbon offsetting scheme for international aviation
50 which starts with a voluntary period (2021–2026) after which it will be mandatory, and it will
51 cover about 80% of carbon dioxide increase in 2021–2035⁴.

52 Whereas renewable energy sources contribute reducing the share of fossil fuels in the energy
53 sector, including ground transportation⁵, this is not currently applicable for aviation⁶.

54 Bio-fuels could be a desirable alternative to fossil fuels in aviation industry. These fuels exhibit
55 several important advantages:

- 56 1. Decreasing dependence on fossil fuel,
- 57 2. Reducing emissions over life cycles using carbon neutral biomass⁷.
- 58 3. Bio-derived jet fuels have low sulfur content and potentially lower emissions, better
59 cold flow properties and higher thermal stability, compared to oil-derived fuels⁸⁻¹⁰.
- 60 4. Using bio-derived jet fuels do not require modifications of engines and fuel quality is n
61 or an issue¹¹.

62 As regards the production of biofuels, there are three generations of bio-fuels:

- 63 1. First-generation biofuels. This generation is not popular because of competition
64 between human diet and fuel production from edible.¹²
- 65 2. Second-generation biofuels are synthesized using non-edible sources, e.g.,
66 lignocellulose from agricultural and forestry residues, municipal waste, halophytes,
67 short rotation woody crops. These kind of bio-fuels can also be produced from
68 camelina, jatropha, used cooking oils, wastes from industry, e.g. tall oil from paper
69 making, oil sediments or acid oils from edible oil refineries.^{6, 13-16}
- 70 3. Third-generation biofuels derive from algae feedstock which contains relatively high oil
71 concentrations. This route to biofuels is considered promising and a potential solution
72 for carbon dioxide sequestration.⁶

73 It is forecasted that the total consumption of jet fuels will grow to 22.88 EJ in 2040.¹⁷
74 Meanwhile, the total available residue biomass energy (lignocellulosic biomass and sugar
75 feedstock) was 42.54 EJ/yr and 6.17 EJ/ yr for 2005, respectively.¹⁸ It is estimated that total
76 production of bio-jet fuels could represent 21.46 EJ, i.e., nearly 94% total jet fuel use in 2040,
77 reducing by ca. 1.5 billion tons GHC emissions.¹⁷

78 On the other hand, although a lot of current research efforts in the combustion field focus on
79 the development of new biofuels¹⁹⁻²¹; reports on their combustion mechanisms, their
80 combustion byproducts and their environmental impact are still scarce.

81 By-products of fuels and biofuels combustion, such as aromatic compounds [AHs (Aromatic
82 Hydrocarbons) and PAC (made up of AHs containing oxygen and/or nitrogen heteroatoms)] are
83 known to be soot precursors²²⁻²³ and account for most of toxic potential and atmospheric
84 reactivity of soot.²⁴⁻²⁵ In spite of the importance of these compounds, data on their analytical
85 profile and concentration in fossil fuels and bio-fuels soot are scarce in literature. Moreover, it
86 lacks efficient, reliable and simple analytical methodologies for determining these highly toxic
87 compounds in soot samples.^{26,27}

88 All these reasons make mandatory developing reliable analytical methodology allowing the
89 precise and accurate determination of AHs and PAC in the mentioned matrices, in the aim of

90 obtaining an as complete as possible inventory of these compounds in soot from different
91 origins (fuels and fossil fuels-biofuels blends) as possible.

92 The aforementioned points were the reasons why our research group undertook the
93 investigation on AHs and PAC in soot samples from Jet A-1, SPK and Jet A-1 - biofuels. This
94 paper continues the research initiated several years ago with the characterization of AHs in
95 soot samples²⁸ and focuses on the identification and estimation of PAC relative abundances in
96 soot from Jet A-1, SPK, and Jet A-1 - biofuels. As PAC, especially oxy-PAHs, are hazardous for
97 human and environment,²⁹ the main goal of this work is evaluating the abundance of these
98 compounds in biofuels soot samples. Moreover, in the aim of evaluation the impact of biofuels
99 from the health and environment point of view as well as the convenience of replacing fossil
100 fuels by biofuels, the PAC concentration in biofuel soot samples were compared with the PAC
101 concentration in soot samples from fossil fuels.

102 The analytical methodology was introduced in previous papers²⁷⁻²⁸ and will be described in the
103 experimental section.

104 More than 130 compounds belonging to the following chemical classes were identified and
105 their relative abundances estimated: a) oxa-AHs (xanthenes, benzoxanthene, alcoxy-AHs,
106 furan...); b) hydroxy-AHs; c) aldehydes-AHs; d) ketones-AHs; e) quinones-AHs; f) aromatic
107 monocarboxylic acids, aromatic hydroxy-acids, aromatic dicarboxylic acids; g) nitrated-AHs
108 (including amines, acridines, cinnoline derivatives, carbazoles...); h) nitro-AHs. To our best
109 acknowledge, this is the first attempt to accomplish so detailed characterization of PAC
110 adsorbed on soot from fossil fuels and from fossil fuels-biofuels blends.

111 **2. EXPERIMENTAL**

112 **2.1. Material and reagents**

113 n-Hexane, water, 2-propanol, and acetonitrile of HPLC grade (Sigma-Aldrich) and glacial acetic
114 acid (Carlo Erba) were used for the analyses. Previous to fractionation, soot samples were
115 filtered through hydrophobic PTFE membranes (0.2 μm , fromAlltech) by using 5 mL glass
116 syringes from Poulten & Graf. A 25 cm x 2.1 mm ID, 5 μm silica column (Supelco) was chosen
117 for fractioning the soot extracts. On the other hand, soot samples were weighing by using an
118 analytical balance Sartorius CP1245.

119 The Jet A-1 - synthetic biofuel mixtures were obtained by blending Jet A-1 with each synthetic
120 biofuel (80 / 20% v / v). The synthetic biofuels used in this work were: (a) 2,5 dimethylfuran
121 ($\text{CH}_3)_2\text{C}_4\text{H}_2\text{O}$ noted 2,5-DMF; (b) methyloctanoate ($\text{CH}_3(\text{CH}_2)_6\text{COOCH}_3$); (c) anhydrous diethyl
122 carbonate ($\text{C}_2\text{H}_5\text{O}$)₂CO noted DEC, and (d) 1-butanol ($\text{CH}_3(\text{CH}_2)_3\text{OH}$), with stated purity $\geq 99\%$.

123 In the experiments, we used a SPK (from Sasol) which has a density of 760.6 g/L at 15 °C, and a
124 derived cetane number (DCN, ASTM D7668) of 23. The Jet A-1 fuel used here has a density of
125 805 g/L at 15 °C and a DCN of 44.7. The chemical composition of the SPK was $\approx 79.9\%$ iso-
126 alkanes, 19.6% n-alkanes, and 0.5% aromatics in mass. The chemical composition of the Jet A-1
127 was 26.3% iso-alkanes, 12.2% n-alkanes, 24.3% of naphthenics, and 33.2% aromatics in mass.

128 **2.2. Soot samples production**

129 We used an in-house flat-flame burner for producing soot samples from the combustion of Jet
130 A-1, SPK, and Jet A-1 - biofuels mixtures under well-characterized and controlled conditions.
131 The apparatus is described in a previous paper.³⁰ Experiments were performed following a
132 procedure documented earlier.³¹⁻³² Soot samples were produced under fuel-rich conditions,
133 equivalence ratio ≈ 2.3 . Soot was collected on the outer surface of a glass tube at 40 mm
134 above the burner surface. Flames were isolated using a cross-shape cylindrical glass tube
135 which prevents flame perturbations from external air streams.³³ The collection tube was

136 introduced perpendicular to the vertical axis of the flame, rotated and moved through the
137 flame. The sampling glass rod was maintained at 318 K by water circulation which limits
138 temperature gradients and allows homogeneous distribution of aromatic products along the
139 sample tube.^{34,35} Soot deposits were weighed after mechanical removal from the glass tube.
140 After dilution in 2 mL of n-hexane, they were stored for future analyses. The thickness of soot
141 deposits was measured using an optical microscope (Reichert meF2)^{32,35} which was
142 alternatively focused on the outer glass surface and soot surface. Homogeneous soot coverage
143 (within 10%) was observed. Soot thickness ranged from 50 to 300 μm , depending on the
144 duration of soot collection.

145 **2.3. Extraction procedure**

146 Although some authors stated that aromatic compounds are strongly attached to soot
147 particles³⁶⁻³⁹ which would require efficient extraction procedures,⁴⁰ other authors claim that
148 these compounds are quite easily extracted because most of them are adsorbed or close to
149 the soot surface.⁴¹ In addition, we found out procedures such as ultrasound-assisted extraction
150 destroy up to 25% of some AHs and PAC even though cold water bath and very short
151 sonication cycles were applied. Consequently, the extraction procedure was abridged; two
152 filtrations through PTFE filters were enough for removing the soot particles and to extract
153 aromatics.^{27,28}

154 **2.4. Cleaning-up and fractioning procedure**

155 Special attention should be paid to the fact that there is no selective extractive methodology in
156 analytical chemistry. That is, under the proper conditions even the most non-polar solvents
157 such as n-hexane can extract polar-AHs. Thus, Viana et al. (2003)⁴² demonstrated that
158 extraction by supercritical CO_2 and Soxhlet extraction with n-hexane or dichloromethane
159 (CH_2Cl_2) were comparably effective in the case of lapachol (a very polar aromatic compound: a
160 hydroxy-quinone) from *Tabebuia avellanedae* wood. Therefore, fractioning procedures are
161 mandatory after extraction in order to isolate the target fractions.

162 The highly complex extracts from Jet A-1, SPK and Jet A-1 - biofuels soot samples were
163 fractionated following a methodology previously published.²⁷ Briefly, the fractionation of the
164 soot extract was achieved by injection of small volumes (about 30 μL) of each soot extract into
165 the column and passing n-hexane as mobile phase against gravity at a flow rate of 0.05 ml/min
166 through a 25 cm length, 2.1 mm ID and 5 μm size particle silica column by using an HPLC pump.
167 Finally, a fraction collector (Shimadzu FRC-10A) was used to collect the content of
168 chromatographic peaks. Unlike conventional methodologies^{40,43} our extraction procedure
169 allowed the efficient fractionation of all the PAC families by using reduced volumes of nontoxic
170 solvents (3.5 ml of n-hexane for elution of the target analytes and about 5 mL of 2-propanol
171 for cleaning the column) and a isocratic programming scheme much simpler than traditional
172 programs using gradient flows of up to 3 solvents at flow rates as high as 4.5 ml/min.⁴⁰

173 **2.5. Pretreatment of the collected fractions**

174 Pretreatment of the collected fractions were optimized for each fuel mixture. Indeed, the
175 combustion of Jet A-1 - Me-octanoate yielded esters-rich soot (see the Results section). As
176 esters co-elute with some other polar aromatic fractions from the silica column during the
177 solid phase extraction, the collected fractions must be pretreated by addition of some μL of
178 glacial acetic acid before HPLC analyses. Under acidic conditions, esters are hydrolyzed and
179 converted into acids and alcohols, which easily elute from the C_{18} column.

180 For Jet A-1 - 2,5-DMF soot samples, the collected fractions were pretreated with sodium
181 hydroxide before being injected into the HPLC column. In this case, large amounts of aromatic
182 hydroxy-acids are present in the soot samples and they co-elute with other PAC fractions from

183 the silica column. Consequently, adding a base (e.g., NaOH) is mandatory to ionize these
184 compounds and elute them in an efficient way from the C₁₈ column. A similar procedure was
185 applied to the SPK samples. Some fractions of soot from Jet A-1 - 2,5-DMF were pretreated
186 with glacial acetic acid due to the presence of some esters also in this sample (see results
187 section). Solid phase extraction fractions from Jet A-1, Jet A-1 - DEC, and Jet A-1 - 1-butanol
188 fractioning did not need pretreatment.

189 **2.6. Chromatography analyses and UV-Visible Identification**

190 A HPLC system consisting of: a binary, high pressure gradient, solvent delivery unit LC-20AB
191 Prominence, a system controller CBM-20A/20 Alite Prominence, a column oven CTO-20A/20AC
192 Prominence, a UV/Visible photodiode array detector SPD-M20A Prominence, and an
193 autosampler SIL-20A/20AC Prominence, (all from Shimadzu) was used. A 201TPC18, 5 μm, 250
194 mm length x 4.6 mm ID Vydac column (Grace Davison Discovery Sciences) was used for the
195 analysis. Acetonitrile and water were used as mobile phase; the flow rate was set up at 0.5 or 1
196 mL min⁻¹ (0.5 mL min⁻¹ for the fractions of nonpolar compounds and 1.0 mL min⁻¹ for the
197 fraction containing polar compounds). The development of the analytical method was
198 described in details in a previous paper.²⁷

199 Fractions eluted from the solid-phase extraction column were injected into the HPLC system in
200 the aim of achieving the unambiguous characterization of the PAHs derivatives. Fractions were
201 re-solved into 2-propanol before injected into the HPLC column. Because of the UV absorbance
202 spectrum of a given PAC is unique to a particular aromatic structure, the target analytes can be
203 identified definitively by matching the compound's UV absorbance spectrum with that of the
204 appropriate UV-VIS spectrum available in standard reference databases. Positive identification
205 of compounds included in this article was confirmed when the UV-visible spectra of standards
206 and unknowns were identical. Tentative identification was done when UV-Visible spectra of
207 standards and unknowns were similar. Retention times and the fraction where the target
208 analyte is collected, also help to identify the compound. For instance, compounds correlating
209 closely with the retention times of very polar AHs are discarded as oxa-PAHs and compounds
210 collected in the same fraction as aromatic carboxylic acid fraction, are discarded as aldehydes-
211 AHs or ketones-AHs. Enhanced resolution was often achieved by using 1ml/min flow rates.

212 Identification was made by using the spectra from the following books:⁴⁴⁻⁵⁹. Some UV spectra
213 of the identified compounds are included in this paper. Figures are included in the Results
214 section.

215 Figure 1 outlines the analytical procedure detailed in previous paragraphs.

216 **2.7 Liquid State NMR (Nuclear Magnetic Resonance) Spectroscopy**

217 Characterization of fuels samples was carried out in the aim of relating the fuels composition
218 with the byproducts of combustion. NMR analysis of Jet A-1 and SPK were thoroughly detailed
219 in a previous paper.^{27-28,31}

220 **2.8 Validation of the methodology**

221 Because suitable reference material is not available, recovery essays have been accomplished
222 by spiking real soot samples from Jet A-1 - 2,5-DMF mixture with standard mixtures of 19 PAHs
223 (16 EPA PAHs, 1- and 2-methylnaphthalene, and coronene) at concentrations comparable to
224 those found in these soot samples in a previous study.²⁸ Recoveries of most of PAHs studied
225 were within the range 95-102% for almost all the compounds except for naphthalene whose
226 recovery was only 75%, and 1- and 2-methylnaphthalene whose recoveries were about 83%.
227 High recoveries along with small standard deviations (within the range 3-7%, n=3) make the
228 methodology presented here appropriate for quantifying AHs and PAC in soot samples.
229 Standard deviations of PAC are a bit higher than those of AHs, within the range 4-15%.

