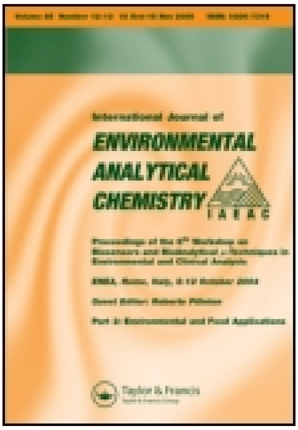

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Determination of oxygenated compounds in secondary organic aerosol from isoprene and toluene smog chamber experiments

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

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

Keywords: secondary organic aerosol; MSTFA; PFBHA; isoprene, toluene

1. Introduction

The photo-oxidation of volatile biogenic and anthropogenic pollutants, such as isoprene and toluene, contributes to the formation of secondary organic aerosol (SOA). A significant portion of aerosol constituents corresponds to polar organic compounds containing oxygenated functional groups hydroxyl, carboxyl and carbonyl. Thus, information on chemical composition is required both for understanding the behaviour of these particles in the atmosphere and for establishing their emission sources. Nevertheless, the identification and quantification are limited by the large number of products having low yields and the subsequent difficulty in analyzing them. SOA can be determined by indirect, off-line and on-line methodologies. A widely used off-line technique is gas chromatography–mass spectrometry (GC-MS) analysis, including

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a prior derivatisation. Although different derivatisation studies have been performed, there is no one universally accepted treatment for the determination of oxygenated organic compounds in SOA [1].

Current procedures for analysing multifunctionalised condensed compounds are based on single-step or multi-step derivatisation techniques, with or without catalyst. The keto and aldehyde moieties are typically transformed using O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine) (PFBHA) [2]. To include the determination of hydroxyl-carbonyl compounds, Yu [3] and Spaulding [4] combine PFBHA with pure bis(trimethylsilyl) trifluoroacetamide (BSTFA) to produce trimethysilyl-derivatives. The silylation of alcohols by means of N-methyl-N-trimethyl-silyltrifluoroacetamide (MSTFA) was evaluated by Edler [5]. In addition, several derivatisation protocols – BF_3/methanol, BSTFA pure with or without trimethylchlrosilylane (TMCS) as catalyst, and a combination with PFBHA - were studied by Jaoui [6]. Finally, Wang [7] studied the fragmentation of synthesised diastereoisomeric 2-methyltetrols with MSTFA/TMCS plus pyridine.

Most of these protocols have been applied for the identification of SOA degradation products in simulation chamber experiments with isoprene under different oxidation conditions. Claeys [8] studied products of the acid-catalysed multiphase reactions with H_2O_2 (hydrogen peroxide) employing BSTFA. Szmigielski [9] and Surratt [10] carried out SOA characterisation under high NO_x conditions employing pure MSTFA/pyridine and MSTFA/TMCS, respectively. A study of PFBHA bifunctional carbonyl derivatives generated by photoirradiation of a mixture of toluene and isoprene was performed by Ortiz [11,12]. Finally, Kleindienst [13] performed a chemical characterisation of isoprene photo-oxidation products under low-NO_x conditions employing BSTFA/pyridine. Furthermore, several studies have been published on the characterisation of SOA from the photo-oxidation of toluene [14–17] and from the photo-oxidation of SOA other molecules such as xylenes, trimethylbenzenes and α-pinene [3,18,19]. Moreover, these derivatisation protocols have been applied to field samples [20–23]. Since only a small mass fraction has been assigned to multi-oxygenated small organic compounds [24], the selection of suitable protocols is still a challenge. For example, BSTFA reagent cannot be recommended for short chain acids or branched compounds that are hindered by steric impediment, since this effect has a strong influence over the rate of derivatisation. Another key point is the formation of artefacts owing to an excess of derivatisation reagent, this can lead to several by-products or unexpected derivatives [25].

