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Additional Information

1 **Determination of oxygenated compounds in secondary organic aerosol**  
2 **from isoprene and toluene smog chamber experiments**

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21 **ABSTRACT**

22       The determination of multifunctional oxygenated compounds in secondary  
23 organic aerosols (SOA) usually requires a derivatization protocol prior to gas  
24 chromatography-mass spectrometry analysis (GC-MS). Our proposed protocol, a  
25 combination of O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) plus diluted  
26 N-methyl-N-trimethyl-silyltrifluoroacetamide (MSTFA) without catalyst, has improved  
27 the determination of carbonyls, polyhydroxyl-compounds, hydroxyl-carbonyls,  
28 hydroxyl-carboxylic acids and di-carboxylic acids. The optimized derivatization  
29 protocol has been successfully used for blanks, standard mixtures and photo-oxidation  
30 products from isoprene and toluene generated in a high-volume simulation chamber  
31 (European Photoreactor, EUPHORE).

32       Some previously identified degradation products for isoprene including tetrols as  
33 threitol, erythritol; 2-methyltetrols and 2-methylglyceric acid; and for toluene including  
34 nitrophenols, methyl-nitrophenols, benzaldehyde, p-cresol, benzoic acid, glyoxylic acid  
35 and methyl-glyoxylic acid, have been identified in our aerosol samples, thus confirming  
36 the successful applicability of the proposed derivatization protocol. Moreover, the  
37 reduction of artifacts and enhanced signal-to-noise ratio, have allowed us to extend the  
38 number of multifunctional compounds determined. These findings have demonstrated  
39 the validity of this analytical strategy, which will contribute to a better understanding of  
40 the atmospheric degradation chemistry of biogenic and anthropogenic pollutants.

41

42 **Keywords:** secondary organic aerosol, MSTFA, PFBHA, isoprene, toluene

43

## 44 **1. Introduction**

45 The photo-oxidation of volatile biogenic and anthropogenic pollutants, such as  
46 isoprene and toluene, contributes to the formation of secondary organic aerosol (SOA).  
47 A significant portion of aerosol constituents corresponds to polar organic compounds  
48 containing oxygenated functional groups - hydroxyl, carboxyl and carbonyl -. Thus,  
49 information on chemical composition is required both for understanding the behaviour  
50 of these particles in the atmosphere and for establishing their emission sources.  
51 Nevertheless, the identification and quantification are limited by the large number of  
52 products having low yields and the subsequent difficulty in analyzing them. SOA can be  
53 determined by indirect, off-line and on-line methodologies. A widely used off-line  
54 technique is gas chromatography - mass spectrometry (GC-MS) analysis, including a  
55 prior derivatization. Although different derivatization studies have been performed,  
56 there is no one universally accepted treatment for the determination of oxygenated  
57 organic compounds in SOA [1].

58 Current procedures for analyzing multifunctionalized condensed compounds are  
59 based on single-step or multi-step derivatization techniques, with or without catalyst.  
60 The keto and aldehyde moieties are typically transformed using O-(2,3,4,5,6-  
61 pentafluorobenzyl)hydroxylamine) (PFBHA) [2]. To include the determination of  
62 hydroxyl-carbonyl compounds, Yu [3] and Spaulding [4] combine of PFBHA with pure  
63 bis(trimethylsilyl) trifluoroacetamide (BSTFA) to produce trimethylsilyl-derivatives.  
64 The silylation of alcohols by means of N-methyl-N-trimethyl-silyltrifluoroacetamide  
65 (MSTFA) was evaluated by Edler [5]. In addition, several derivatization protocols –  
66 BF<sub>3</sub>/methanol, BSTFA pure with or without trimethylchlorosilylamine (TMCS) as catalyst,  
67 and a combination with PFBHA - were studied by Jaoui [6]. Finally, Wang [7] studied  
68 the fragmentation of synthesized diastereoisomeric 2-methyltetrols with MSTFA/TMCS  
69 plus pyridine.

70 Most of these protocols have been applied for the identification of SOA  
71 degradation products in simulation chamber experiments with isoprene under different  
72 oxidation conditions. Claeys [8] studied products of the acid-catalysed multiphase  
73 reactions with H<sub>2</sub>O<sub>2</sub> employing BSTFA. Szmigielski [9] and Surratt [10] carried out  
74 SOA characterization under high NO<sub>x</sub> conditions employing pure MSTFA/pyridine and  
75 MSTFA/TMCS, respectively. A study of PFBHA bifunctional carbonyl derivatives  
76 generated by photoirradiation of a mixture of toluene and isoprene was performed by

77 Ortiz [11,12]. Finally, Kleindienst [13] performed a chemical characterization of  
78 isoprene photo-oxidation products under low-NO<sub>x</sub> conditions employing  
79 BSTFA/pyridine. Furthermore, several studies have been published on the  
80 characterization of SOA from the photo-oxidation of toluene [14-17] and from the  
81 photo-oxidation of SOA other molecules such as xylenes, trimethylbenzenes and  $\alpha$ -  
82 pinene [3,18-19]. Moreover, these derivatization protocols have been applied to field  
83 samples [20-23]. Since only a small mass fraction has been assigned to multi-  
84 oxygenated small organic compounds [24], the selection of suitable protocols is still a  
85 challenge. For example, BSTFA reagent cannot be recommended for short chain acids  
86 or branched compounds that are hindered by steric impediment, since this effect has a  
87 strong influence over the rate of derivatization. Another key point is the formation of  
88 artifacts, due to an excess of derivatization reagent, this can lead to several by-products  
89 or unexpected derivatives [25].