230 3. RESULTS

231 3.1. Identification and estimation of relative abundances of PAC on soot

232 PAC accounts for most of the toxic potential and atmospheric reactivity of soot.^{25,26} A detailed
233 list of the polar compounds identified is given in Tables 1-8. The PAC families determined
234 were: a) oxa-AHs (xanthenes, benzoxanthene, methoxy-AHs, furan, ethers...), b) hydroxy-AHs;
235 c) aldehydes-AHs; d) ketones-AH; e) quinones-AHs; f) aromatic monocarboxylic acids/ aromatic
236 hydroxy-acids/ aromatic dicarboxylic diacids; g) nitrated-AHs (including amines, acridines,
237 cinnoline derivatives, carbazoles...); h) nitro-AHs. In this paper no quantitative data are
238 presented (except for the nitro-AHs group) due to the high cost and/or the unavailability of
239 most of standards. Instead, relative abundances of PAC (i.e., normalized concentrations) were
240 estimated for each compound identified in the analyzed soot samples.

241 Analytical profile of soot from Jet A-1 - Me-octanoate previously published²⁷ was completed
242 here with the identification of new compounds. The goal of our former study was only to
243 develop the analytical methodology and validate it with complex real samples.

244 3.1.1. Oxa-AHs (Ethers/xanthenes/benzoxanthenes...)

245 The present measurements show that oxa-AHs richest soot samples are those from Jet A-1 -
246 2,5-DMF and Jet A-1 - DEC closely followed by those from Jet A-1, Jet A-1 - Me-octanoate and
247 Jet A-1 - 1-butanol which contain similar relative abundances of oxa-AHs; whereas soot
248 samples from SPK contain the lowest concentration of Oxa-AHs (Figure 2, Table 1).

249 22 oxa-AHs in total were identified in the analyzed soot samples. However, the profiles of
250 relative abundances are quite different from each other. As we can see from Table 1, soot
251 from Jet A-1 is rich in 9H-xanthene, alkyl-xanthene, benzo[]xanthene and 2'-methoxy-1-
252 phenylnaphthalene. Conversely, soot from SPK is rich in methoxy-biphenyl isomers and 2'-
253 methoxy-1-phenylnaphthalene, soot from Jet A-1 - Me-octanoate is rich in methylchromone
254 and 9H-xanthene, and soot from Jet A-1 - 2,5-DMF in derivatives of furan. Finally, soot from Jet
255 A-1 - DEC is rich in coumarins and chromones as well as soot from Jet A-1 - 1-butanol, although
256 their profiles are different from each other. On the other hand, whereas soot from Jet A-1 -
257 DEC contains one isomer of benzo[]xanthene, this compound is absent from Jet A-1 - 1-butanol
258 soot (Table 1).

259 3.1.2. Hydroxy-AHs

260 14 different hydroxy-AHs (including two hydroxy-benzaldehydes) were identified and their
261 relative abundances estimated in all the soot samples analyzed (Figure 2, Table 2). The
262 hydroxy-AHs richest soot samples are those from Jet A-1 - 1-butanol, followed far by those
263 from Jet A-1 - Me-octanoate and those from Jet A-1 - 2,5-DMF. On the other hand, soot
264 samples from Jet A-1, SPK and from the Jet A-1 - DEC mixture contain the lowest
265 concentrations in hydroxy-AHs (Figure 3). Soot samples from Jet A-1 - 1-butanol contain the
266 highest concentrations in hydroxyphenanthrenes and they are the only ones containing
267 dihydroxy-naphthalene isomers. Concerning hydroxy-benzaldehydes, they are very abundant
268 in soot from Jet A-1 - 1-butanol and they were also found at very low concentration in soot
269 from Jet A-1 - DEC.

270 As we can see from Figure 3 and Table 2, 1- and 2-naphthol are present in almost all the soot
271 samples analyzed and they are especially abundant in soot from Jet A-1 - 2,5-DMF and in soot
272 from Jet A-1 - 1-butanol. Conversely, soot samples from Jet A-1 - Me-octanoate contain very
273 low concentrations of 1-naphthol and 2-naphthol.

274 On the other hand, soot from Jet A-1 - Me-octanoate contains another hazardous substance:
275 1-hydroxypyrene (also called 3-hydroxypyrene); whereas 2-hydroxypyrene was only found in
276 soot from SPK. Ketones of fluorene are abundant in soot samples from Jet A-1 - Me-octanoate.

277 **3.1.3. Aldehydes-AHs**

278 9 carboxaldehydes-AHs in total, including those from Table 3 and another one identified at low
279 concentrations in soot from Jet A-1 - Me-octanoate, were the most abundant and the most
280 common: 1-naphthalene-carboxaldehyde, 2-naphthalene-carboxaldehyde and acenaphthene-5-
281 carboxaldehyde are found in almost all the soot samples analyzed. From Table 3, we can say
282 that whereas Jet A-1 - 2,5-DMF and SPK mainly produces very low concentrations of
283 carboxaldehydes-AHs; Jet A-1 - Me-octanoate, Jet A-1 - DEC and Jet A-1 - 1-butanol produce
284 larger amounts of light and heavy carboxaldehydes-AHs such as pyrene-carboxaldehyde and
285 fluoranthene-carboxaldehyde. In the next sections we will see that Jet A-1 - 1-butanol also
286 produces significant amounts of nitro-benzaldehydes.

287 On the other hand, Jet A-1 - DEC produces aliphatic aldehydes such as hexadienal isomers.
288 Although aliphatic aldehydes are out of the scope of this paper, we also report on their
289 presence in soot extracts analyzed in the present work.

290 As can be seen from Table 3, the relative abundance of carboxaldehydes-AHs in soot from Jet
291 A-1 - 1-butanol are almost twice those found in soot from Jet A-1. On the contrary, soot from
292 SPK and Jet A-1 - 2,5-DMF blends are poor in carboxaldehydes-PAH (Figure 4). In conclusion,
293 we can say that blending Jet A-1 with biofuels gives rise to a significant increasing of
294 carboxaldehydes concentrations except in the case of 2,5-DMF.

295 Although it was not included in Table 3, small concentrations of p-terphenyl-2,2',5',2''-
296 tetracarboxaldehyde were found in soot samples from Jet A-1 - Me-octanoate.

297 **3.1.4. Ketones**

298 The number of keto-AHs detected in the analyzed samples is the highest; it is constituted of 27
299 compounds (Table 4, Figure 5). This group of compounds can be divided into two subgroups:

- 300 a) Keto-AHs with the carbonyl group outside a ring structure (like acetophenone), and
- 301 b) Keto-AHs with the carbonyl group inside the aromatic structure (like fluorene-1-one).

302 As we can see from Table 4, the largest relative abundances of keto-AHs were found in soot
303 samples from Jet A-1 - 2,5-DMF followed by far by those from Jet A-1 - 1-butanol, whereas the
304 other soot samples are much poorer in keto-AHs. Soot from Jet A-1 - 2,5-DMF contains larger
305 concentrations of heavy keto-AHs, such as benzanthrone and 6H-benzo[cd]pyrene-6-one, than
306 the other soot samples, whereas benzo[b]fluorenone isomers are abundant in soot samples
307 from Jet A-1 - 2,5-DMF and from Jet A-1 - Me-octanoate. Finally, although it is beyond the
308 scope of this paper, one must report that SPK produces large amounts of aliphatic ketones like
309 methyl-vinyl ketone, cyclohexenones and ketones from isoprene. Soot from Jet A-1 - 1-butanol
310 also contains aliphatic ketones such as 2,3,4,4a,5,6,7,8-octahydro-1-methyl-2oxanaphthalene.

311 As reported in a previous work,²⁷ isomers of phenyl-naphthalene were found in all the samples
312 analyzed but on those from Jet A-1 - 2,5-DMF, their concentrations were extremely low.
313 However, one polar derivative of the aforementioned AH (phenyl-2-naphthylketone) was
314 found at high concentration in soot samples from Jet A-1 - 2,5-DMF. It seems that isomers of
315 phenyl-naphthalene are transformed into its main polar derivative (phenyl-2-naphthylketone) in
316 the soot samples from Jet A-1 - 2,5-DMF.

317 **3.1.5. Identification and relative abundances of quinones**

318 Quinones-AHs might be referred in the keto-AHs subsection due to their functionality (-C=O).
319 However, we decided to present them separately due to the different trend observed.
320 Particularly, the widest distribution and the highest relative abundance of quinones-AHs were
321 observed in soot samples from Jet A-1 - DEC and in soot samples from Jet A-1 - Me-octanoate
322 followed by far by those from SPK but they are scarce in soot from Jet A-1, Jet A-1 - 2,5-DMF
323 and Jet A-1 - 1-butanol as we can see from Figure 6.

324 16 aromatic quinones in total were identified in our soot samples (Table 5 and Figure 6). Two
325 aliphatic quinones (5,5-dimethylcyclohexane-1,3-dione and camphorquinone), were also
326 tentatively identified in soot samples from Jet A-1 - DEC.

327 Small quinone-AHs like 1,4-naphthoquinone are abundant in soot from Jet A-1, SPK, and Jet A-
328 1 - 1-butanol, whereas heavier quinone-AHs are much more abundant in Jet A-1 - DEC and Jet
329 A-1 - Me-octanoate blends. Conversely, soot from SPK is the only one containing one isomer of
330 methyl-1,4-naphthoquinone. As we observed previously, SPK tends to produce methyl branched
331 compounds.²⁸

332 **3.1.6. Aromatic monocarboxylic Acids/Aromatic Hydroxy-Acids /Aromatic dicarboxylic acids**

333 17 aromatic monocarboxylic acids, hydroxy-acids, and aromatic dicarboxylic acids were
334 identified in the analyzed soot samples (Table 6). The presence of aromatic monocarboxylic
335 acids and aromatic dicarboxylic acids was verified in all soot samples except in those from Jet
336 A-1 - DEC. They are much more abundant in soot from Jet A-1 - Me-octanoate than in the
337 other soot samples (Figure 7). Regarding aromatic hydroxy-acids were found in all the soot
338 samples except in those from Jet A-1 - DEC and those from SPK. They are very abundant in soot
339 samples from Jet A-1 - 2,5-DMF.

340 The widest distribution of compounds was detected in soot samples from Jet A-1 - Me-
341 octanoate (9 compounds from this group were found in these soot samples).

342 All in all, aromatic monocarboxylic acids/aromatic dicarboxylic acids/aromatic hydroxy-acid
343 compounds richest soot samples are those from Jet A-1 - Me-octanoate as depicted in Figure
344 6.

345 **3.1.7. N-Aromatics**

346 N- aromatic compounds (N-AHs) are generated from e.g., coal gasification, shale oil
347 extraction^{48,60}. 26 compounds belonging to this group were identified in the analyzed soot
348 samples. They are very abundant in soot from Jet A-1 - Me-octanoate blends (Table 7, Figure
349 8).

350 N-AHs represent ~18% of the total number of PAC determined in soot. Derivatives of
351 quinolines, acridines and cinnolines were the most abundant N-AHs identified in the analyzed
352 soot samples. A wide distribution of these compounds was observed in all samples except in
353 those from SPK and Jet A-1 - 1-butanol where they appeared at low concentrations.

354 The distribution of this group of compounds is largely dependent on the sample analyzed. In
355 soot samples from Jet A-1, acridines are the predominant compounds, whereas in soot
356 samples from Jet A-1 - Me-octanoate the predominant groups of N-AHs are carbazol and their
357 derivatives and cinnoline derivatives. In soot samples from Jet A-1 - DEC the predominant
358 group is quinoxaline and their derivatives (Table 7 and Figure 8). Although the origin of
359 quinoxaline is usually synthetic and it is very rare in nature, some authors claimed that this
360 compound might be produced through the condensation of o-phenylenediamine (found in
361 soot samples from Jet A-1 and from Jet A-1 - DEC) with α -dicarbonyl compounds.⁶¹ The empty
362 cells mean "Not Detected".

363 Especially interesting is the fact that Jet A-1 - Me-octanoate and Jet A-1 - DEC emit PAC with
364 several functional groups. As can be seen from Table 7, Jet A-1 - Me-octanoate produces
365 several isomers of methoxy-cinnoline and Jet A-1 - DEC emits 3-pyridyl-methylketone (with an
366 amine group and a carbonyl group) and di-amino anthraquinone (with two carbonyl groups
367 and two amino groups). Something similar was observed in soot from Jet A-1 - 1-butanol,
368 which contains large amounts of nitro-benzaldehydes as presented in the next section.

369 **3.1.8. Nitro-PAHs**

370 The formation of nitro-PAHs is much concerning because of their potential mutagenicity and
371 atmospheric reactivity.⁶³ These compounds may be emitted from incomplete combustion
372 processes such as fossil fuel and biomass burning⁶³⁻⁶⁵ or produced by heterogeneous or

373 homogeneous reactions of AHs with atmospheric oxidants such as the hydroxyl radical, the
374 nitrate radical, or ozone.^{25,26} On the other hand, some oxy-PAHs have been reported to
375 transform into nitro-PAHs via atmospheric reaction.^{67,68}

376 Due to heating occurring in most of the extraction methodologies in the literature (Soxhlet,
377 microwave-assisted extraction or supercritical fluid extraction) and/or dichloromethane for
378 extracting nitro-PAHs⁶⁹⁻⁷¹, most nitro-PAHs in soot samples can be lost. On the other hand,
379 important contradictions have been found in literature about concentrations of nitro-PAHs on
380 soot samples. Indeed, whereas Barreto et al., 2007⁷⁰ published concentrations about 0.50 ng
381 of 1-nitro-pyrene/mg in diesel soot samples, Paschke et al. (1992)⁷² had reported
382 concentrations of 1-nitropyrene in bus soot (a very similar matrix) about 540 ng/mg.

383 Unlike other papers already quoted, in this paper neither heat nor dichloromethane has been
384 used for extracting or fractioning nitro-PAHs and higher recoveries are expected.

385 As we can see from Table 8 and Figure 9 the nitro-AHs richest soot samples are those from Jet
386 A-1 - DEC and from Jet A-1 - 1-butanol.