In this study, the aim was to achieve a better GC-MS characterisation of condensed oxygenated organic compounds, based on an optimised derivatisation procedure. Two detection modes – electron impact ionisation (EI) and chemical ionisation (CI) – standard compounds, bibliographic reference compounds and mass spectra libraries have been used to assess the correct identification of products. The strategy has been applied to aerosol filter samples from smog chamber photo-oxidations of isoprene and toluene. These pollutants were selected because of the low number of SOA products have been determined. Isoprene is emitted almost exclusively during daytime, in tropical forests or remote areas [26]. For this reason, our focus has been the identification and quantification of isoprene condensed products formed under low-NO_x conditions in the absence of acidified conditions. In contrast toluene is mainly a traffic-related emissions, and thus constant urban NO_x levels have been simulated.

2. Experimental

2.1 *Reagents*

The derivatisation reagents employed were MSTFA (Lancaster, Morecambe, England), BSTFA (Fluka, Steinheim, Germany) and PFBHA (Sigma Aldrich, Steinheim, Germany). Silylation agents were combined with TMCS, supplied by Fluka. Formaldehyde, 4-fluorobenzaldehyde, glycolaldehyde, glyoxal, 4-hydroxybenzaldehyde, glyoxylic acid, isoprene, levoglucosan, 2-methyl-4-nitrophenol, 2-methyl-5-nitrophenol, 3-methyl-4-nitrophenol, malic acid, malonic acid, methacrolein, methyl vinyl ketone, 4-nitrophenol, p-cresol, succinic acid and toluene were obtained from Sigma Aldrich. Methylglyoxal and 1-phenyldodecane were supplied by Fluka. Hydrogen peroxide (H_2O_2) and solvents of HPLC grade were purchased from Scharlau Chemie (Barcelona, Spain).

2.2 *Derivatisation study*

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

The standard mixture consisted of 1-hexanol, benzaldehyde, hydroxyacetone, levoglucosan, octanoic acid, glutaric acid, 2-ketoglutaric acid, 4-oxopentanoic acid, pentadecafluorooctanoic acid (Sigma Aldrich) and benzoic acid, oxalic acid and stearic acid (Fluka). The standard solutions were prepared in CH_2Cl_2/CH_3CN (1 : 1) in a range of 0.5–20 mg/L^{-1}. Blank and spiked control samples were also measured to guarantee a satisfactory level of quality.

2.3 *Simulation chamber*

The experiments were carried out at the European Photoreactor (EUPHORE). This atmospheric simulation chamber (Valencia, Spain) consists of two half-spherical fluorinated ethene/propene covers of 200 m^3, highly transparent to solar irradiation and enabling a homogeneous mix of pollutants. A more detailed description of the chambers is found in Martin-Reviejo and Wirtz [27]. The facility was equipped with a white-type mirror system coupled to a Fourier transform infrared spectrometer; model Magna 550 (Nicolet Instrument Corporation, Madison, USA). The isoprene and toluene concentrations were recorded with an absorption path length of 553.5 m, a spectral resolution of 1 cm^{-1}. Simultaneously, an Eco Physics AG model AL-ppt-77312 (Duernten, Switzerland) was used for measuring NO, NO_2 and NO_x in the ppbV range. Aerosol profiles were recorded with a scanning mobility particle sizer (SMPS), model 3080 (TSI Incorporated, Shoreview, USA). This system consists of a differential mobility analyser, model 3081, and a condensation particle counter, model 3022A, which measure size distributions in the 11–982 nm diameter range in real time with a 5 min scan rate. Sheath and aerosol sampling flows were 4 $L\,min^{-1}$ and 0.30 $L\,min^{-1}$, respectively.

2.3.1 *Set-up experiments*

Since reactor walls could be a source of gas and/or particles, owing to the off-gassing of compounds, preliminary test are required before each run. For that, a chamber blank experiment was performed to assure the absence of possible artefacts. First, the high-volume chamber was flushed for 24 h with purified air. A blank pre-baked filter was sampled during 1 h, after the exposure of smog chamber to the same solar radiation time. In all cases, the background was negligible, no aerosol compounds were detected. An outdoor photoreactor also requires the routinely characterisation of chamber losses. Dilution process was determined using SF_6 [28] as a gas tracer and the aerosol losses were measured injecting ammonium nitrate by triplicate [29].

2.3.2 *Photo-oxidation smog chamber experiments*

The photoreactor was filled with air from an air purification system which included absorption driers (type HEA 1400, Zander, Essen, Germany) with a molecular sieve (ECO 30%, MOL 70% Sogimair, Barcelona, Spain), providing air that had non-detectable hydrocarbons, NO_x and particles - aerosol background of $0.010 \pm 0.005\,\mu g\,m^{-3}$. Photo-oxidation experiments of isoprene and toluene were carried out by duplicate with a high reproducibility in the aerosol formation (calculated from aerosol mass concentration).