90 In this study, the aim was to achieve a better GC-MS characterization of  
91 condensed oxygenated organic compounds, based on an optimized derivatization  
92 procedure. Two detection modes - electron impact ionization (EI) and chemical  
93 ionization (CI) -, standard compounds, bibliographic reference compounds and mass  
94 spectra libraries have been used to assess the correct identification of products. The  
95 strategy has been applied to aerosol filter samples from smog chamber photo-oxidations  
96 of isoprene and toluene. These pollutants were selected because of the low number of  
97 SOA products have been determined. Isoprene is emitted almost exclusively during  
98 daytime, in tropical forests or remote areas [26]. For this reason, our focus has been the  
99 identification and quantification of isoprene condensed products formed under low-NO<sub>x</sub>  
100 conditions in the absence of acidified conditions. In contrast toluene is mainly a traffic-  
101 related emissions, and thus constant urban NO<sub>x</sub> levels have been simulated.

102

## 103 **2. Experimental Section**

104 **2.1 Reagents.** The derivatization reagents employed were MSTFA (Lancaster,  
105 Morecambe, England), BSTFA (Fluka, Steinheim, Germany) and PFBHA (Sigma  
106 Aldrich, Steinheim, Germany). Silylation agents were combined with TMCS, supplied  
107 by Fluka. Formaldehyde, 4-fluorobenzaldehyde, glycolaldehyde, glyoxal, 4-  
108 hydroxybenzaldehyde, glyoxylic acid, isoprene, levoglucosan, 2-methyl-4-nitrophenol,  
109 2-methyl-5-nitrophenol, 3-methyl-4-nitrophenol, malic acid, malonic acid,  
110 methacrolein, methyl vinyl ketone, 4-nitrophenol, p-cresol, succinic acid and toluene

111 were obtained from Sigma Aldrich. Methylglyoxal and 1-phenyldodecane were  
112 supplied by Fluka. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and solvents of HPLC grade were  
113 purchased from Scharlau Chemie (Barcelona, Spain).

114 **2.2 Derivatization study.** Complete factorial designs were performed to study  
115 the effect of the silylation parameters, including derivatization reagent, concentration,  
116 catalyst, temperature and reaction time. In this set of experiments, different conditions  
117 were investigated: catalyst percentage in the 0 % - 10% range, reagent excess ranged in  
118 the 1:2 – 1:150 range and reaction time in the stove at 40-100 °C for a range of 1 h – 5  
119 h.

120 The standard mixture consisted of 1-hexanol, benzaldehyde, hydroxyacetone,  
121 levoglucosan, octanoic acid, glutaric acid, 2-ketoglutaric acid, 4-oxopentanoic acid,  
122 pentadecafluorooctanoic acid (Sigma Aldrich) and benzoic acid, oxalic acid and stearic  
123 acid (Fluka). The standard solutions were prepared in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (1:1) in a range  
124 of 0.5 – 20 mg/L. Blank and spiked control samples were also measured to guarantee a  
125 satisfactory level of quality.

126 **2.3 Simulation chamber.**

127 The experiments were carried out at the European Photoreactor (EUPHORE).  
128 This atmospheric simulation chamber (Valencia, Spain) consists of two half-spherical  
129 fluorinated ethene/propene covers of 200 m<sup>3</sup>, highly transparent to solar irradiation and  
130 enabling a homogeneous mix of pollutants. A more detailed description of the chambers  
131 is found in M. Martin-Reviejo et al., 2005 [27]. The facility was equipped with a white-  
132 type mirror system coupled to a Fourier Transform Infrared spectrometer; model Magna  
133 550 (Nicolet Instrument Corporation, Madison, USA). The isoprene and toluene  
134 concentrations were recorded with an absorption path length of 553.5 m, a spectral  
135 resolution of 1 cm<sup>-1</sup>. Simultaneously, an Eco Physics AG model AL-ppt-77312  
136 (Duernten, Switzerland) was used for measuring NO, NO<sub>2</sub> and NO<sub>x</sub> in the ppbV range.  
137 Aerosol profiles were recorded with a scanning mobility particle sizer (SMPS), model  
138 3080 (TSI Incorporated, Shoreview, USA). This system consists of a differential  
139 mobility analyzer, model 3081, and a condensation particle counter, model 3022A,  
140 which measure size distributions in the 11 – 982 nm diameter range in real time with a 5  
141 min scan rate. Sheath and aerosol sampling flows were 4 L/min and 0.30 L/min,  
142 respectively.

143 **2.3.1 Set-up experiments.** Since reactor walls could be a source of gas and/or  
144 particles, due to the off-gassing of compounds, preliminary test are required before each

145 run. For that, a chamber blank experiment was performed to assure the absence of  
146 possible artifacts. First, the high-volume chamber was flushed for 24 h with purified air.  
147 A blank pre-baked filter was sampled during 1h, after the exposure of smog chamber to  
148 the same solar radiation time. In all cases, the background was negligible, no aerosol  
149 compounds were detected. An outdoor photoreactor also requires the routinely  
150 characterization of chamber losses. Dilution process was determined using SF<sub>6</sub> [28] as a  
151 gas tracer and the aerosol losses were measured injecting ammonium nitrate by  
152 triplicate [29].

153 *2.3.2 Photo-oxidation smog chamber experiments.* The photoreactor was filled  
154 with air from an air purification system which included absorption driers (type HEA  
155 1400, Zander, Essen, Germany) with a molecular sieve (ECO 30%, MOL 70%  
156 Sogimair, Barcelona, Spain), providing air that had non-detectable hydrocarbons, NO<sub>x</sub>  
157 and particles - aerosol background of  $0.010 \pm 0.005 \mu\text{g}/\text{m}^3$  -. Photo-oxidation  
158 experiments of isoprene and toluene were carried out by duplicate with a high  
159 reproducibility in the aerosol formation (calculated from aerosol mass concentration).