387 Extinction coefficients of nitro-AHs are within the range $[(0.5-1)\times 10^4 \text{ M}^{-1}\text{cm}^{-1}]$, were used for
388 calculating the absolute concentrations of this group of compounds in soot samples. Thus,
389 extinction coefficients of o-nitrotoluene, m-nitrotoluene and p-nitrotoluene are 5890, 8190,
390 and 10100 $\text{M}^{-1}\text{cm}^{-1}$ respectively⁷³ whereas extinction coefficients of o-nitrobenzaldehyde (in
391 hexane or methanol), m-nitrobenzaldehyde and p-nitrobenzaldehyde at 250-252 nm are 5000
392 $\text{M}^{-1}\text{cm}^{-1}$, 8000 $\text{M}^{-1}\text{cm}^{-1}$, and 10000 $\text{M}^{-1}\text{cm}^{-1}$ respectively.²¹ On the other hand, the extinction
393 coefficient of 2-nitronaphthalene is $3\times 10^4 \text{ M}^{-1}\text{cm}^{-1}$, and for 6-nitrochrysene is $5.37\times 10^4 \text{ M}^{-1}\text{cm}^{-1}$
394 .²²

395 As we can see from Figure 9, the total concentrations of nitro-AHs in soot samples reaches
396 almost 6000 ng/(mg soot) in Jet A-1 - 1-butanol soot samples and about 1800 ng/mg soot in
397 samples from Jet A-1. These values are much higher than those found in literature for similar
398 samples.⁶⁹ found concentrations near 7.5 ng of 1-nitropyrene/(mg of total suspended
399 particulate matter) at workplaces associated with the use of Diesel engines. On the other
400 hand, Oukebdane et al. (2010)⁷¹ found concentrations near 3 ng of Nitro-PAHs/mg on Diesel
401 soot samples. In the former study the sum of 1-nitronaphthalene, 2-nitrofluorene, 9-
402 nitroanthracene, 3-nitrofluoranthene, and 1-nitropyrene concentrations was used.

403 According to a number of authors, blending conventional fuels with biofuels, diminishes the
404 emissions of nitro-PAHs but our measurements indicate that nitro-PAHs concentrations
405 increase in Jet A-1 - biofuels compared to the Jet A-1 reference case.

406 **3.2. Other polar compounds on soot Aromatic S-compounds**

407 Dibenzothiophene was detected in soot samples from SPK and also in those from Jet A-1 - Me-
408 octanoate but it is absent from the other soot samples analyzed. Thioanisole and benzenethiol
409 were found exclusively in SPK.

410 **3.3. Esters**

411 Soot from Jet A-1 - Me-octanoate is the only one showing high concentrations of esters.
412 Fluorenone-1-carboxylate, methyl-fluoranthene-1-carboxylate, ethylfluoranthene-1-
413 carboxylate were detected whereas methyl- β -(5,6,7,8-tetrahydro-2-naphthol)acrylate was
414 detected in soot samples from Jet A-1 - 2,5-DMF.

415 **4. DISCUSSION**

416 In order to interpret the present results, we considered the physico-chemical properties of the
417 fuels together with the flames conditions, the fuels tendency to produce soot and PAHs, the
418 ranking of PACs for the different fuels, chemical mechanisms which could explain the
419 formation of PACs, when available.

420 Table 9 presents the sooting tendency of each fuel determined previously²⁸ together with O/C
421 ratios in the neat biofuel and in fuel mixtures, and C/H ratios for the neat biofuels. Fuel sooting

422 tendency is based on our measurements of soot mass.²⁸ Fuel tendencies were: 1 for Jet A-1
423 (reference fuel), 0.33 for SPK, 1.77 for Jet A-1 - 2,5-DMF, 1.17 for Jet A-1 - Me-octanoate, 0.5
424 for Jet A-1 - DEC, and 0.37 for Jet A-1 - 1-butanol. However, we reported that sooting
425 tendencies were not proportional to the mass fraction of PAHs adsorbed on soot. We also
426 reported that whereas Lemaire et al. (2013)⁷³ proposed that fuels with high oxygen content
427 tend to produce less soot, that trend was not observed in our experiments, and no clear
428 relationship between C/O in the fuels and sooting tendency could be delineated.

429 From Table 9, one can see that the addition of 2,5-DMF increases the most the production of
430 soot, likely because of its aromatic character. Methyl octanoate has no significant effect
431 whereas diethyl carbonate and 1-butanol addition both reduce sooting, as reported earlier.²⁸
432 In Table 10, we compare the total concentration of PAHs per mass unit of soot, and the impact
433 of fuel composition on adiabatic flames temperature. From this Table, one can note that the
434 total fresh gas flowrate varies by -0.39 to +1.3% only from the Jet A-1 reference flame.
435 Therefore, this parameter should not significantly impact the results. However, the variation of
436 the adiabatic flame temperature by -4.8 to +11.5% from the reference flame can affect the
437 formation of PACs.

438 For oxa-AHs, we observed a relatively small variation of the total amount of oxa-AHs formation
439 with fuel composition while the fuel containing 2,5-DMF produces the highest concentration of
440 oxa-AHs, among them, furanic compounds are the most abundant chemicals. The observed
441 trend for oxa-AHs production was: Jet A-1 - 2,5-DMF > Jet A-1 - DEC ≥ Jet A-1 - Me-octanoate ≥
442 Jet A-1 - 1-butanol Jet A-1 > SPK. However, it is difficult to directly link the biofuel structure to
443 the identified oxa-AHs whereas in the literature, oxa-AHs formation is only described for
444 simple furans, e.g., the formation of benzofuran is proposed to proceed via the oxidation of
445 dibenzyl by radicals (O, OH) yielding 2-phenyl phenol which further oxidizes to form
446 benzofuran.⁷⁴

447 For hydroxy-AHs, it is interesting to note that there is a large variation of the yield with fuels
448 composition, the Jet A-1 -1-butanol fuel producing the highest concentration of hydroxy-AHs.
449 The observed trend for hydroxy-AHs production was: Jet A-1 - 1-butanol >> Jet A-1 - Me-
450 octanoate > Jet A-1 - 2,5-DMF > Jet A-1 ≥ SPK ≥ Jet A-1 - DEC. The formation of these products
451 is expected to follow the mechanism of formation of phenol which involves an initial H-atom
452 abstraction by radicals (H, O, OH, HO₂ ...) to form a phenyl radical which yields phenoxy by
453 oxidation with oxygen. The recombination of phenoxy and H yields phenol.⁷⁵ Again, it is
454 difficult to link the higher concentration of hydroxy-AHs in Jet A-1 - 1-butanol flames to a
455 particular alcohol chemistry. What was observed could result from the higher flame
456 temperature which favors H-atom abstractions but still, the Jet A-1 - 1-butanol flame produces
457 the lowest amounts of PAHs.

458 The production of aromatic aldehydes is enhanced by methyl octanoate, diethyl carbonate,
459 and 1-butanol blending. The observed trend for aromatic aldehydes production was: Jet A-1 -
460 1-butanol > Jet A-1 - Me-octanoate > Jet A-1 - DEC > Jet A-1 >> SPK >> Jet A-1 - 2,5-DMF. That
461 could indicate that the presence of these oxygenates favor the oxidation of aromatics rather
462 than their growth, as observed earlier during the oxidation of indane and dimethoxymethane-
463 doped indane oxidation.⁷⁵

464 The effect of fuel blending on keto-AHs production is mostly observed with 2,5-DMF which is
465 forming the highest concentrations of keto-AHs. The observed trend for keto-AHs production
466 was: Jet A-1 - 2,5-DMF >> Jet A-1 - 1-butanol > SPK > Jet A-1 > Jet A-1 - Me-octanoate > Jet A-1
467 - DEC. The formation of aromatic ketones has been described in the literature.⁷⁶ The highest
468 concentrations of PAHs observed for the Jet A-1 - 2,5-DMF soot samples could explain the
469 important formation of keto-AHs with that fuel.

470 The blending effect on quinones production is mainly observed for the fuels containing diethyl
471 carbonate and methyl octanoate. The observed trend for quinones production was: Jet A-1 -

472 DEC > Jet A-1 - Me-octanoate >> SPK > Jet A-1 - 1-butanol \geq Jet A-1 \geq Jet A-1 - 2,5-DMF. In the
473 literature,⁷⁶ the formation of quinone was reported to proceed via the oxidation of an
474 aromatic radical, e.g., ortho-benzoquinone was observed as an initial production of oxidation
475 of the phenyl radical by O₂. A synergistic effect between jet fuel and diethyl carbonate is thus
476 suspected to be responsible for the higher production of quinones.

477 Aromatic acids production was increased by biofuels blending, except in the case of diethyl
478 carbonate. The observed trend for aromatic acids production was: Jet A-1 - Me-octanoate >>
479 SPK > Jet A-1 - 2,5-DMF > Jet A-1 - 1-butanol > Jet A-1 >> Jet A-1 - DEC. These acids could derive
480 from the oxidation of aromatic aldehydes. This could well be the case for 1-naphtalene
481 carboxylic acid. For the other acids, no link to the corresponding aldehydes was observed,
482 which could indicate that other routes of formation are involved.

483 The production of nitro-HAPs is enhanced by jet fuel blending with 1-butanol and diethyl
484 carbonate. The observed trend for nitro-PAHs production was: Jet A-1 - 1-butanol > Jet A-1 -
485 DEC > Jet A-1 > SPK > Jet A-1 - Me-octanoate >> Jet A-1 - 2,5-DMF. These highly toxic pollutants
486 are known to be formed by reaction of NO₂ with polyaromatic radicals which are produced by
487 H-atom abstraction on PAHs by OH in particular.⁷⁷ One can expect a higher production of nitro-
488 PAHs if the flame temperature increases since the thermal-NO mechanism should dominate in
489 the present flames. In the burnt gases, NO oxidizes forming NO₂ which can react with
490 polyaromatic radicals, producing nitro-PAHs. With hotter Jet A-1 - 1-butanol and Jet A-1 - DEC
491 flames (+11.5% and + 5.9%), one can expect higher nitro-PAHs production. However, that does
492 not explain the low production of nitro-PAHs in Jet A-1 - 2,5-DMF flames which produce the
493 highest quantities of PAHs.

494 In the aim of improving the methodology described here, PAC might be analyzed by using polar
495 columns with smaller particle size, smaller inner diameter and larger length than that here
496 used. These columns are expected to retain the PAC longer into the column, achieving a more
497 efficient separation, especially if an appropriate gradient is applied

498 5. CONCLUSIONS

499 The soot samples were obtained from pre-mixed flames, the lab conditions being far from the
500 industrial conditions, particularly in terms of pressure; nevertheless, the chemistry going on
501 should not be so different that our findings could not be extrapolated to industrial conditions.
502 Soot from JetA-1 blended with synthetic biofuels is richer in PAC than soot from Jet A-1 and
503 from SPK. Soot from Jet A-1 - 2,5-DMF has the highest keto-AHs concentrations and in general
504 oxa-AHs. Soot from Jet A-1 - methyloctanoate presents the highest concentrations in aromatic
505 monocarboxylic-aromatic, dicarboxylic acids-aromatic, aromatic hydroxy-acids, and aldehydes-
506 AHs. Soot from Jet A-1 - diethylcarbonate has the highest concentrations in the quinones-AHs
507 and nitrated-AHs. Soot from Jet A-1 - 1-butanol contains the largest concentrations of nitro-
508 AHs and hydroxy-AHs. As observed previously (Andrade-Eiroa et al., 2015), in general blending
509 a fossil fuel with synthetic biofuels diminishes the emission of AHs (except in the case of 2,5-
510 DMF) but increases the production of PAC.

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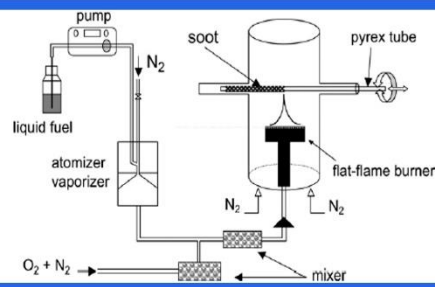
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Sampling collection and pretreatment

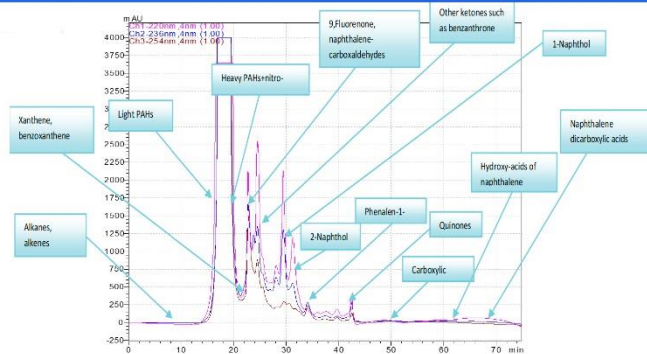
- 1 Collection of soot samples on the outer surface of a Pyrex road tube at height 4 cm above the head of the burner.



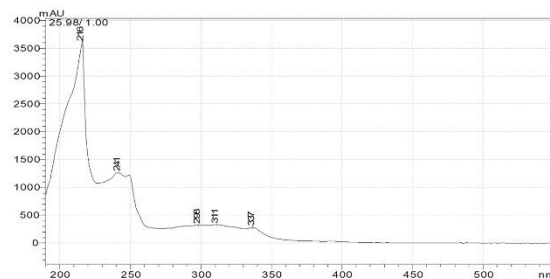
- 2 Weighted soot samples (about 15 mg) were solved into 2 mL of hexane. Filtration twice through two PTFE filter was accomplished in the aim of removing particles and extracting PAHs and their derivatives.



- 3 30 μ L of the extracts obtained in the previous step, were directly injected into a silica SPE column 25 cm length, 2.1 mm ID, 5 μ m particle size) against gravity, at very low pressure, by using hexane as mobil phase. Several fractions were collected using a fraction collector.



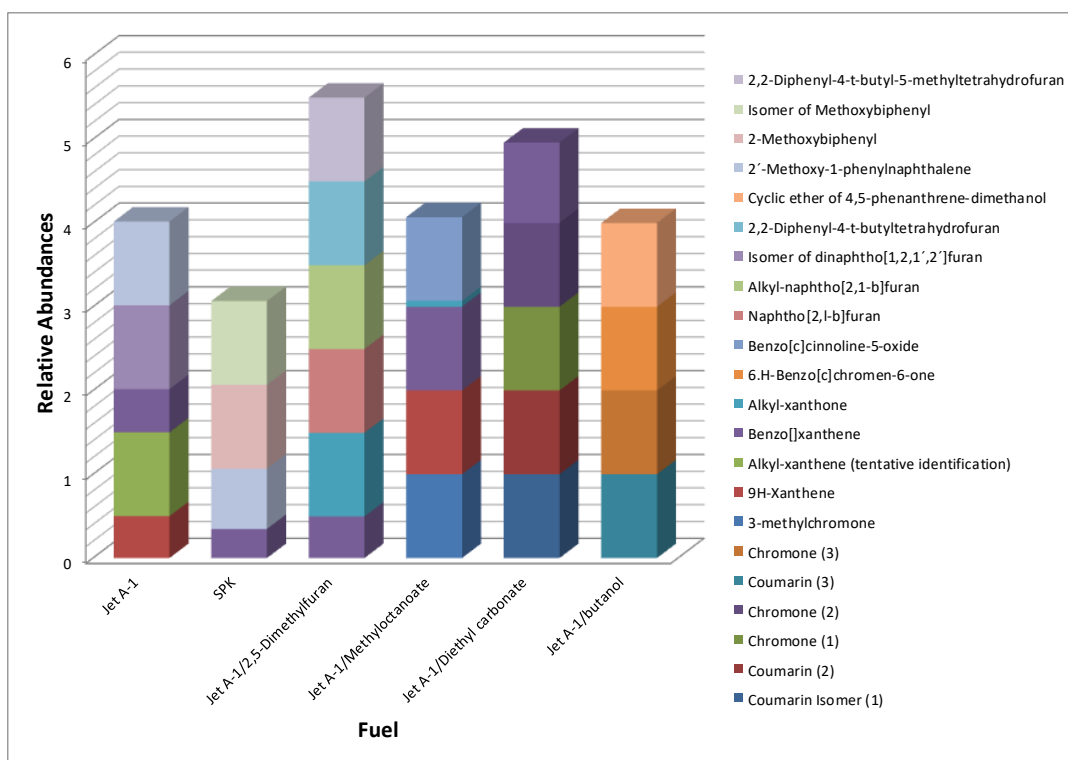
- 4 Jet A-1/methyloctanoate SPE soot extracts were pretreated with acetic acid before being injected into the HPLC system whereas 2,5-dimethylfuran SPE soot extracts were pretreated with sodium hydroxide before injection into the HPLC system. Identification was carried out by UV-Visible spectrometry.