The experiments consisted of the photo-decomposition of aromatic hydrocarbons under dry conditions (<2% RH) in the absence of inorganic seed aerosols. Isoprene (2.1 ppm) was introduced in the photo-reactor via heated air stream; H_2O_2 (7 ppm) was injected by a sprayer. The photo-oxidation of toluene (2.6 ppm) was performed following a similar protocol with constant NO_x (30 ppb). Later, all the reactants were mixed with high power fans for 10 min before exposing them to sunlight. The sunlight exposure was conducted until the aerosol mass was steady; after that, the house of the chamber was closed. Measurements then continued for at least two hours to observe the aerosol decay behaviour. Finally, particles were collected at maximum aerosol formation, at a flow rate of $80\,L\,min^{-1}$, for h, with quartz fibre filters of GF/A 47 mm of diameter (Whatman, Brentford, England), pre-baked at 500°C, 12 h to avoid organic binders. After weighting in a microbalance MC21S (Sartorius, Goettingen, Germany), filters were kept in the freezer at −4°C.

2.3.3 *Aerosol total mass*

Aerosol volume concentrations from SMPS were converted to aerosol mass concentrations by assuming a density of $1\,g\,cm^{-3}$, spherical shapes and multi-charge correction for the condensed organic material [29–31]. Correction of wall losses were performed by fitting the decrease of the integrated particle number concentrations over time to an exponential decay function after closure of the chamber to sunlight for each experiment. Size-resolved wall-loss corrections were not needed, since negligible variations were observed during filter sampling for particle number concentration. Then, first-order loss coefficients – $1.0 \times 10^{-4}\,s^{-1}$ and $1.4 \times 10^{-4}\,s^{-1}$, respectively – were determined from measured changes in aerosol volume concentration using the equation proposed by McMurry *et al.*, 1985 [32]. Similar coefficients were used to correct the measured aerosol volume concentrations [12,29–31]. Finally, the total mass concentrations obtained from SMPS system data were compared with gravimetric measurements of pre-baked filters sampled.

2.4 *Sample treatment*

Half of the filter was extracted with 5 ml of CH_2Cl_2/CH_3CN (1 : 1) mixture and with sonication. The extract solution was centrifuged at 2000 rpm for 20 min, and the supernatant was concentrated in a nitrogen stream to dryness and dissolved in 1.5 ml of CH_2Cl_2/CH_3CN (1 : 1). The extract was divided into three equal portions and each one was brought to dryness by a nitrogen stream. After this, the following reagents were added: 0.5 ml of CH_3CN, 150 µL of PFBHA solution of 1000 mg L^{-1} in CH_3CN and 50 µl of a 4-fluorobenzaldehyde solution (15 mg L^{-1}) as an internal standard of carbonyl derivatisation. This mixture was left in darkness at room temperature for 24 hours, after it was dried. It was then dissolved in 145 µL of MSTFA solution (1 : 150 in hexane), adding 5 µl of a chlorosuccinic acid solution (5 mg L^{-1}) as an internal standard of hydroxyl derivatisation and heated at 90°C for 1 h. Finally, 1 µl was injected in the GC-MS.

2.5 *Chromatographic conditions*

TRACE-DSQ II GC-MS was used (Thermo Fisher Scientific Co., Waltham, MA, USA). An HP-5MS column of 30 m × 0.25 mm I.D × 0.25 µm film thickness (Crosslinked 5% Ph Me Siloxane) was supplied by Agilent Technologies (Santa Clara, USA). The chromatograph was programmed at 60°C for 1 min, then ramped at a rate of 10°C min^{-1} to 250°C, 5°C min^{-1} to 280°C and held at 280°C for 10 min. The injection port was held at 280°C and the transfer line from GC to MS was held at 300°C. Samples were injected in split (1 : 20) mode via an automatic injector, using on column helium flow of 1 mL min^{-1}. The EI-voltage was 70 eV, while, in the CI mode was 120 eV,with a CH_4 flow of 1.3 L min^{-1}. We worked in full scan mode (m/z 50–650) with the ion source temperature at 200°C and the quadrupole temperature at 100°C.