160 The experiments consisted of the photo-decomposition of aromatic  
161 hydrocarbons under dry conditions (< 2% RH) in the absence of inorganic seed  
162 aerosols. Isoprene (2.1 ppm) was introduced in the photo-reactor via heated air stream;  
163 H<sub>2</sub>O<sub>2</sub> (7 ppm) was injected by a sprayer. The photo-oxidation of toluene (2.6 ppm) was  
164 performed following a similar protocol with constant NO<sub>x</sub> (30 ppb). Later, all the  
165 reactants were mixed with high power fans for 10 min before exposing them to sunlight.  
166 The sunlight exposure was conducted until the aerosol mass was steady; after that, the  
167 house of the chamber was closed. Measurements then continued for at least two hours to  
168 observe the aerosol decay behaviour. Finally, particles were collected at maximum  
169 aerosol formation, at a flow rate of 80 L/min, for 1 h, with quartz fibre filters of GF/A  
170 47 mm of diameter (Whatman, Brentford, England), pre-baked at 500 °C, 12 h to avoid  
171 organic binders. After weighting in a microbalance MC21S (Sartorius, Goettingen,  
172 Germany), filters were kept in the freezer at -4 °C.

173 *2.3.3 Aerosol total mass.* Aerosol volume concentrations from SMPS were  
174 converted to aerosol mass concentrations by assuming a density of 1 g cm<sup>-3</sup>, spherical  
175 shapes, multi-charge correction for the condensed organic material [29-31]. Correction  
176 of wall losses were performed by fitting the decrease of the integrated particle number  
177 concentrations over time to an exponential decay function after closure of the chamber  
178 to sunlight for each experiment. Size-resolved wall-loss corrections were not needed,

179 since negligible variations were observed during filter sampling for particle number  
180 concentration. Then, first-order loss coefficients –  $1.0 \times 10^{-4} \text{ s}^{-1}$  and  $1.4 \times 10^{-4} \text{ s}^{-1}$ ,  
181 respectively - were determined from measured changes in aerosol volume concentration  
182 using the equation proposed by McMurry et al., 1985 [32]. Similar coefficients were  
183 used to correct the measured aerosol volume concentrations [12,29-31]. Finally, the  
184 total mass concentrations obtained from SMPS system data were compared with  
185 gravimetric measurements of pre-baked filters sampled.

186 **2.4 Sample treatment.** Half of the filter was extracted with 5 ml of  
187  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  (1:1) mixture and with sonication. The extract solution was centrifuged  
188 at 2000 rpm for 20 min, and the supernatant was concentrated in a nitrogen stream to  
189 dryness and dissolved in 1.5 ml of  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  (1:1). The extract was divided into  
190 three equal portions and each one was brought to dryness by a nitrogen stream. After  
191 this, the following reagents were added: 0.5 ml of  $\text{CH}_3\text{CN}$ , 150  $\mu\text{L}$  of PFBHA solution  
192 of 1000 mg/L in  $\text{CH}_3\text{CN}$  and 50  $\mu\text{l}$  of a 4-fluorobenzaldehyde solution (15 mg/L) as an  
193 internal standard of carbonyl derivatization. This mixture was left in darkness at room  
194 temperature for 24 hours, after it was dried. It was then dissolved in 145  $\mu\text{L}$  of MSTFA  
195 solution (1:150 in hexane), adding 5  $\mu\text{l}$  of a chlorosuccinic acid solution (5 mg/L) as an  
196 internal standard of hydroxyl derivatization and heated at 90 °C for 1 h. Finally, 1  $\mu\text{L}$   
197 was injected in the GC-MS.

198 **2.5 Chromatographic conditions.** TRACE-DSQ II GC-MS was used (Thermo  
199 Fisher Scientific Co., Waltham, MA, USA). An HP-5MS column of 30 m  $\times$  0.25 mm  
200 I.D  $\times$  0.25  $\mu\text{m}$  film thickness (Crosslinked 5% Ph Me Siloxane) was supplied by  
201 Agilent Technologies (Santa Clara, USA). The chromatograph was programmed at 60  
202 °C for 1 min, then ramped at a rate of 10 °C/min to 250 °C, 5 °C/min to 280 °C and held  
203 at 280 °C for 10 min. The injection port was held at 280 °C and the transfer line from  
204 GC to MS was held at 300 °C. Samples were injected in split (1:20) mode via an  
205 automatic injector, using on column helium flow of 1 ml/min. The EI-voltage was 70  
206 eV, while, in the CI mode was 120 eV -with a  $\text{CH}_4$  flow of 1.3 L/min-. We worked in  
207 full scan mode ( $m/z$  50 – 650) with the ion source temperature at 200 °C and the  
208 quadrupole temperature at 100 °C.

209  
210  
211



### 212 **3. Results and discussion**

213 **3.1 Derivatization study.** The silylation process was studied under different  
214 conditions (BSTFA or MSTFA reagent, solvent, reaction time, temperature and catalyst  
215 percentage) - maintaining the carbonyl derivatization conditions -. For this, the  
216 derivatization yields were calculated for the standard mixture, including a primary  
217 alcohol, a polyhydroxylated compound, an aldehyde, a hydroxyl-ketone and several  
218 acids (two carboxylic linear, one aromatic, two dicarboxylic, two keto-carboxylic and  
219 one fluorinated). The best results were obtained for PFBHA plus BSTFA concentrated  
220 with 1% TMCS (yield > 95%) and PFBHA plus MSTFA in a 1:150 hexane dilution  
221 without catalyst (yield > 99%), except for pentafluorooctanoic acid with lower  
222 recoveries in all the conditions evaluated. Table 1a summarised the results obtained for  
223 all derivatization combinations under optimized conditions. In all cases, the reaction  
224 occurred at room temperature for 24 hours and then at 90 °C for an hour without  
225 addition of pyridine. Since a single derivatization may not be sufficient to identify  
226 aromatic or hydroxyl-carbonyl compounds – misidentification problems – [22], the  
227 mixture was previously derivatized with PFBHA. In this sense, the reaction yields of  
228 four critical model compounds – benzaldehyde, hydroxyacetone, 2-ketoglutaric acid,  
229 and 4-oxopentanoic acid - were specially evaluated. Quantitative recoveries (90-102%)  
230 demonstrated that this double derivatization treatment permits the proper determination  
231 of hydroxyl-carbonyl compounds even with  $\alpha$ -hydrogen. Reproducibility greater than  
232 90% and high coefficients for linear correlation ( $r^2 > 0.99$ ) were obtained.