Chromatoraphic Analysis

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Figure 1. Schema of the analytical procedure applied.



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764 **Figure 2. Relative abundances of oxa-PAHs on every soot samples analyzed. Data are**
 765 **normalized to the main oxa-AH formed for each fuel.**

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769 **Table 1. Relative abundances of oxa-AHs in the analyzed soot samples. Data are normalized**
 770 **to the main oxa-AH formed for each fuel.**

COMPOUNDS	SOOT SAMPLES					
	Jet A-1	SPK	Jet A-1/2,5-Dimethylfuran	Jet A-1/Methyloctanoate	Jet A-1/Diethylcarbonate	Jet A-1/Butanol
Coumarin Isomer (1)					1,00	
Coumarin (2)					1,00	
Chromone (1)					1,00	
Chromone (2)					1,00	
Coumarin (3)						1,00
Chromone (3)						1,00
3-methylchromone				1,00		
9H-Xanthene	0,500			1,00		
Alkyl-xanthene (tentative identification)	1,00					
Benzo[<i>j</i>]xanthene	0,516	0,348	0,496	1,00	0,959	
Alkyl-xanthone			1,00	0,07		
6.H-Benzo[<i>c</i>]chromen-6-one						1,00
Benzo[<i>c</i>]cinnoline-5-oxide				1,00		
Naphtho[2, <i>l</i> - <i>b</i>]furan			1,00			
Alkyl-naphtho[2, <i>l</i> - <i>b</i>]furan			1,00			
Isomer of dinaphtho[1,2, <i>l</i> ,2' <i>l</i>]furan	1,00					
2,2-Diphenyl-4- <i>t</i> -butyltetrahydrofuran			1,00			
Cyclic ether of 4,5-phenanthrene-dimethanol						1,00
2'-Methoxy-1-phenylnaphthalene	1,00	0,720				
2-Methoxybiphenyl		1,00				
Isomer of Methoxybiphenyl		1,00				
2,2-Diphenyl-4- <i>t</i> -butyl-5-methyltetrahydrofuran			1,00			

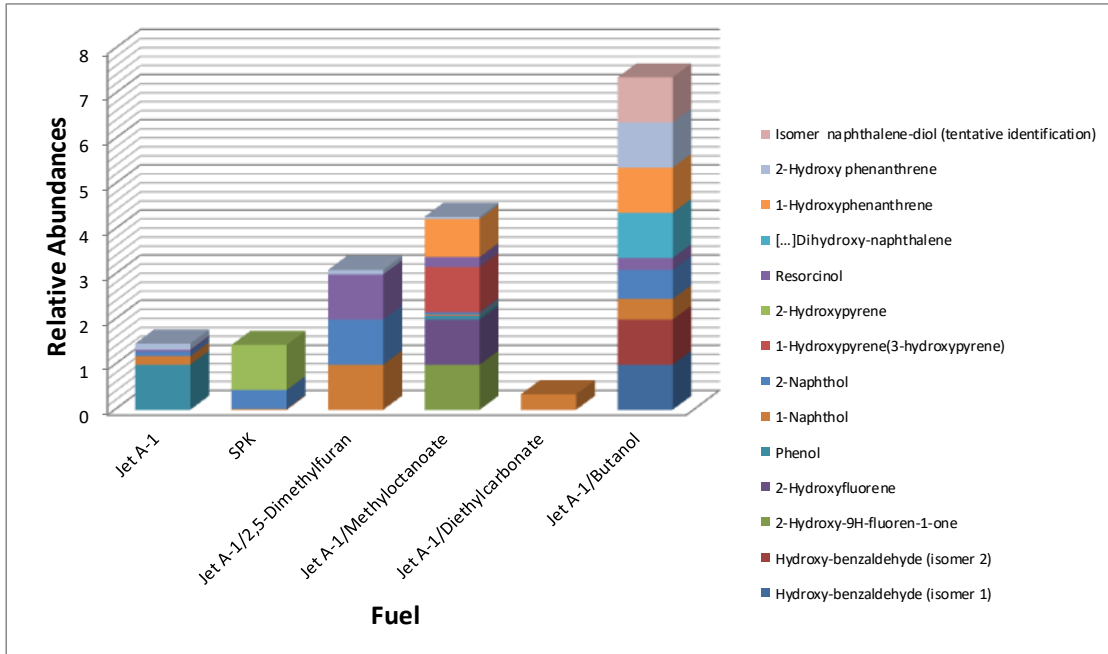
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Figure 3. Relative abundances of hydroxy-AHs in the soot samples analyzed. Data are normalized to the main hydroxy-AH formed for each fuel.

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782 **Table 2. Hydroxy-PAHs and hydroxy-acids PAHs found in the soot samples analyzed. Data are**
 783 **normalized to the main hydroxy-AH formed for each fuel.**

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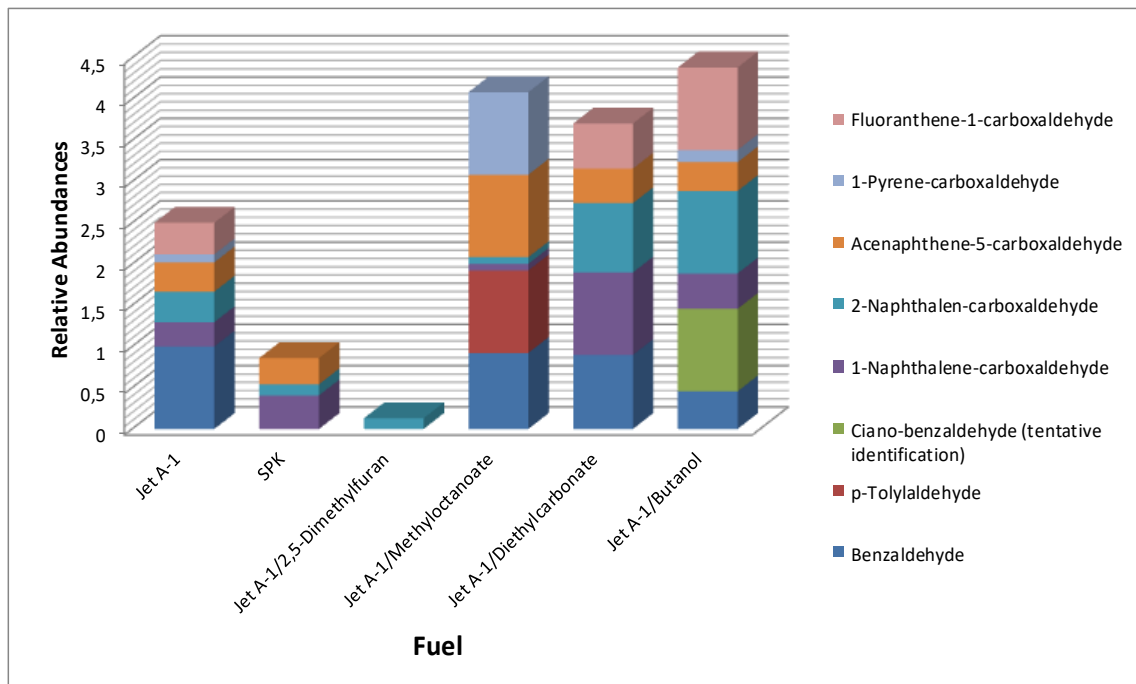
COMPOUNDS	SOOT SAMPLES					
	Jet A-1	SPK	Jet A-1/2,5-Dimethylfuran	Jet A-1/Methyloctanoate	Jet A-1/Diethylcarbonate	Jet A-1/Butanol
Hydroxy-benzaldehyde (isomer 1)					0,0120	1,00
Hydroxy-benzaldehyde (isomer 2)					0,00940	1,00
Phenol	1,00			0,0800		
Resorcinol	0,0424		1,00	0,223		0,265
1-Naphthol	0,190	0,0210	1,00	0,0250	0,345	0,456
2-Naphthol	0,0980	0,417	1,00	0,0580		0,644
2-Hydroxy-9H-fluoren-1-one				1,00		
2-Hydroxyfluorene				1,00		
2-Hydroxy phenanthrene	0,137		0,100	0,0500		1,00
1-Hydroxypyrene(3-hydroxypyrene)				1,00		
2-Hydroxypyrene		1,00				
[...]Dihydroxy-naphthalene						1,00
Isomer naphthalene-diol						1,00
Isomer naphthalene-diol (tentative identification)						1,00

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Figure 4. Relative abundances of the most representative aldehydes in the analyzed soot samples. Data are normalized to the main aromatic aldehyde formed for each fuel.

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796 **Table 3. Relative abundances of carboxaldehydes-AHs in every soot sample analyzed. Data**
 797 **are normalized to the main aromatic aldehyde formed for each fuel.**

COMPOUNDS	SOOT SAMPLES					
	Jet A-1	SPK	Jet A-1/2,5-Dimethylfur	Jet A-1/Methyloctanoate	Jet A-1/2,5-Diethylcarbon	Jet A-1/Butanol
Benzaldehyde	1,00			0,921	0,897	0,456
p-Tolylaldehyde				1,00		
Ciano-benzaldehyde (tentative identification)						1,00
1-Naphthalene-carboxaldehyde	0,295	0,407		0,0810	1,00	0,429
2-Naphthalen-carboxaldehyde	0,370	0,134	0,129	0,0800	0,840	1,00
Acenaphthene-5-carboxaldehyde	0,355	0,318		1,00	0,419	0,348
1-Pyrene-carboxaldehyde	0,0979			1,00		0,149
Fluoranthene-1-carboxaldehyde	0,381				0,546	1,00

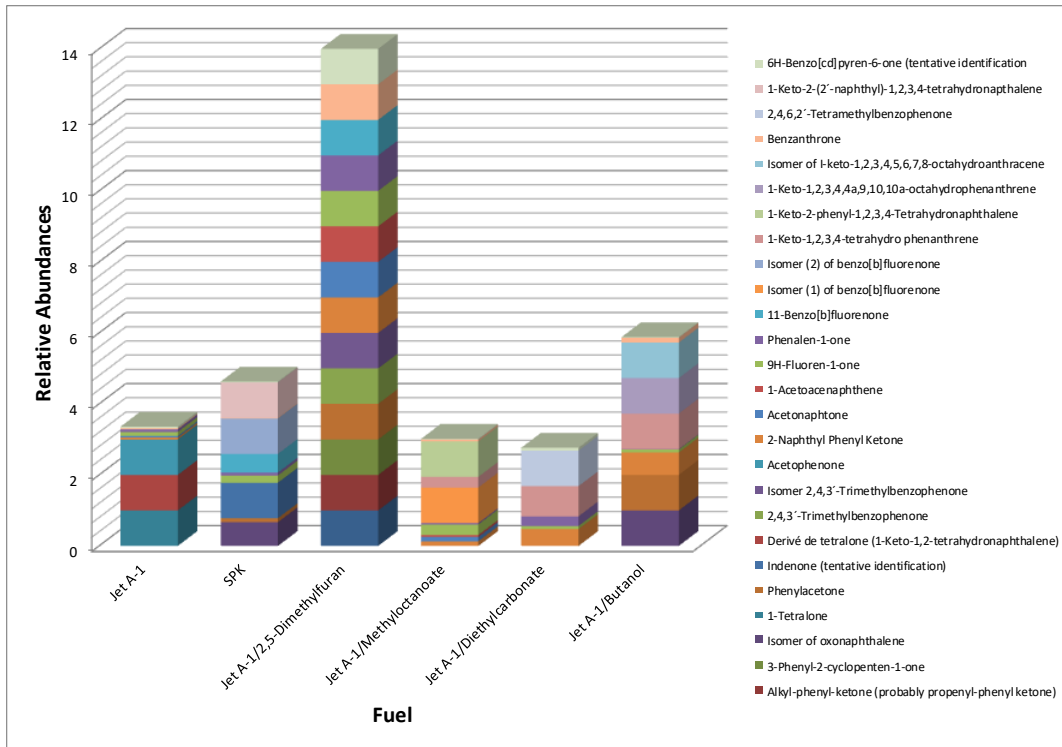
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Figure 5. Relative abundances of ketones-AHs in the analyzed soot samples. Data are normalized to the main aromatic ketone formed for each fuel.