3. Results and discussion

3.1 *Derivatisation study*

The silylation process was studied under different conditions (BSTFA or MSTFA reagent, solvent, reaction time, temperature and catalyst percentage), maintaining the carbonyl derivatisation conditions. For this, the derivatisation yields were calculated for the standard mixture, including a primary alcohol, a polyhydroxylated compound, an aldehyde, a hydroxyl-ketone and several acids (two carboxylic linear, one aromatic, two dicarboxylic, two keto-carboxylic and one fluorinated). The best results were obtained for PFBHA plus BSTFA concentrated with 1% TMCS (yield >95%) and PFBHA plus MSTFA in a 1 : 150 hexane dilution without catalyst (yield >99%), except for pentafluorooctanoic acid with lower recoveries in all the conditions evaluated. Table 1a summarised the results obtained for all derivatisation combinations under optimised conditions. In all cases, the reaction occurred at room temperature for 24 h and then at 90°C for an hour without addition of pyridine. Since a single derivatisation may not be sufficient to identify aromatic or hydroxyl-carbonyl compounds – misidentification problems – [22], the mixture was previously derivatised with PFBHA. In this sense, the reaction yields of four critical model compounds – benzaldehyde, hydroxyacetone, 2-ketoglutaric acid, and 4-oxopentanoic acid – were specially evaluated. Quantitative recoveries (90–102%) demonstrated that this double derivatisation treatment permits the proper determination of hydroxyl-carbonyl compounds even with α-hydrogen.

Table 1(a). Comparative analysis of derivatisation protocols: recovery percentages for standard solution.

Compounds	r.t	PFBHA/ MSTFA	PFBHA/ MSTFA +1% TMCS	PFBHA/ BSTFA	FFBHA/ BSTFA +1% TMCS	FFBHA/ BSTFA +10% TMCS
1-Hexanol	5.3	110 ± 11	95 ± 10	97 ± 10	103 ± 10	97 ± 10
Oxalic acid	7.3	100 ± 10	88 ± 9	83 ± 8	106 ± 11	69 ± 7
4-Oxopentanoic acid	7.5	99 ± 10	99 ± 10	100 ± 10	71 ± 7	52 ± 5
Malonic acid	8.1	98 ± 10	98 ± 10	97 ± 10	97 ± 10	96 ± 10
Octanoic acid	8.6	104 ± 10	95 ± 9	94 ± 9	80 ± 8	64 ± 6
Benzoic acid	9.1	87 ± 9	100 ± 10	80 ± 8	94 ± 9	75 ± 7
Glurtaric acid	11.1	91 ± 9	90 ± 9	100 ± 10	105 ± 11	58 ± 6
Hydroxyacetone	11.4	98 ± 10	96 ± 10	95 ± 10	96 ± 10	95 ± 10
Levoglucosan	13.7	96 ± 10	95 ± 10	91 ± 9	100 ± 10	93 ± 9
Benzaldehyde	15	94 ± 9	94 ± 9	94 ± 9	94 ± 9	94 ± 9
2-Ketoglutaric acid	16.5	94 ± 9	94 ± 9	95 ± 10	96 ± 10	95 ± 10
Pentaflurooctanoic acid	18.5	40 ± 4	40 ± 4	35 ± 4	30 ± 3	33 ± 3
Stearic acid	20	103 ± 10	95 ± 9	95 ± 10	90 ± 9	91 ± 9

Table 1(b). Comparative analysis of derivatisation protocols: artefact data for filter samples.

		PFBHA/BSTFA[1]	PFBHA/MSTFA[2]
Chromatogram m/z 73	Number of peaks	20	13
	Average peak area	$(53 \pm 5) \cdot 10^5$	$(36 \pm 7) \cdot 10^5$
	Retention time interval (min)	4.0–9.5	4.0–6.1
Chromatogram m/z 181	Number of peaks	28	28
	Average peak area	$(10 \pm 6) \cdot 10^6$	$(10 \pm 6) \cdot 10^6$
	Retention time interval (min)	4.0–19.4	4.0–19.4

[1] PFBHA sofotion of 200 mg L^{-1} and BSTFA concentrated with 1% TMCS.
[2] PFBHA solution of 200 mg L^{-1} and MSTFA in a dilution 1:150 in hexane without catalyst.