233 The main problems with derivatization protocols are the memory column effects  
234 for gas chromatography and the high amount of artifacts that reagents produce in the  
235 chromatogram. In our case, the analysis of blank filters showed the absence of artifacts  
236 due to sampling material. Moreover, the chromatograms of blank derivatized filters  
237 were analyzed by extracting the m/z 73 ion fragment  $[\text{Si}(\text{CH}_3)_3]^+$  and the m/z 181 ion  
238 fragment  $[\text{C}_6\text{F}_5\text{CH}_2]^+$ , since they are specific for hydroxyl and carboxylic compounds  
239 and for carbonyl compounds, respectively [1,33] (see Table 1b).

240 According to the results shown in Table 1, the combined derivatization protocol  
241 of PFBHA plus MSTFA under diluted conditions promoted fewer and smaller artifacts  
242 and a wide region free from overlap peaks than PFBHA plus pure BSTFA, enabling a  
243 better determination of small polar compounds that elute at the beginning of the  
244 chromatogram. To confirm these better chromatographic characteristics, we carried out  
245 a comparison of both derivatization protocols for spiked control filters. Small size

246 compounds and hindered compounds such as oxalic acid, malonic acid and 4-  
247 oxopentanoic acid were better determined by the PFBHA plus diluted MSTFA reagents,  
248 which avoided overlapping elution and showed better derivatization recoveries.

### 249 ***3.2 Photochemical oxidation of isoprene: qualitative results.***

250 The maximum mass concentration of aerosol formation obtained 5.5 hours after  
251 the reaction started, was 31  $\mu\text{g}/\text{m}^3$ , with an aerosol yield of 1%, which coincides with  
252 Kleindienst [13], even in the absence of seed aerosol. Aerosol yield was determined as  
253 the aerosol mass concentration formed as a function of the precursor consumption [13].  
254 Figure 1 shows the extracted ion chromatogram characteristic of the PFBHA/MSTFA  
255 derivatization ( $m/z$  73 and 181).

256 The degradation products herein determined have been classified in different  
257 categories. Standard compounds are those that their identification on the basis of  
258 commercial reagents; tentative compounds are those whose structure can be proposed  
259 on the basis of experimental information ( $m/z$  fragments and their intensity of MS  
260 spectrum, chemical properties and comparison with MS spectra in bibliographic  
261 references), but cannot be confirmed; and, finally, unknown compounds are those for  
262 which no specific structure can be proposed due to their low response or undefined MS  
263 spectra.

264 Some of the major SOA compounds here determined, tetrols and methyl-tetrols -  
265 threitol, erythritol, 2-methylthreitol and 2-methylerythritol-, have been observed  
266 previously using the BSTFA reagent. These poly-hydroxylated compounds were  
267 identified according to EI-mass spectra [7,13,22,34]. In our study, the 2-methyl tetrols  
268 are products of isoprene photo-oxidation with low  $\text{NO}_x$  in the absence of acidic aerosol  
269 seeds. Regarding minor SOA compounds, 2-methylglyceric was detected at a retention  
270 time of 11.39 min with the  $m/z$  219 as the main fragment and the same fragmentation  
271 path described by Szmigielski [9]. Additionally, several gas phase products are often  
272 observed in particulate phase as artifacts or due to their gas/particle partitioning [12].  
273 Methyl-butenediols are major gaseous products reported at low concentrations in  
274 particle phase from the degradation of isoprene in the absence of  $\text{NO}_x$  [8,13,26].  
275 Although, they have not been identified in our samples, two C4-polyhydroxyl  
276 compounds (MW 112) have been registered at 11.64 and 12.25 min. Neither, C5-  
277 alkenetriol compound or hydroperoxide compounds (which require other analytical  
278 conditions to be detected but have been identified previously [10,13]) have not been  
279 identified in our samples; however, other more oxidized compounds, C5-hydroxyl

280 carboxylic acids have been detected. Methacrolein, methyl vinyl ketone, glycolaldehyde  
281 and hydroxyacetone have been also detected.

282 Moreover, the use of our optimized derivatization process has allowed us to  
283 determine new condensed products consistent with isoprene degradation mechanisms  
284 [22,26,35]. The identification of dicarboxylic acids with short retention times - oxalic,  
285 malonic, butenedioic and succinic acids-, has been supported from standards. Under  
286 conditions of absence of NO<sub>x</sub>, SO<sub>2</sub> and seed particles, their formation can be justified  
287 by the oxidation of intermediate 1,2 diols, described in isoprene - H<sub>2</sub>O<sub>2</sub> photo-oxidation  
288 [20]. Moreover, malic acid has been identified using a standard ( $t_r = 13.35$  min).  
289 Although described in field samples and proposed as late products of forest vegetation  
290 emissions [20], malic acid is first reported here *in a chamber study*. Several unknown  
291 compounds have been observed, but we cannot propose any specific structure due to  
292 their low response or undefined MS spectra. Finally, the following tentative compounds  
293 have been identified based on their EI and CH<sub>4</sub>-CI mass spectra, which appear in  
294 *Appendix A. Supplementary data 1*.