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808 **Table 4. Relative abundances of ketones-AHs found in the soot samples analyzed. Data are**
 809 **normalized to the main aromatic ketone formed for each fuel.**

COMPOUNDS	SOOT SAMPLES					
	Jet A-1	SPK	Jet A-1/2,5-Dimethylfuran	Jet A-1/Methyloctanoate	Jet A-1/Diethylcarbonate	Jet A-1/Butanol
Cyclohexyl-phenyl-ketone			1,00			
Alkyl-phenyl-ketone (probably propenyl-phenyl ketone)			1,00			
3-Phenyl-2-cyclopenten-1-one			1,00			
Isomer of oxonaphthalene		0,67				1,00
1-Tetralone	1,00					
Phenylacetone		0,112	1,00			1,00
Indenone (tentative identification)		1,00				
Derivé de tetralone (1-Keto-1,2-tetrahydronaphthalene)	1,00					
2,4,3'-Trimethylbenzophenone			1,00			
Isomer 2,4,3'-Trimethylbenzophenone			1,00			
Acetophenone	1,00					
2-Naphthyl Phenyl Ketone	0,0517		1,00	0,131	0,476	0,629
Acetonaphthone	0,04418		1,00	0,119957		
1-Acetoacenaphthene			1,00	0,05841		
9H-Fluoren-1-one	0,113	0,203	1,00	0,296	0,085	0,0848
Phenalen-1-one	0,0785	0,0822	1,00	0,0386	0,273	0,0132
11-Benzo[b]fluorenone		0,525	1,00			
Isomer (1) of benzo[b]fluorenone				1,00		
Isomer (2) of benzo[b]fluorenone		1,00				
1-Keto-1,2,3,4-tetrahydro phenanthrene				0,300	0,850	1,00
1-Keto-2-phenyl-1,2,3,4-Tetrahydronaphthalene				1,00		
1-Keto-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (or isomer)						1,00
Isomer of 1-keto-1,2,3,4,5,6,7,8-octahydroanthracene						1,00
Benzanthrone	0,0278	0,0156	1,00	0,0534		0,138
2,4,6,2'-Tetramethylbenzophenone					1,00	
1-Keto-2-(2'-naphthyl)-1,2,3,4-tetrahydronaphthalene		1,00				
6H-Benzo[cd]pyren-6-one (tentative identification)	0,0440	0,0213	1,00	0,0177	0,0813	0,0157

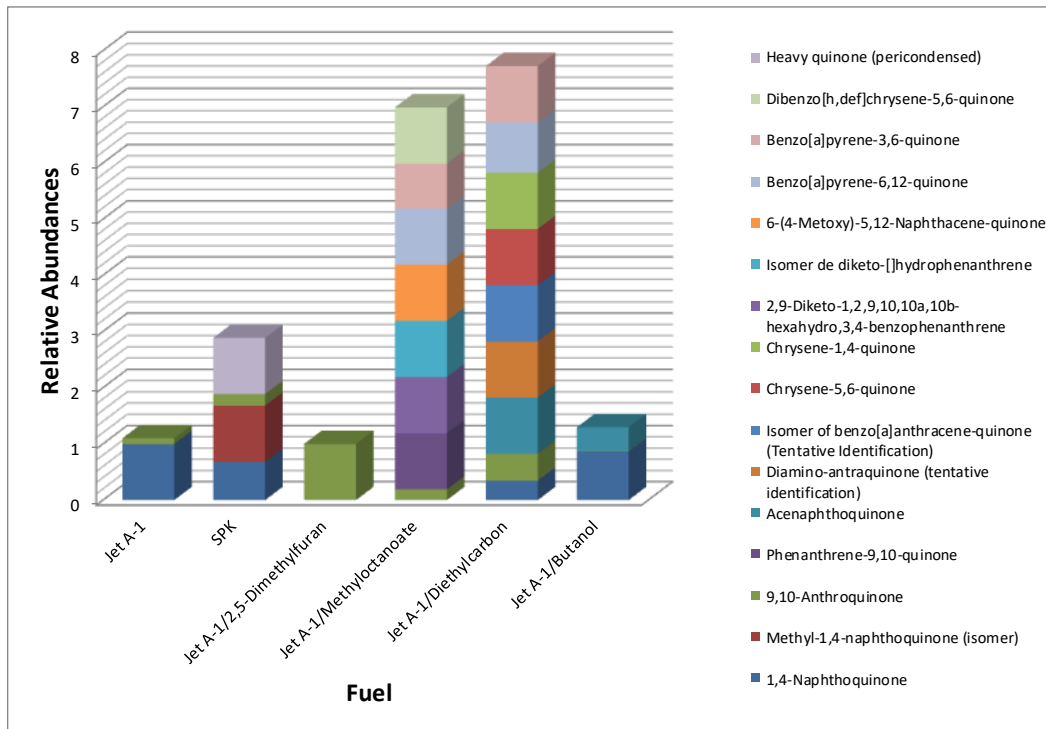
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Figure 6. Relative abundances of quinones in soot from Jet A-1, SPK and Jet A-1 blended with biofuels. Data are normalized to the main quinone formed for each fuel.

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821 **Table 5. Relative abundances of quinone-AHs in soot samples from the fuels analyzed. Data**
 822 **are normalized to the main quinone formed for each fuel.**

COMPOUNDS	SOOT SAMPLES					
	Jet A-1	SPK	Jet A-1/2,5-Dimethylfuran	Jet A-1/Methyloctanoate	Jet A-1/Diethylcarbonate	Jet A-1/Butanol
1,4-Naphthoquinone	1,00	0,682			0,348	0,866
Methyl-1,4-naphthoquinone (isomer)		1,00				
9,10-Anthroquinone	0,1	0,205	1,00	0,190	0,477	0,00800
Phenanthrene-9,10-quinone				1,00		
Acenaphthoquinone					1,00	0,422
Diamino-antraquinone (tentative identification)					1,00	
Isomer of benzo[a]anthracene-quinone (Tentative Identification)					1,00	
Chrysene-5,6-quinone					1,00	
Chrysene-1,4-quinone					1,00	
2,9-Diketo-1,2,9,10,10a,10b-hexahydro,3,4-benzophenanthrene				1,00		
Isomer de diketo-[]hydrophenanthrene				1,00		
6-(4-Metoxy)-5,12-Naphthacene-quinone				1,00		
Benzo[a]pyrene-6,12-quinone				1,00	0,900	
Benzo[a]pyrene-3,6-quinone				0,810	1,00	
Dibenzo[h,def]chrysene-5,6-quinone				1,00		
Heavy quinone (pericondensed)		1,00				

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827 **Table 6. Relative abundances of aromatic monocarboxylic acids, aromatic dicarboxylic acids**
 828 **and aromatic hydroxy-acids in the soot samples analyzed. Data are normalized to the**
 829 **main aromatic acid formed for each fuel.**

COMPOUNDS	SOOT SAMPLES					
	Jet A-1	SPK	Jet A-1/2,5-Dimethylfuran	Jet A-1/Methyloctanoate	Jet A-1/Diethylcarbonate	Jet A-1/butanol
Benzoic acid		1,00				
Isomer of hydroxy-benzoic acid	1,00					
Isomer benzoic diacid (tentative identification)				1,00		
Benzofuran-2-carboxylic Acid			1,00			
1-naphthalene-carboxylic acid		0,387		1,00		
2-naphthalene-carboxylic acid						
Isomer du Pyrene-carboxylic acid		1,00				
Hydroxy-2-naphthoic acid (tentative identification)				1,00		
2-hydroxy-1-naphthoic acid			1,00	0,150		
[...]hydroxy-1-naphthoic acid			1,00	0,180		
Naphthalene-1,2-dicarboxylic acid						1,00
Naphthalene-2,3-dicarboxylic acid						1,00
Naphthalene-1,8-dicarboxylic acid anhydride(*)		1,00				
Naphthalene-2,7-dicarboxylic acid				1,00		
Naphthalene-1,6-dicarboxylic acid				1,00		
Naphthalene-1,7-dicarboxylic acid				1,00		
Alkyl-fluoranthene carboxylic acid				1,00		

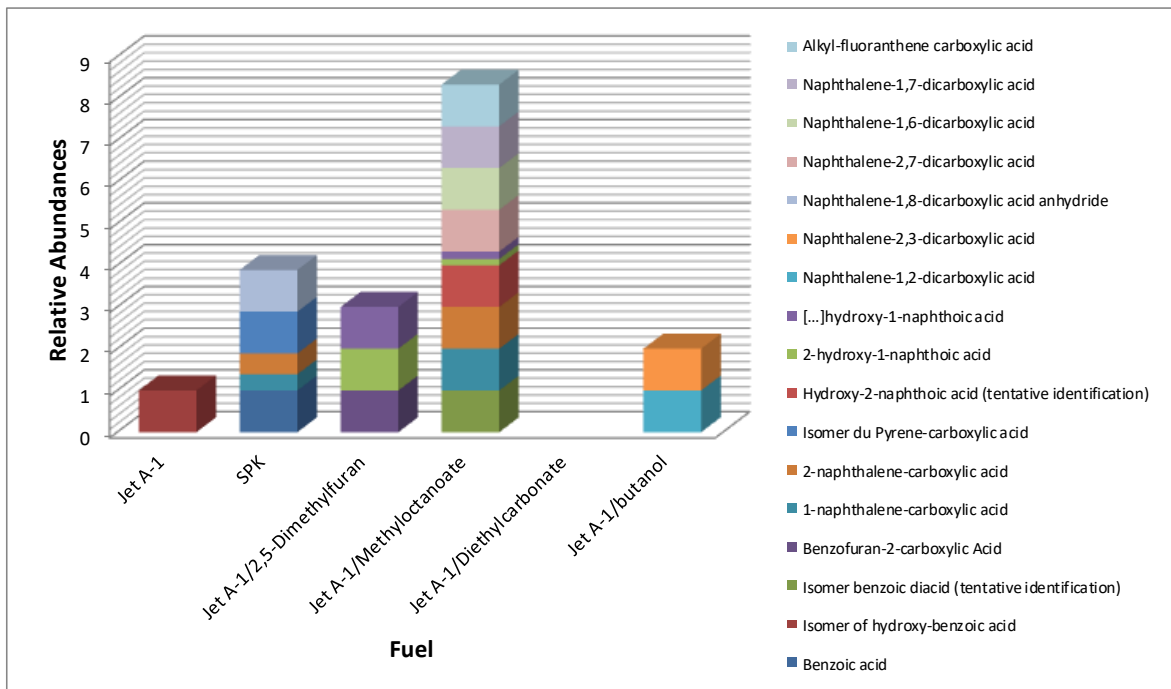
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831 * Identified directly during the fractionation through silica column (hexane as mobile phase).

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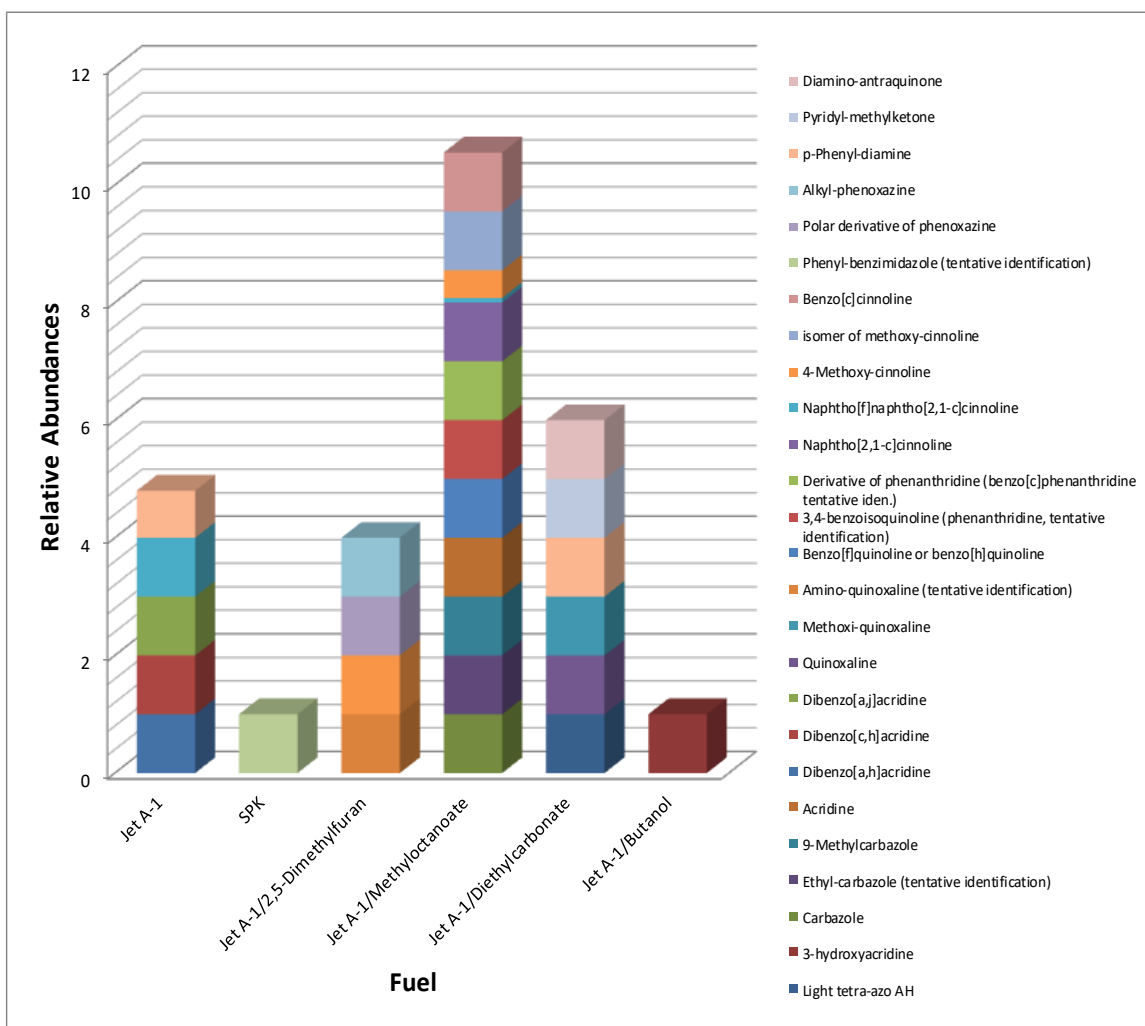
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Figure 7. Relative abundances of aromatic monocarboxylic acid/aromatic dicarboxylic acid/aromatic hydroxy-acids compounds in the soot samples analyzed. Data are normalized to the main aromatic acid formed for each fuel.

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Figure 8. Relative abundances of nitrated-AHs in every soot sample analyzed. Data are normalized to the main N-AH formed for each fuel.

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Table 7. Relative abundances of nitrated-AHs in every soot sample analyzed. Data are normalized to the main N-AH formed for each fuel.

COMPOUNDS	SOOT SAMPLES					
	Jet A-1	SPK	Jet A-1/2,5-Dimethylfuran	Jet A-1/Methyloctanoate	Jet A-1/Diethylcarbonate	Jet A-1/Butanol
Light tetra-azo AH					1,00	
3-hydroxyacridine						1,00
Carbazole				1,00		
Ethyl-carbazole (tentative identification)				1,00		
9-Methylcarbazole				1,00		
Acridine				1,00		
Dibenzo[a,h]acridine	1,00					
Dibenzo[c,h]acridine	1,00					
Dibenzo[a,j]acridine	1,00					
Quinoxaline					1,00	
Methoxy-quinoxaline					1,00	
Amino-quinoxaline (tentative identification)			1,00			
Benzo[f]quinoline or benzo[h]quinoline				1,00		
3,4-benzoisoquinoline (phenanthridine, tentative identification)				1,00		
Derivative of phenanthridine (benzo[c]phenanthridine tentative iden.)				1,00		
Naphtho[2,1-c]cinnoline				1,00		
Naphtho[f]naphtho[2,1-c]cinnoline	1,00			0,0810		
4-Methoxy-cinnoline			1,00	0,470		
Methoxy-cinnoline (isomer 1)				1,00		
Benzo[c]cinnoline				1,00		
Phenyl-benzimidazole (tentative identification)		1,00				
Polar derivative of phenoxazine			1,00			
Alkyl-phenoxazine			1,00			
p-Phenyl-diamine	0,800				1,00	
Pyridyl-methylketone					1,00	
Diamino-antraquinone					1,00	

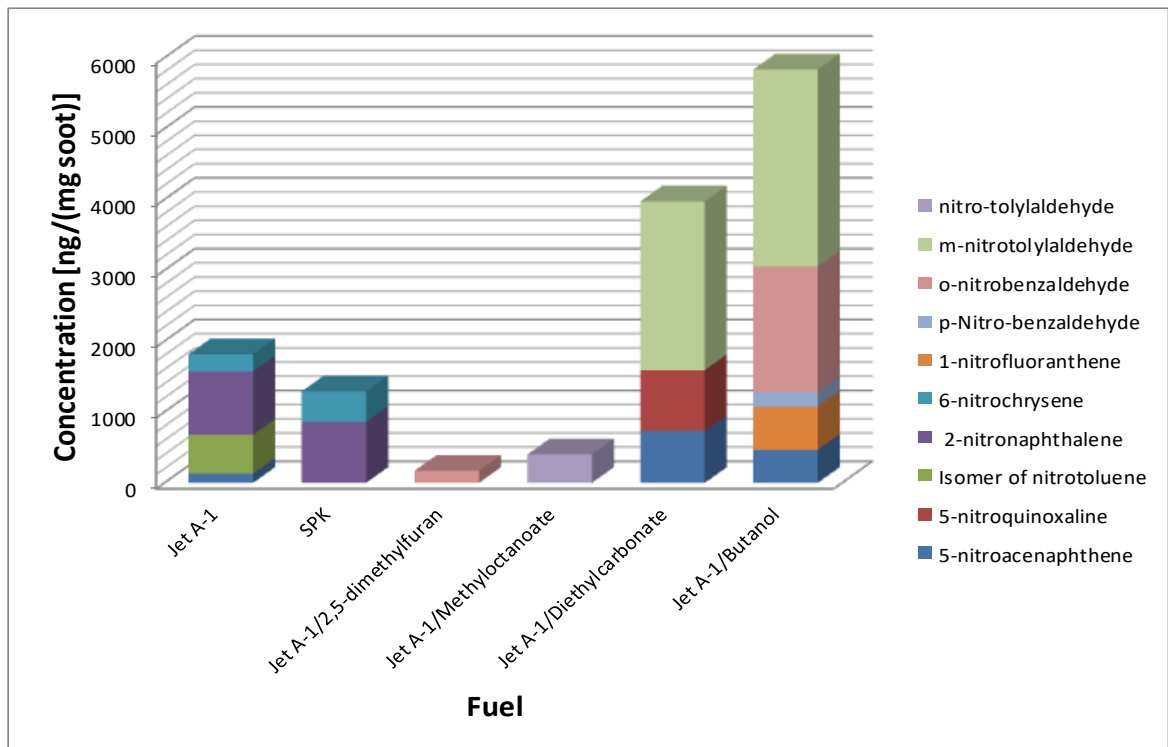
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Figure 9. Concentrations of nitro-PAHs and nitro-PAHs derivatives in soot from every fuel included in this paper. Data are normalized to the main nitro-PAH formed for each fuel.

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Table 8. Concentrations of nitro-AHs in the soot samples analyzed. Data are normalized to the main nitro-PAH formed for each fuel.

Compounds	Soot samples [ng/(mg soot)]					
	Jet A-1	SPK	Jet A-1/2,5-dimethylfuran	Jet A-1/Methyloctanoate	Jet A-1/Diethylcarbonate	Jet A-1/Butanol
5-nitroacenaphthene	131				734	467
5-nitroquinoxaline					858	
Isomer of nitrotoluene	550					
2-nitronaphthalene	890	860				
6-nitrochrysene	245	429				
1-nitrofluoranthene						610
p-Nitro-benzaldehyde						201
o-nitrobenzaldehyde			169			1774
m-nitrotolylaldehyde					2380	2781
nitro-tolylaldehyde				400		

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LQ. Limit of Quantification.

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866 **Table 9. Fuels properties and sooting tendencies.** The data are from Eiroa-Andrade et al.

867 (2015)⁸⁵.

Fuel	C/O biofuel	C/O in mixture	C/H biofuel	Sooting tendency relative to Jet A-1 (\pm 20%)	Oxygenated structure
Jet A-1	-	∞	-	1	none
SPK	-	∞	-	0.33	none
Jet A-1/DEC	1.67	10.9	0.5	0.50	O-C(=O)-O
Jet A-1/Butanol	4	24.9	0.4	0.37	C-O-H
Jet A-1/Methyl octanoate	9	25.1	0.5	1.17	O=C-O-C
Jet A-1/2,5-DMF	6	30.3	0.75	1.77	C-O-C, aromatic

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Table 10. Fuels and flames properties. The data are from Eiroa-Andrade et al. (2015)⁸⁵.

Parameter	Fuels					
	Jet A-1	SPK	Jet A-1/2,5-DMF	Jet A-1/DEC	Jet A-1/Me-octanoate	Jet A-1/butanol
Total PAHs (ng/mg of soot)	3551	3412	4662	1978	819	253
Relative sooting tendency ($\pm 20\%$)	1	0.33	1.77	0.5	1.17	0.37
Δ Flame temperature % *	0	-	+6.4	+5.9	-4.8	+11.5
Δ Flame input flowrate %	0	-	-0.79	+0.46	-0.48	+1.3

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*Computed using the Equil program of the Chemkin II library (Kee, R. J.; Rupley, F. M.; Miller, J. A. CHEMKIN-II: A Fortran Chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics; SAND89-8009; Sandia National Laboratories: Livermore, CA, 1989).

Supporting information
**Polar Aromatic Compounds (PAC) in Soot From Premixed Flames of Kerosene,
 Paraffinic Synthetic Kerosene, and Kerosene-Synthetic Biofuels**
 Maria Auréa Andrade-Eiroa, Philippe Dagaut and Guillaume Dayma

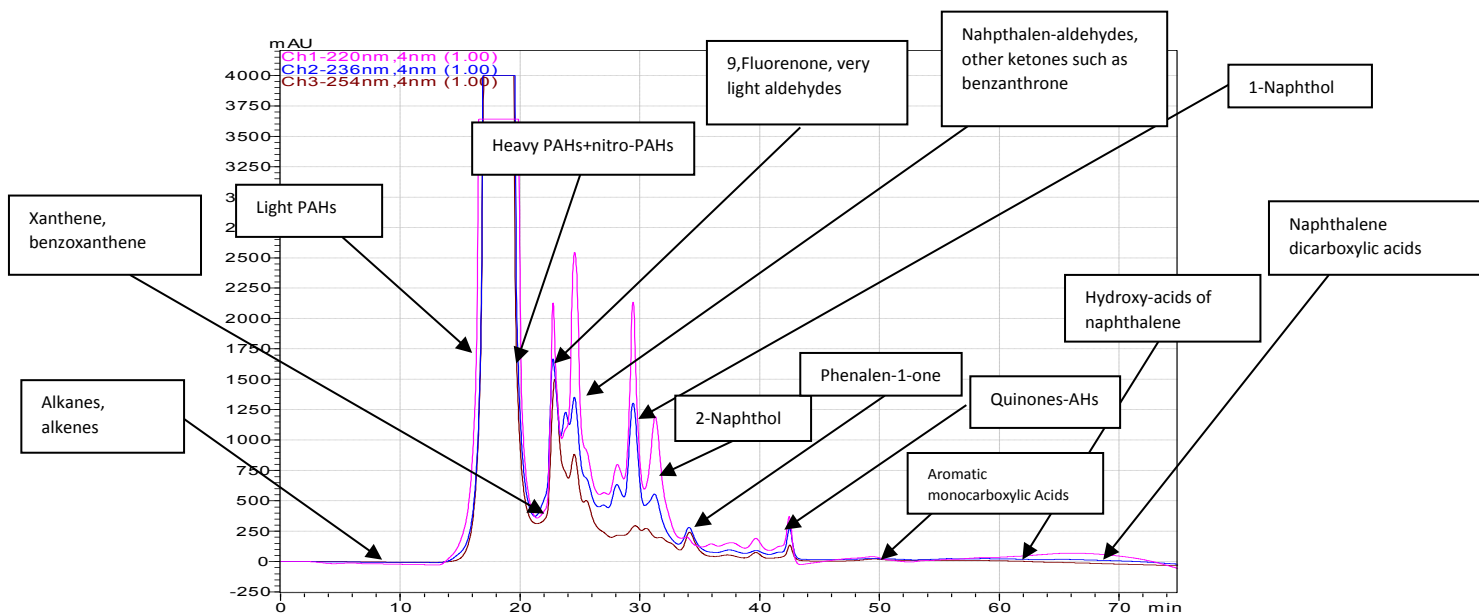


Figure S1. Fractioning of the methyloctanoate-kerosene (20% v/v methyloctanoate) soot extract into hexane blends through the silica column described in the experimental part. Experimental conditions: $V_{inj}=50\mu\text{L}$ of the pure extract of soot (15.8mg/2mL). Mobile phase: 100%hexane at speed flow of 0.05ml/min.

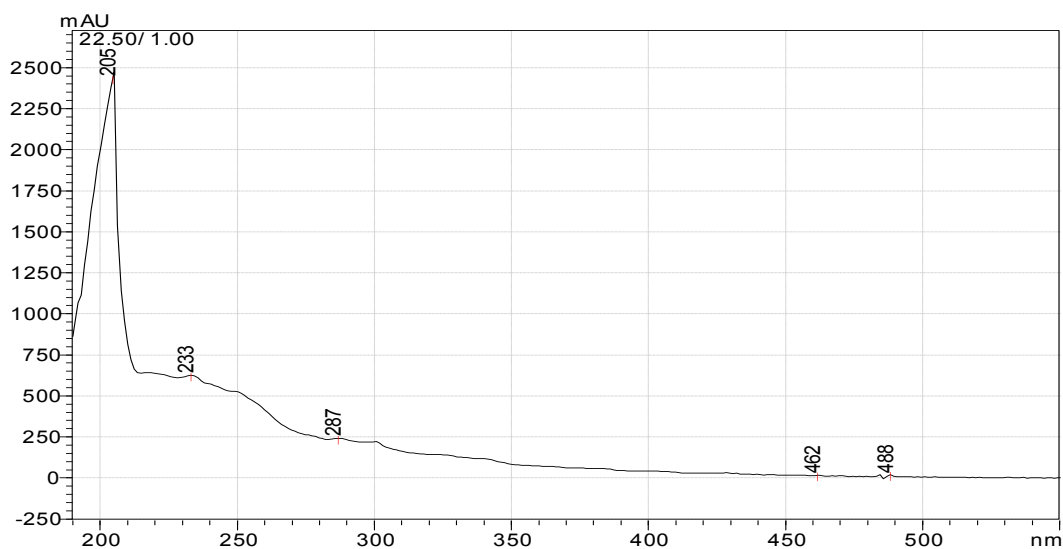


Figure S2. UV spectrum of the fraction eluting at 22.50 minute. In the Solid-Phase extraction eluted from the extraction column between 22.00-23.00 min we found some oxy-PAHs and 9-fluorenone.

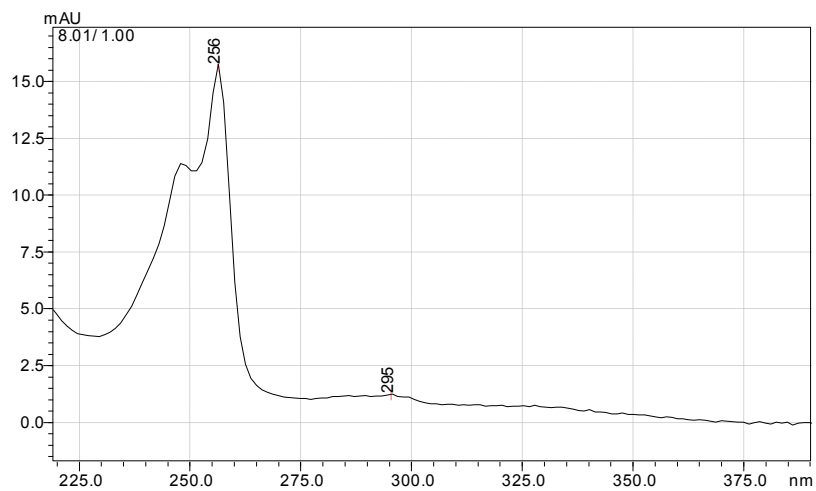


Figure S3. Reinjection of the fraction eluted from the HPLC system between 22-23 min, also allowed to obtained the clear and precise identification of 9-fluorenone, as we can see from this figure. UV spectrum of 9-fluorenone at 8.01 min.

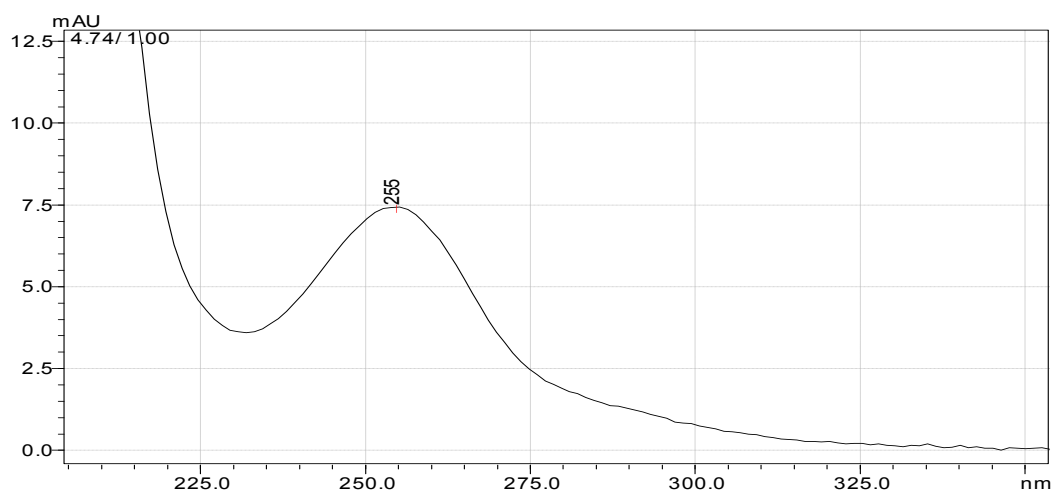


Figure S4. Fraction obtained between 23.01-24.00 min was re-injected into the HPLC system and, as can see from this figure, at 4.74 min we obtained the UV spectrum of tolylaldehyde.

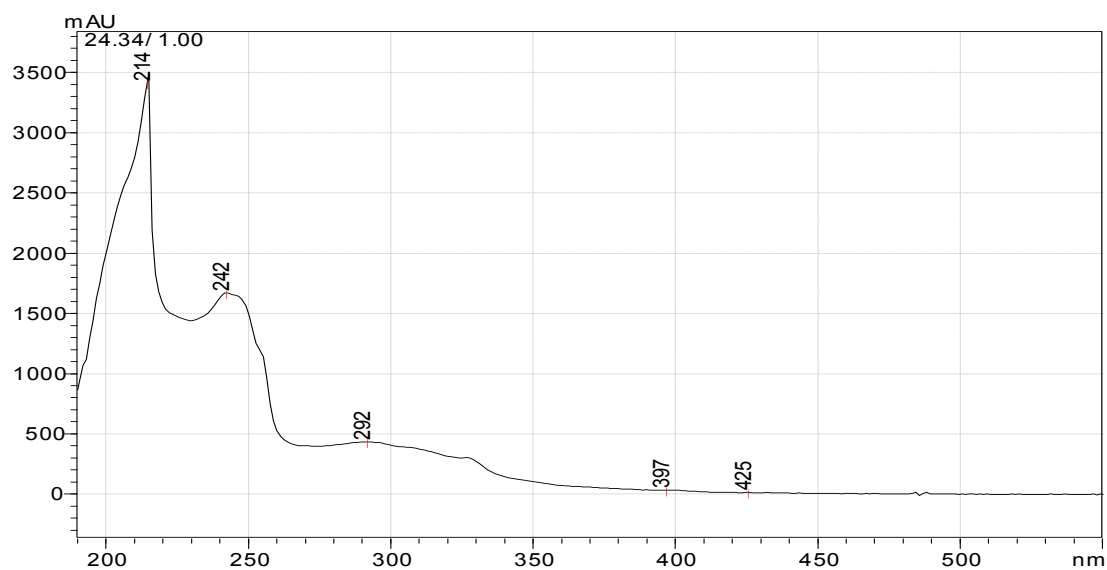


Figure S5. UV spectrum of the fraction eluting at 24.34 minute. This profile corresponds to aldehydes (naphthalen-aldehydes isomers).