295 *2-Methyl-propene-1,3-diol*. The mass spectrum of the derivative showed  
296 fragments at  $m/z$  232 [M]<sup>+</sup>, 217 [M-15]<sup>+</sup>, 189 [M-43]<sup>+</sup>, 159 [M-73]<sup>+</sup> and 147,  
297 corresponding to the fragment [(CH<sub>3</sub>)<sub>3</sub>Si-O-Si(CH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Ion fragment 143 [M-89]<sup>+</sup>  
298 presents high intensity due to the fact that it can be originated from both parts of the  
299 molecule. We also observed ions at  $m/z$  132 [M-100]<sup>+</sup>, attributed to the loss of [CH-O-  
300 Si(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>, 103 [CH<sub>2</sub>-O-Si(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup> and 73 [Si(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>. Moreover, the fragments at  $m/z$   
301 132 and 103 strongly suggested the presence of a double carbon bond and a primary  
302 alcohol proposed by Little et al., [25]. The CI-spectrum confirmed its molecular weight  
303 with a high intensity of [M+1] fragment. The detection of this diol agrees with the fact  
304 that the degradation of isoprene in the absence of NO<sub>x</sub> follows the mechanism of  
305 peroxy radicals proposed by [22,26].

306 *2-Hydroxy-2-methylpropionic acid*. The derivative fragments were  $m/z$  246  
307 [M]<sup>+</sup>, 231 [M-15]<sup>+</sup>, 155 [M-89]<sup>+</sup> and 147. Moreover, we detected the characteristic ion  
308 of carboxylic acids and hydroxyl group ( $m/z$  117 and 73). The ion at  $m/z$  143 [M-103]<sup>+</sup>,  
309 is the base peak in the EI mass spectra, explained by the loss of [(CH<sub>2</sub>-O-Si(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>.  
310 The fragments observed were consistent with the presence of a compound with both a  
311 primary alcohol and a carboxylic group. These assumptions of a double oxidized C4-  
312 isoprene product were confirmed by its high polarity - retention time of 7.12 min – and  
313 the presence of ions at  $m/z$  103 and 117.

314 *2-Methyl-buta-1,3-diene-1,3-diol*. The fragmentation pattern of the derivative  
315 provided fragments at  $m/z$  244, 229, 185, 147 and 73 corresponding to  $[M]^+$ ,  $[M-15]^+$ ,  
316  $[M-59]^+$ ,  $[(CH_3)_3Si-O-Si(CH_3)_2]^+$  and  $[Si(CH_3)_3]^+$ . The high intensity of the ion at  $m/z$   
317 142  $[M-102]^+$  was related to the loss of  $[(CH-O-Si(CH_3)_3)]^+$ . Due to the short retention  
318 time, we postulated that a highly polar molecule would result from the oxidation of the  
319 first and third carbon atoms of isoprene, following the peroxy radical pathway.

320 *2-Methylen-butandioic acid or 2-methylbutenedioic acid (and related*  
321 *compounds)*. The derivative showed the fragments at  $m/z$  259, 231, 215 and 157,  
322 interpreted as  $[M-15]^+$ ,  $[M-43]^+$ ,  $[M-59]^+$  and  $[M-117]^+$ , respectively. The mass  
323 spectrum showed the fragments  $[(CH_3)_3Si-O-Si(CH_3)_2]^+$ ,  $[(COO-Si(CH_3)_3)]^+$  and  
324  $[Si(CH_3)_3]^+$ . The detection of these ions indicated the presence of two hydroxyl groups,  
325 at least one of them being a carboxylic acid group. Although the CI-spectrum was not  
326 conclusive, there were some facts that allowed us to propose these dicarboxylic acids.  
327 The presence of their saturated homologue with comparable EI-fragmentation pattern,  
328 detected at 11.11 min, supports our proposal since Jang [15] and Edney [36]  
329 independently reported similar unsaturated and saturated serial compounds in photo-  
330 oxidation reactions. Unsaturated compounds, generated as primary products, could form  
331 saturated secondary products in the system during the reaction. On the other hand, the  
332 formation of both C5-hydroxyl carboxylic acids is also reinforced by the detection of a  
333 C5-hydroxyl dicarboxylic acid (MW 148) and a C5-polyhydroxyl carboxylic acid (MW  
334 148) eluted at 9.50 and 13.73 min, respectively. The probable precursors of these related  
335 compounds may be the intermediate 1,2-diol isomers ( $C_5H_{10}O_2$ ) proposed by Claeys  
336 [20] and the C5-triols proposed by Kleindienst [13].

### 337 ***3.3 Photochemical oxidation of isoprene: quantitative results.***

338 The use of calibration solutions for standard compounds and appropriate  
339 surrogate compounds for newly tentative compounds, allowed us the estimation of the  
340 concentrations of the multi-oxygenated compounds formed. The concentrations ( $\mu g/m^3$ )  
341 of all the compounds determined are provided in Table 2. The classification of the  
342 products determined was also based on standard, tentative and unknown compounds, as  
343 previously defined.

344 The most abundant compounds were threitol, erythritol, 2-methylthreitol and 2-  
345 methylerythritol. The concentrations obtained from the methyl-tetrols - 2-methylthreitol  
346 and 2-methylerythritol – are quite consistent with previously reported product yields  
347 [13,20]. The main newly identified products were 2-hydroxy-3-methylsuccinic, 2-

348 methyl-propene-1,3-diol and 2-hydroxy-2-methylpropionic acid, indicating that these  
349 compounds can serve as suitable tracers for low-NO<sub>x</sub> isoprene photo-oxidation but  
350 additional confirmation should be accomplished with further experimentation. In  
351 comparison with previous studies, the total contribution of alcohols, aldehydes and  
352 ketones is reduced, while the amount of dicarboxylic and hydroxyl-carboxylic acids is  
353 increased. Therefore, the photo-oxidation of isoprene in the absence of NO<sub>x</sub>, performed  
354 in our high-volume smog chamber and induced by natural sunlight, seems to promote  
355 the formation of more oxidized products. The percentage of identified SOA fraction was  
356 12% using authentic standards. These values could increase to ~55% if the isoprene  
357 degradation tentative products are confirmed.– unknown compounds were not taken  
358 into account -, increasing the identified SOA fraction. Previous reported values were  
359 ranged between 12 – 34% [10]. This improvement is the result of using our  
360 PFBHA/MSTFA optimized protocol, which facilitated the determination of more  
361 oxidized multifunctionalized compounds ( $t_r < 9$  min).