Reinjection of the fraction obtained from the Solid Phase Extraction system between 24.00-25.00 min, into the HPLC system, allowed to obtained the clear and precise identification of several naphthalene-aldehydes, such as the 2-naphthalen-aldehyde.

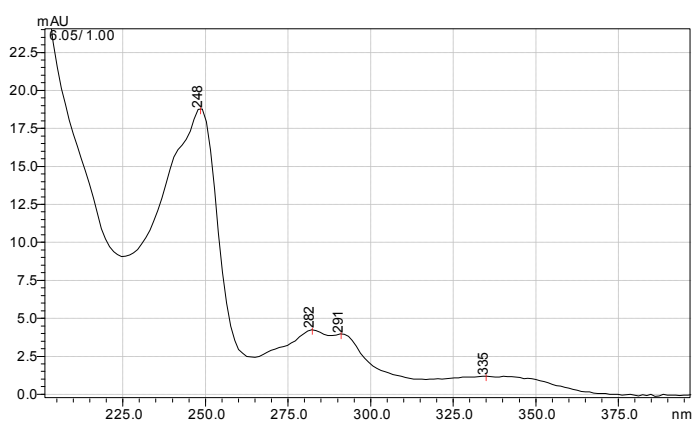


Figure S6. UV-Vis spectrum of 2-naphthalen-aldehyde. Reinjection of the fraction above mentioned allowed the unambiguous identification of sereral aldehydes, among the, the 2-naphthalen-aldehyde, eluted from the HPLC column at 6.05 min.

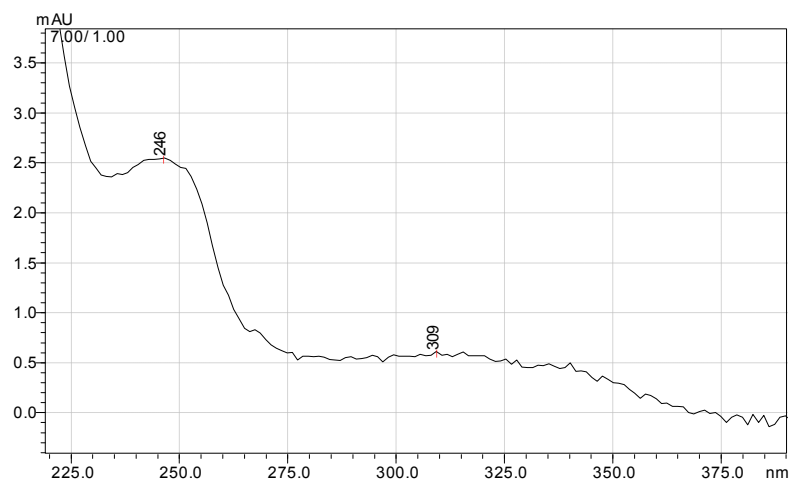


Figure S7. UV-Vis spectrum of 1-naphthalen-aldehyde. Reinjection of the fraction eluted from the HPLC system between 24.00-25.00 min, allowed to obtained the clear and precise identification of several naphthalene-aldehydes, such as the 1-naphthalen-aldehyde, eluted at 7.00 min.

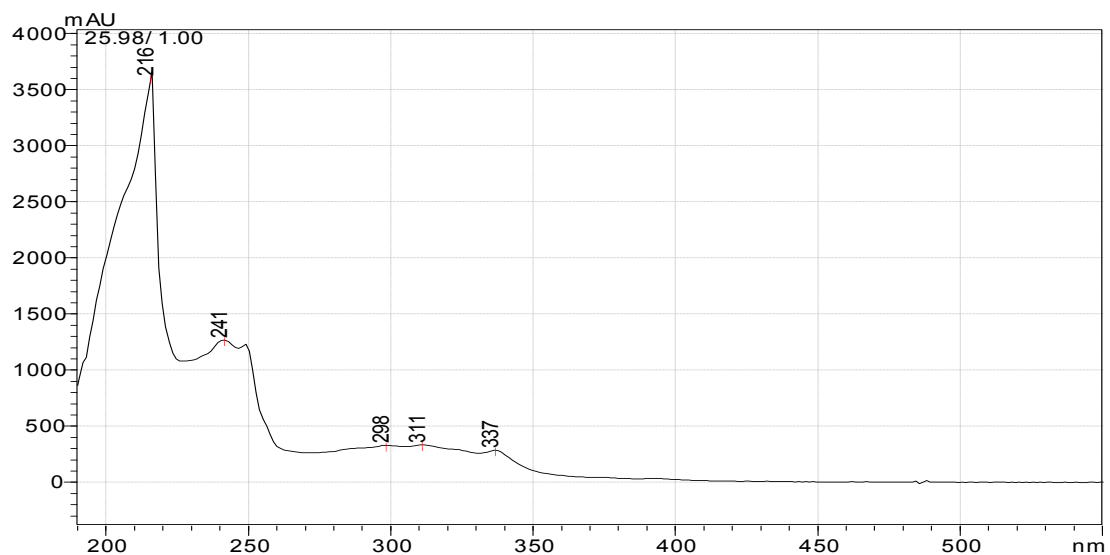


Figure S8. UV spectrum of the fraction eluting at 25.98 minute from the solid-phase extraction column. In this fraction (25-27 min) we find 9-vinylcarbazole and other nitrated-PAHs.

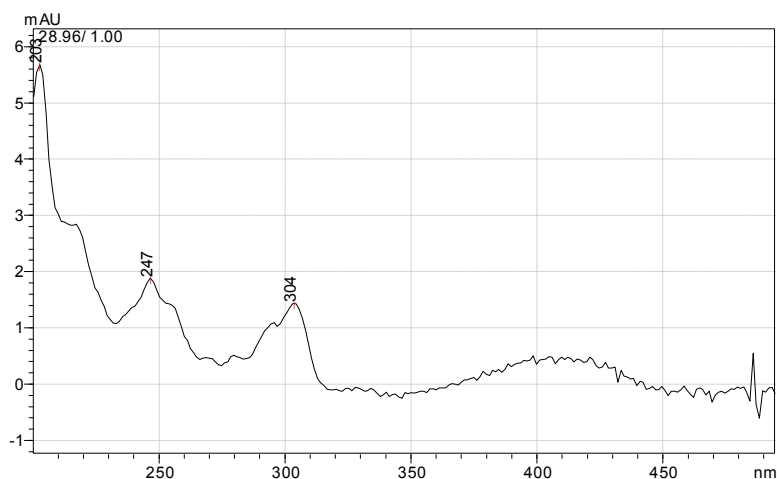


Figure S9. The fraction eluting at 25-27 minute from the solid-phase extraction column was re-injected into the HPLC system. Here we can see the UV spectrum of benzo[c]cinnoline eluted from the HPLC system at 28.96 min.

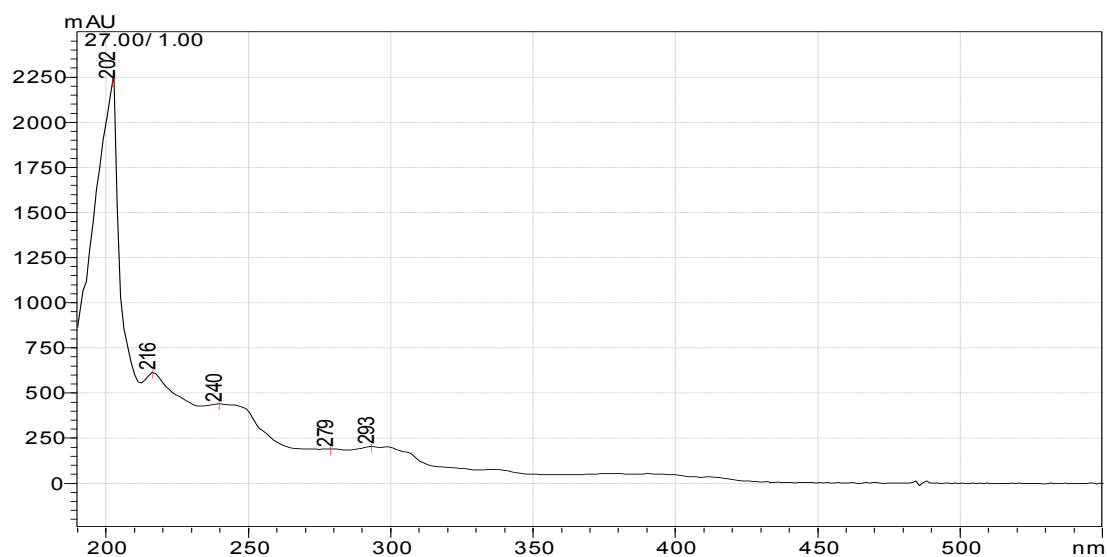


Figure S10. UV spectrum of the fraction eluting at 27.00 minute. In the fraction collected between 27-30 min, we find quinones (which absorb at wavelengths above 400 nm). The re-injection of the fraction collected from the Solid Phase Extraction column between 27-29 min, into the HPLC system allowed to identified several quinones, as we can see in the following figures. The highest quinones eluted after 41 min from the solid-phase extraction system.

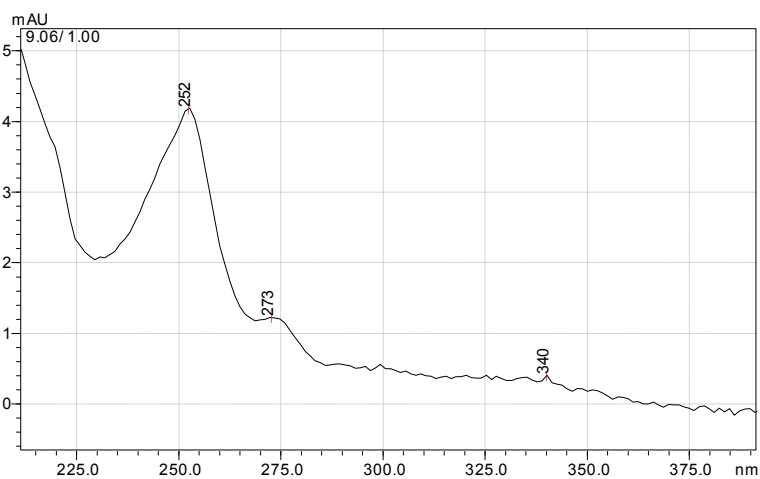


Figure S11. UV spectrum of the fraction eluting at 27-29 minute was reinjected into the HPLC system. In this UV spectrum we can see the spectrum of 9,10-anthraquinone eluted at 9.06 min from the HPLC column.

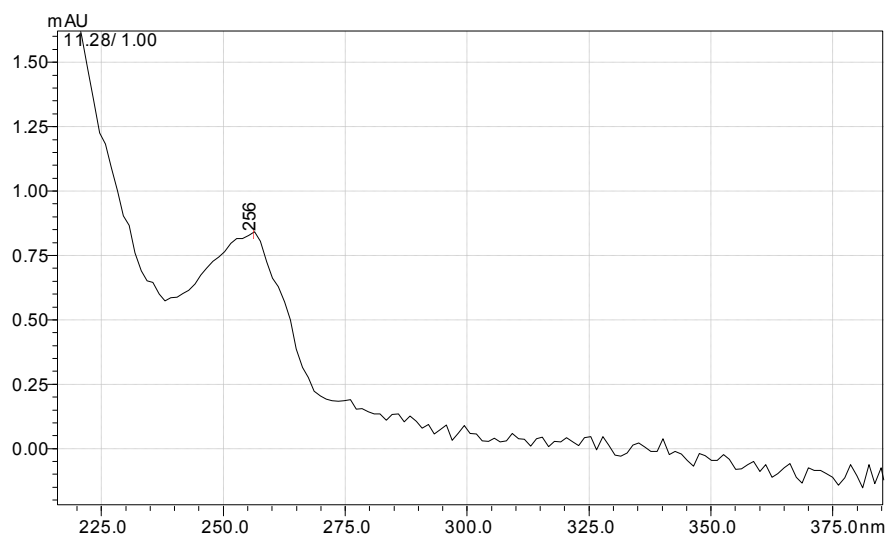


Figure S12. UV-Vis spectrum of phenanthrene-9,10-quinone eluted at 11.28 min from the HPLC column after injection of the fraction eluted from the solid-phase extraction column between 27-29 min.

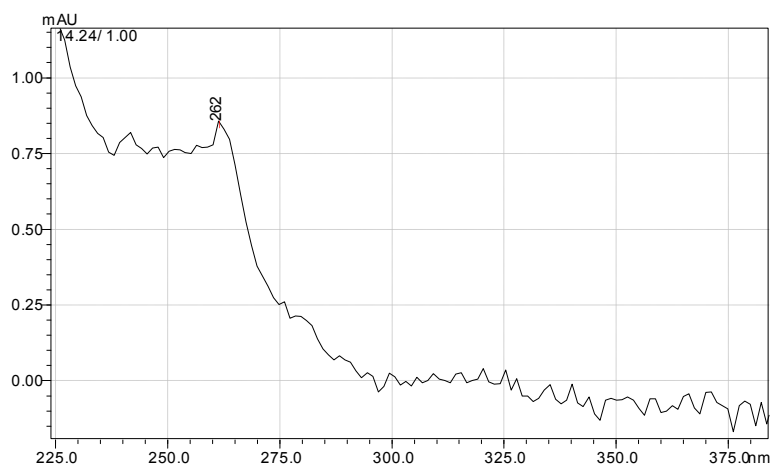


Figure S13. UV spectrum of benzo[a]pyrene-6,12-quinone eluted at 14.24 min. from the HPLC column after re-injection of the solid phase fraction eluted between 27-29 min.



Figure S14. The fraction eluted from the solid-phase extraction column between 27.00-29.00 min was re-injected into the HPLC system. In this figure we can see UV spectrum of pyrene-3-carboxaldehyde eluted from the HPLC column at 24.31 min.

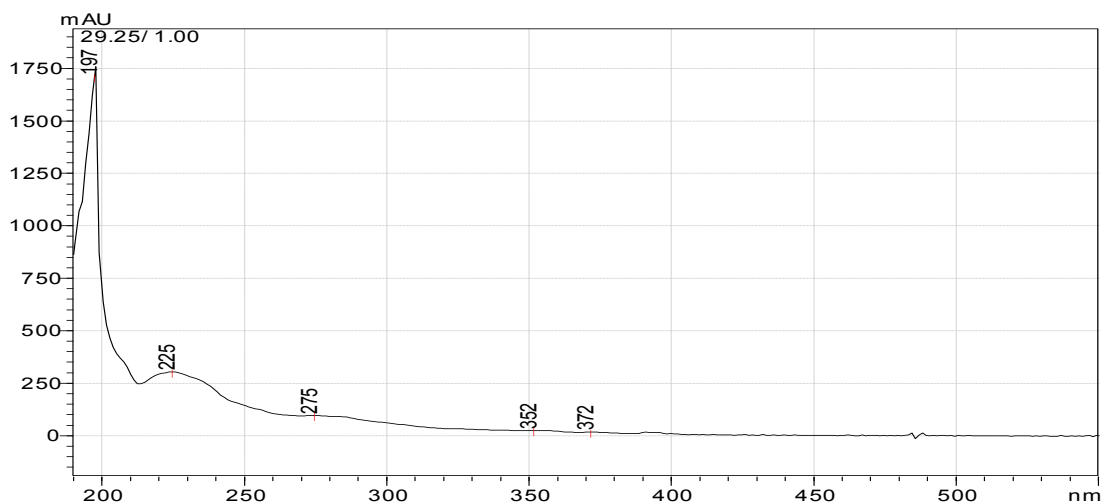


Figure S15. UV spectrum of the fraction eluting at 29.25 minute. In the fraction eluting from the Solid-Phase Extraction column between 29-38 min, we found some medium-size PAH derivatives, such as 2-hydroxy-phenanthrene.

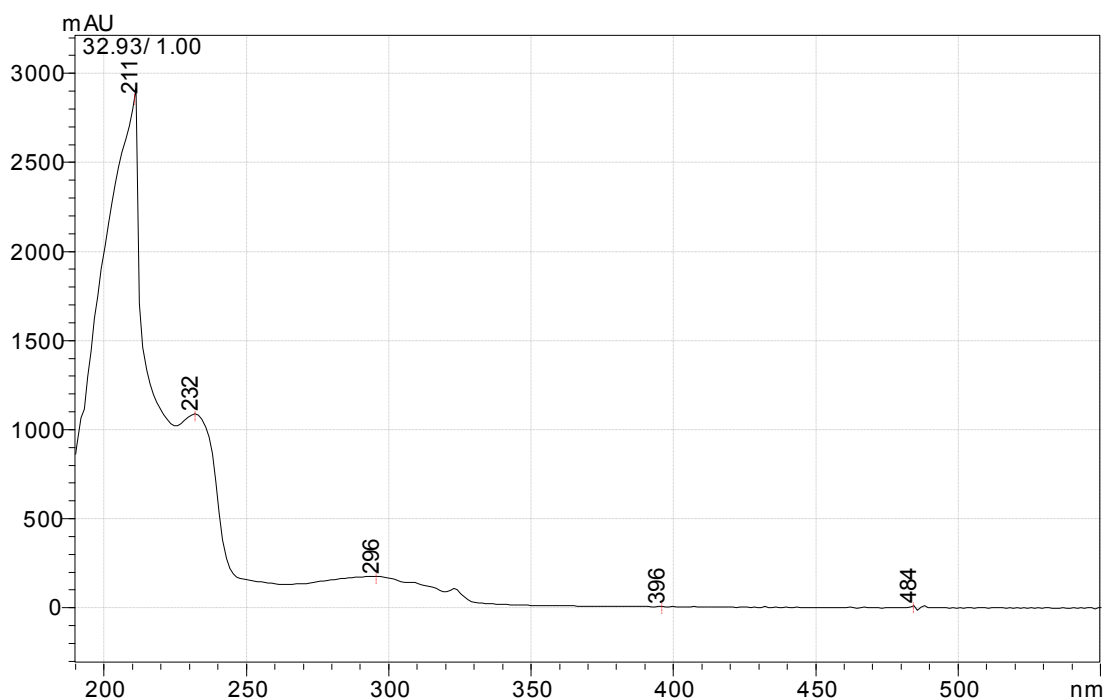


Figure S16. UV spectrum of the fraction eluting at 32.93 minute. In this fraction (29-38 min) we find several hydroxyl-PAHs, among them, 2-naphthol.

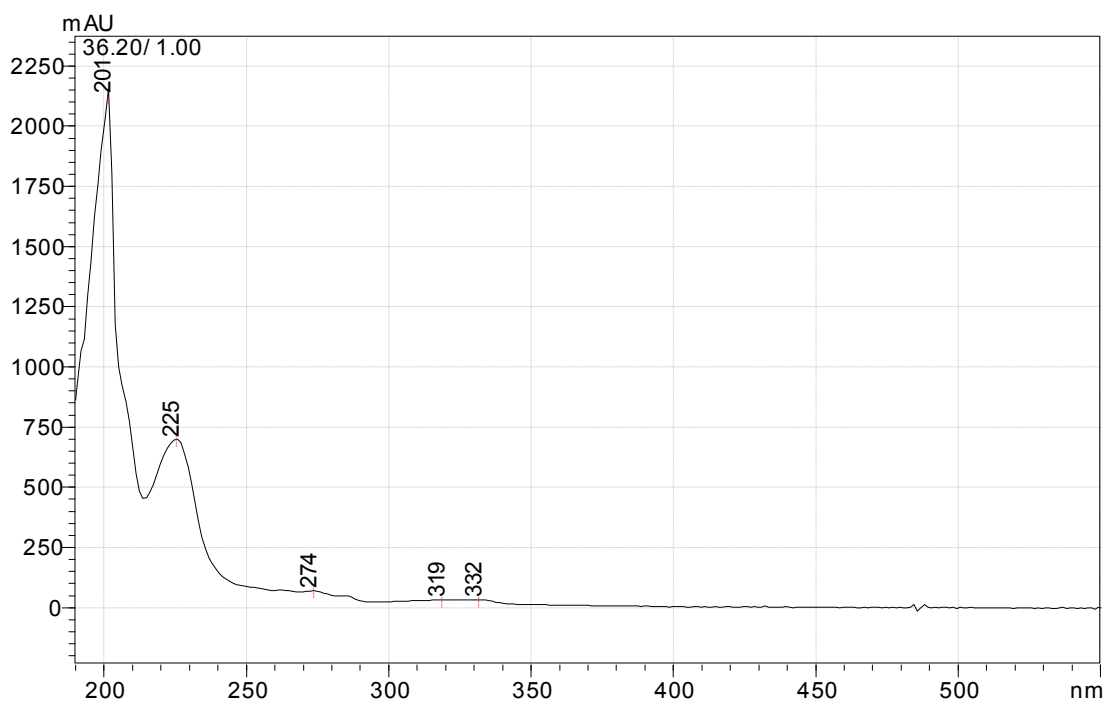


Figure S17. UV spectrum of the fraction eluting at 36.20 minute. It seems that 1-naphthol is present at high concentration. Reinjection of this fraction (29-38 min) into the HPLC system will allow us to identify unambiguously of several hydroxy-PAHs, among them, 1 and 2-naphthol and the 2-hydroxy-phenanthrene as we can below.

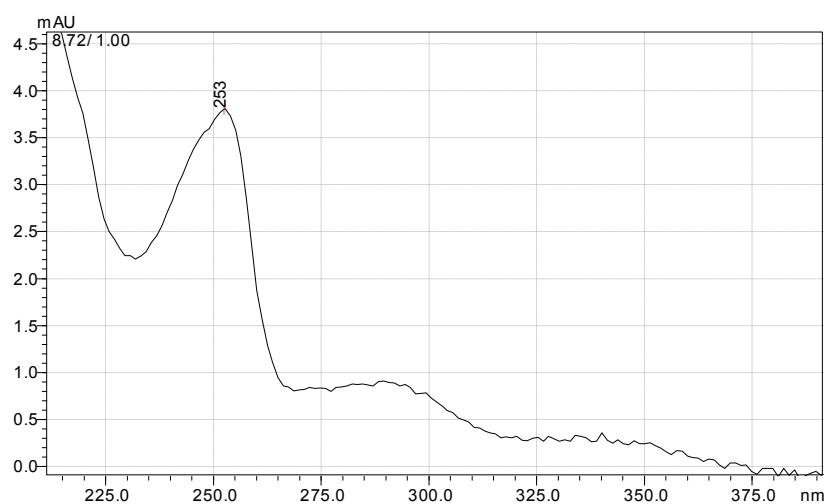


Figure S18. The fraction eluting at 29-38 minute from the solid-phase extraction column was re-injected into the HPLC column. Here we can see the UV spectrum of 2-hydroxyphenanthrene eluted from the HPLC column at 8.72 min.

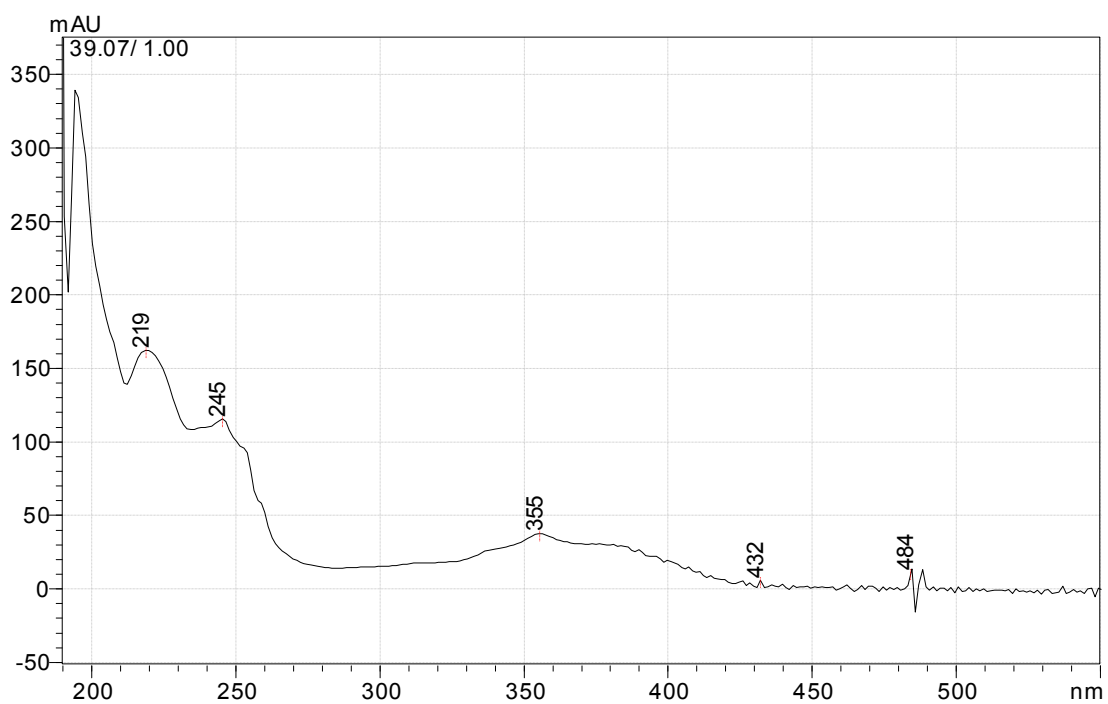


Figure S19. UV spectrum of the fraction eluting at 39.01 min. In the fraction eluting from the solid-phase extraction system between 39-45 min, we found, among other compounds, some heavy ketones and quinones.

Re-injection of this fraction into the HPLC system allowed the identification of several ketones.

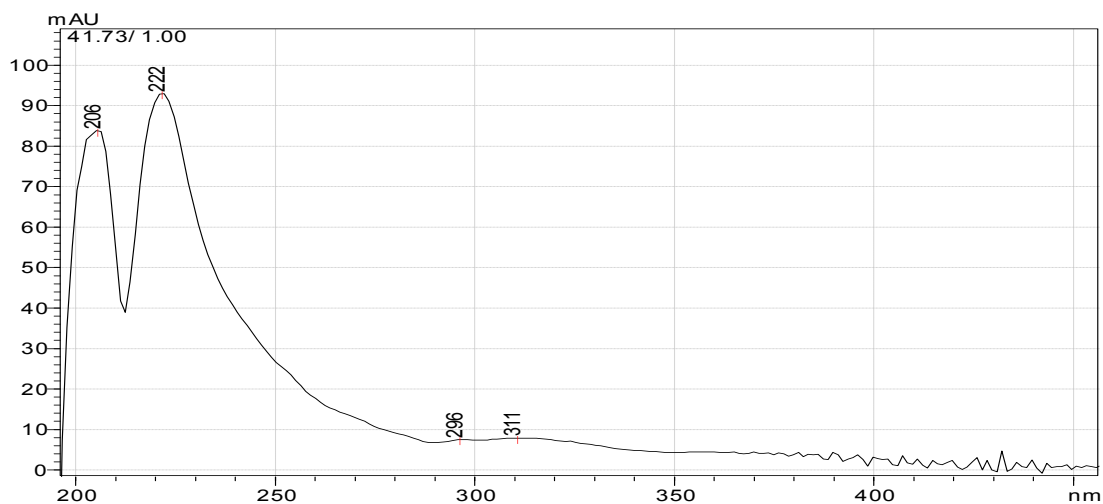


Figure S20. UV spectrum of the fraction eluting at 41.73 minute. In the Solid Phase Fraction collected between 41 and 45 min, we found carboxylic acids, some heavy quinones and anhydrides as we said above.

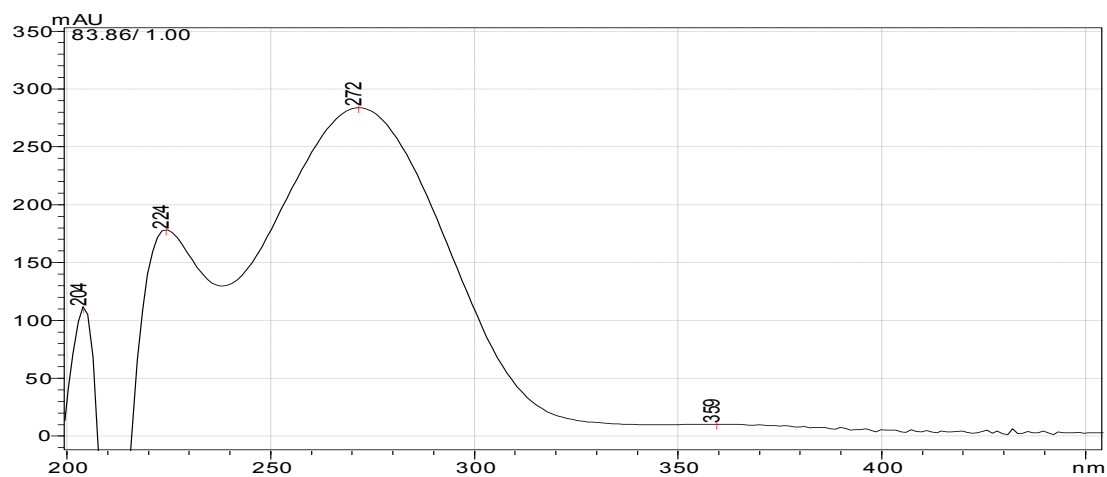


Figure S21. UV spectrum of the fraction eluting at 83.86 minute. This compound could not be identified but it is likely one ester.