362

### 363 ***3.4 Photochemical oxidation of toluene: qualitative results.***

364 SOA compounds were obtained from the toluene photo-oxidation reaction under  
365 constant low NO<sub>x</sub> concentrations, simulating traffic emissions in an urban zone. The  
366 maximum mass concentration of aerosol formation, obtained 7 hours after the reaction  
367 start, was 1050  $\mu\text{g}/\text{m}^3$  with an aerosol yield of 33%. A typical extracted ion  
368 chromatogram of PFBHA/MSTFA derivatives in EI-mode is shown in Figure 2. Some  
369 of the ring-retaining products and ring-opening products have been previously detected  
370 [14-16]. The p-cresol was formed from an initial OH attack; meanwhile, the addition of  
371 NO<sub>2</sub> to the oxidized aromatic ring leads to the formation of 4-nitrophenol, 2-methyl-5-  
372 nitrophenol, 3-methyl-4-nitrophenol and 2-methyl-4-nitrophenol. Moreover, the small  
373 amount of benzaldehyde and the high concentration of benzoic acid registered are due  
374 to the fact that benzaldehyde further reacts with the OH radical, forming a  
375 benzoylperoxy radical and leading to benzoic acid. As the photo-oxidation reaction  
376 advances, oxygenated ring-opening products are also generated, such as glycolaldehyde,  
377 hydroxyacetone, n-oxopentenoic acid, glyoxylic acid and methyl-glyoxylic acid.  
378 Compounds such as glyoxylic and n-oxopentanoic acid were previously identified [17].  
379 The detection of glyoxal and methylglyoxal in the particle phase was interpreted as the  
380 result of the cleavage process of condensed polymeric or oligomeric compounds [37].  
381 However, polyketones and hydroxyl polyketones, expected at lower NO<sub>x</sub> initial

382 conditions [36], were not present. This absence could be due to our experimental  
383 conditions (constant NO<sub>x</sub> addition, lower toluene concentrations and natural sunlight).

384 Other multifunctional products have been newly determined in this study. The  
385 ring-retaining products were two dihydroxynitrotoluene isomers from the OH and NO<sub>2</sub>  
386 attack, and 4-hydroxybenzaldehyde, from the OH ring addition at the para-position in  
387 benzaldehyde, which eluted at 16.19, 16.56 and 18.04 min, respectively. In addition,  
388 reactions leading to the formation of ring-opening compounds can be deduced from the  
389 mechanisms described in [14,15]. Thus, 2-methylbutendial - identified using a  
390 laboratory synthesized standard- came from the direct oxidative ring cleavage, malonic  
391 acid from the oxidation of ring-opening carbonyl products and succinic acid from the  
392 oxidation of 4-oxo-2-butenoic acid. Although, several additional products were  
393 observed, only a few tentative compounds were identified from EI and CH<sub>4</sub>-CI mass  
394 spectra (*Appendix B. Supplementary data 2*).

395 *n-Oxopentanoic acid*. The fragmentation pattern of the derivative provided at  
396 m/z 188, 173, 129, 117 and 73 corresponded to [M]<sup>+</sup>, [M-15]<sup>+</sup>, [M-59]<sup>+</sup>, [COO-  
397 Si(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>, and [Si(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>. The carbonyl group of this ring-opening oxocarboxylic  
398 acid (MW 116) should be in the C2 or C3 position since its MS spectrum is similar to  
399 the reference compound of 4-oxopentanoic acid; however, it appeared at a different  
400 retention time. Moreover, the unsaturated homologue n-oxopentenoic acid was observed  
401 at 8.10 min.

402 *Butenedioic acid*. The mass spectrum of the derivative showed fragments at m/z  
403 260 [M]<sup>+</sup>, 245 [M-15]<sup>+</sup>, 217 [M-43]<sup>+</sup>, 201 [M-59]<sup>+</sup>, 117 [COO-Si(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>, and 73  
404 [Si(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>. The structure of double-derivatized dicarboxylic acid agrees with an  
405 elution at 0.4 minutes later to the succinic acid (saturated homologue). The CI mass  
406 spectrum reinforces this identified C4-carboxylic acid, probably formed from the  
407 oxidative ring opening of toluene.

408 *Methylmuconaldehyde*. The mass spectrum of the derivative showed the  
409 fragments at m/z 311 [M]<sup>+</sup> and the characteristic fragments of the PFBHA derivatization  
410 m/z 195, 181 and 116 [M-181]<sup>+</sup>. For benzene photo-oxidation reactions  
411 muconaldehyde, has been proposed as an intermediate SOA precursor [27]. However,  
412 this is the first time that it has been experimentally determined in toluene photo-  
413 oxidation.

414  
415

416 **3.5 Photochemical oxidation of toluene: quantitative results.**

417 The concentrations ( $\mu\text{g}/\text{m}^3$ ) of the identified compounds are provided in Table 3.  
418 As in the case of the isoprene experiments, the use of calibration solutions for standard  
419 compounds or appropriate surrogate compounds for newly tentative compounds,  
420 allowed us to estimate the concentrations of the multi-oxygenated compounds formed.  
421 The more abundant species were 2-methyl-4-nitrophenol, 3-methyl-4-nitrophenol,  
422 succinic acid, butenedioic acid and benzoic acid. Some of these compounds had been  
423 previously quantified by Hamilton et al. [17]. The aerosol mass concentration obtained  
424 in our experiment was higher than in Hamilton et al., 2005, who used a similar initial  
425 toluene concentration but a doubled NO<sub>x</sub> level. Our methodology was better for the  
426 determination of some species like glyoxylic, 4-oxopentanoic and 4-  
427 hydroxybenzaldehyde, because standard calibration solutions could be used and no co-  
428 elution problems were observed. For other compounds, e.g. benzaldehyde, results of  
429 both studies were comparable. However, for compounds, such as benzoic acid and 3-  
430 methyl-4-nitrophenol, the levels herein quantified were higher.

431 The percentage of identified SOA fraction was 5.5% using authentic standards.  
432 These values could increase to ~15% if the toluene degradation tentative products are  
433 confirmed, improving previous studies – although the experimental conditions are not  
434 exactly the same - [12,17]. The constant low NO<sub>x</sub> concentrations in our experiment,  
435 which simulate traffic emissions in an urban zone – instead of a high initial NO<sub>x</sub>  
436 concentration of a short-term emission-, promote more extensively oxidized pathways.  
437 Under our photo-oxidation conditions, 80% of the identified products are associated  
438 with multifunctional ring-opening products (oxo-carboxylic acids and dicarboxylic  
439 acids).

440 This improvement can be attributed to some of the determined products, first  
441 quantified in this study, eluted at the beginning of the chromatogram (artifact free zone  
442 enhanced by our proposed methodology).

443

444 **4. Conclusion**

445 A better understanding of the atmospheric degradation of biogenic and  
446 anthropogenic pollutants involves the development of high throughput analytical  
447 protocols. Our optimized derivatization, based on PFBHA/MSTFA, has improved the  
448 detection and quantification of multi-oxygenated photochemical products by GC-MS.  
449 The interpretation of chromatograms has been easier, since enhanced features have been

450 achieved for small molecules, containing hydroxyl, carbonyl and/or carboxylic groups.  
451 These advantages have allowed us to obtain satisfactory results in the application of this  
452 methodology to high-volume photoreactor samples. The number of secondary organic  
453 compounds identified has been extended, increasing the SOA fraction quantified from  
454 isoprene and toluene photo-oxidations. Similar results using our proposed derivatization  
455 protocol are also expected for other aerosol samples.

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460

461 **Appendix A. Supplementary data 1.** Mass spectra obtained for derivative products  
462 from isoprene photo-oxidation.

463 **Appendix B. Supplementary data 2.** Mass spectra obtained for derivative products  
464 from toluene photo-oxidation.

465

#### 466 **References**

- 467 [1] M. Hallquist, J.C. Wenger, U. Baltensperger, Y. Rudich, D. Simpson, M. Claeys, J.  
468 Dommen, N. M. Donahue, C. George, A. H. Goldstein, J. F. Hamilton, H. Herrmann, T.  
469 Hoffmann, Y. Iinuma, M. Jang, M. E. Jenkin, J. L. Jimenez, A. Kiendler-Scharr, W.  
470 Maenhaut, G. McFiggans, Th. F. Mentel, A. Monod, A. S. H. Prevot, J. H. Seinfeld, J.  
471 D. Surratt, R. Szmigielski, J. Wildt, *Atmos. Chem. Phys.* **9**, 3555 (2009).
- 472 [2] J. Yu, H.E. Jeffries, R.M. Le Lacheur, *Environ. Sci. Technol.* **29**, 1923 (1995).
- 473 [3] J. Yu, R. Flagan, J. Seinfeld, *Environ. Sci. Technol.* **32**, 2357 (1998).
- 474 [4] R.S. Spaulding and M.J. Charles, *Anal. Bioanal. Chem.* **372**, 808 (2002).
- 475 [5] M. Edler, D. Metzger, N. Jakubowski, M. Linscheid, *J. Anal. Atom. Spectrom.* **17**,  
476 1209 (2002).
- 477 [6] M. Jaoui, T.E. Kleindienst, M. Lewandowski, J.H. Offenberg, E.O. Ednby, *Anal.*  
478 *Chem.* **76**, 4765 (2004).
- 479 [7] W. Wang, G. Vas, R. Dommisse, K. Loones, M. Claeys, *Rapid. Comm. Mass.*  
480 *Spectrom.* **18**, 1787 (2004).
- 481 [8] M. Claeys, W. Wang, A.C. Ion, I. Kourtev, A. Gelencser, W. Maenhaut, *Atmos.*  
482 *Environ.* **38**, 4093 (2004).



483 [9] R. Szmigielski, J.D. Surratt, R. Vermeylen, K. Szmigielski, J.H. Kroll, N.L. Ng,  
484 M.S. Murphy, A. Sorooshian, J.H. Seinfeld, M. Claeys, M. J. Mass. Spectrom. **42**, 101  
485 (2007).

486 [10] J.D. Surratt, S.M. Murphy, J.H. Kroll, N.L. Ng, L. Hildebrandt, A. Sorooshian, R.  
487 Szmigielski, R. Vermeylen, W. Maenhaut, M. Claeys, R.C. Flagan, J.H. Seinfeld, J.  
488 Phys. Chem. A. **110**, 9665 (2006).

489 [11] R. Ortiz, K. Enya, K. Sekiguchi, K. Sakamoto, Atmos. Environ. **43**, 382, (2009).

490 [12] R.M. Healy, J.C. Wenger, A. Metzger, J. Duplissy, M. Kalberer, J. Dommen  
491 Atmos. Chem. Phys. **8**, 3215 (2008).

492 [13] T.E. Kleindienst, M. Lewandowski, J.H. Offenberg, M. Jaoui, E.O. Edney, Atmos.  
493 Chem. Phys. **9**, 6541 (2009).

494 [14] H.J.L. Forstner, R. Flagan, J. Seinfeld, Environ. Sci. Technol. **31**, 1345 (1997).

495 [15] M. Jang and R.M. Kamens, Environ. Sci. Technol. **35**, 3626 (2001).

496 [16] T.E. Kleindienst, T.S. Conver, C.D. McIver, E.O. Edney, J. Atmos. Chem. **47**, 79  
497 (2004).

498 [17] J. F. Hamilton, P.J. Webb, A. C. Lewis, M. M. Reviejo, Atmos. Environ. **39**, 7263,  
499 (2005)

500 [18] G.E. Orzechowska, H.T. Nguyen, S.E. Paulson, J. Phys. Chem. A. **109**, 5366  
501 (2005).

502 [19] M. Claeys, R. Szmigielski, I. Kourtchev, P. Van Der Veken, R. Vermeylen, W.  
503 Maenhaut, M. Jaoui, T.E. Kleindienst, M. Wandowski, J. Offenberg, E.O. Edney,  
504 Environ. Sci. Technol. **41**, 1628 (2007).

505 [20] M. Claeys, B. Graham, G. Vas, W. Wang, R. Vermeylen, V. Pashynska, J.  
506 Cafmeyer, P. Guyon, M.O. Andreae, P. Artaxo, W. Maenhaut, Science. **313**, 1173  
507 (2004b).

508 [21] M. Jaoui, T.E. Kleindienst, M. Lewandowski, J.H. Offenberg, E.O. Edney,  
509 Environ. Sci. Technol. **39**, 5661 (2005).

510 [22] O. Böge, Y. Miao, A. Plewka, H. Herrmann, Atmos. Environ. **40**, 2501 (2006).

511 [23] I. Kourtchev, J. Warnke, W. Maenhaut, T. Hoffmann, M. Claeys, Chemosphere.  
512 **73**, 1308 (2008).

513 [24] C. Pio, C. Alves, A. Duarte, Atmos. Environ, **35**, 389 (2001).

514 [25] J.L. Little, J. Chromat. A. **844**, 1 (1999).

515 [26] L. Ruppert and K.H. Becker, Atmos. Environ, **34**, 1529 (2000).

516 [27] M. Martin-Reviejo and K Wirtz, Environ. Sci. Technol. **39**, 1045 (2005).

517 [28] R. Volkamer, B. Klotz, I. Barnes, T. Imamura, K. Wirtz, N. Washida, K.H. Becker,  
518 U. Platt. *Phys. Chem. Chem. Phys.* **4**, 1598 (2002).

519 [29] M.D. Hurley, O. Sokolov, T.J. Wallington, H. Tatekawa, M. Karasawa, B. Klotz, I.  
520 Barnes, K. H. Becker. *Environ. Sci. Technol.*, **35**, 1358 (2001).

521 [30] D. Paulsen, J. Dommen, M. Kalberer, A.S.H. Prevot, R. Richter, M. Sax, M.  
522 Steinbacher, E. Weingartner, U. Baltensperger. *Environ. Sci. Technol.*, **39**, 2668 (2005).

523 [31] U. Baltensperger, M. Kalberer, J. Dommen, D. Paulsen M. R. Alfarra, H. Coe, R.  
524 Fisseha, A. Gascho, M. Gysel, S. Nyeki, M. Sax, M. Steinbacher, A. S. H. Prevot, S.  
525 Sjogren, E. Weingartner, R. Zenobi. *Faraday Discuss.*, **130**, 265, (2005).

526 [32] P. H. McMurry, D. J. Rader. *Aerosol Science and Technology*, **4**, 249 (1985).[33]  
527 J.M. Halket, V.G. Zaikin, *J. Mass. Spectrom.* **9**, 1 (2003).

528 [34] A.L. Clements and J.H. Seinfeld, *Atmos. Environ*, **41**, 1825 (2007).

529 [35] W.F. Rogge, M.A. Mazurek, L.M. Hildemann, G.R. Cass, B.R.T. Simoneit,  
530 *Atmos. Environ*, **27**, 1309 (1993).

531 [36] E.O. Edney, D.J. Driscoll, W.S. Weathers, T.E. Kleindienst, T.S. Conner, C.D.  
532 McIver, W. Li, *Aerosol. Sci. Technol.* **35**, 998 (2001).

533 [37] B. Temime, R. M. Healy, J.C. Wenger. *Environ. Sci. Technol.*, **41**, 6514 (2007)  
534

535 **FIGURE CAPTIONS**

536

537 **Figure 1.** Chromatogram of the m/z 73+181 for an aerosol sample obtained from  
538 isoprene photo-oxidation (see code Table 2).

539

540 **Figure 2.** Chromatogram of the m/z 73+181 for an aerosol sample obtained from  
541 toluene photo-oxidation (see code Table 3).

542

543 **Table 1** Comparative analysis of derivatization protocols. a) Recovery percentages for  
544 standard solution and b) Artifact data for filter samples

545

546 **Table 2** Concentrations of oxygenated organic compounds identified in isoprene photo-  
547 oxidation.

548

549 **Table 3** Concentrations of oxygenated organic compounds identified in toluene photo-  
550 oxidation.

551

552 **Appendix A. Supplementary data 1.** Mass spectra obtained for derivative products  
553 from isoprene photo-oxidation. (a) 2-Methylpropene-1,3-diol in EI, (b) 2-  
554 Methylpropene-1,3-diol in CI, (c) 2-Hydroxy-2methylpropionic acid in EI, (d) 2-  
555 Methylbuta-1,3-diene-1,3-diol in EI, (e) 2-Methylen-butandioic acid or 2-  
556 methylbutenedioic acid in EI.

557

558 **Appendix B. Supplementary data 2.** Mass spectra obtained for derivative products  
559 from toluene photo-oxidation. (a) n-Oxopentanoic acid in EI, (b) Oxopentenoic acid in  
560 EI, (c) Butenedioic acid in EI, (d) Butenedioic acid in CI, (e) Methylmuconaldehyde.

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562