Reproducibility greater than 90% and high coefficients for linear correlation ($r^2 > 0.99$) were obtained.

The main problems with derivatisation protocols are the memory column effects for gas chromatography and the high amount of artefacts that reagents produce in the chromatogram. In our case, the analysis of blank filters showed the absence of artefacts owing to sampling material. Moreover, the chromatograms of blank derivatised filters were analysed by extracting the m/z 73 ion fragment $[Si(CH_3)_3]^+$ and the m/z 181 ion fragment $[C_6F_5CH_2]^+$, since they are specific for hydroxyl and carboxylic compounds and for carbonyl compounds, respectively [1,33] (see Table 1b).

According to the results shown in Table 1, the combined derivatisation protocol of PFBHA plus MSTFA under diluted conditions promoted fewer and smaller artefacts and a wide region free from overlap peaks than PFBHA plus pure BSTFA, enabling a better determination of small polar compounds that elute at the beginning of the chromatogram. To confirm these better chromatographic characteristics, we carried out a comparison of both derivatisation protocols for spiked control filters. Small size compounds and hindered compounds such as oxalic acid, malonic acid and 4-oxopentanoic acid were better determined by the PFBHA plus diluted MSTFA reagents, which avoided overlapping elution and showed better derivatisation recoveries.

3.2 *Photochemical oxidation of isoprene: qualitative results*

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

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

Some of the major SOA compounds here determined, tetrols and methyl-tetrols -threitol, erythritol, 2-methylthreitol and 2-methylerythritol-, have been observed previously using the BSTFA reagent. These poly-hydroxylated compounds were identified

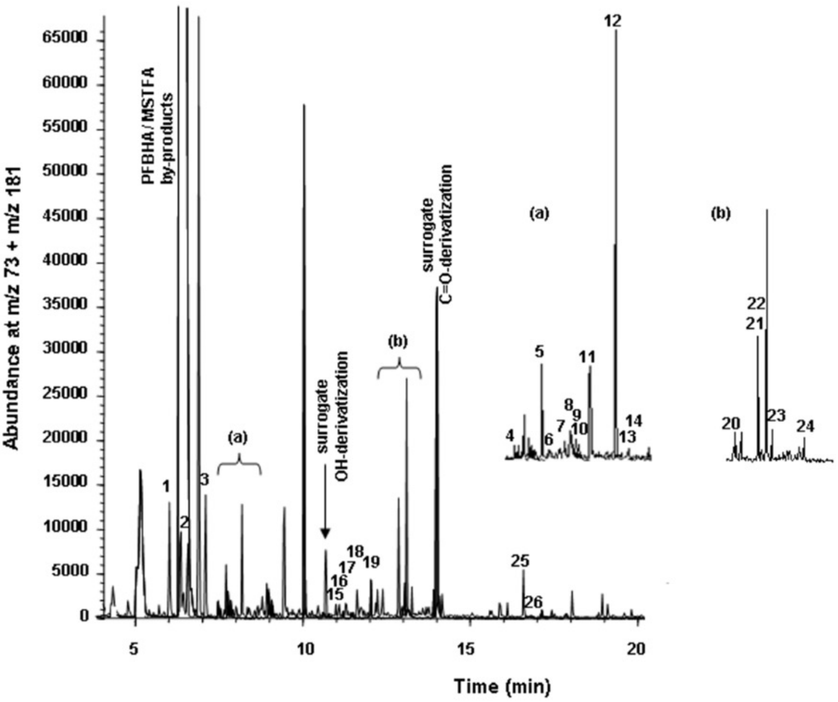

Figure 1. Chromatogram of the m/z 73+181 for an aerosol sample obtained from isoprene photo-oxidation (see code Table 2).

according to EI-mass spectra [7,13,22,34]. In our study, the 2-methyl tetrols are products of isoprene photo-oxidation with low NO_x in the absence of acidic aerosol seeds. Regarding minor SOA compounds, 2-methylglyceric was detected at a retention time of 11.39 min with the m/z 219 as the main fragment and the same fragmentation path described by Szmigielski [9]. Additionally, several gas phase products are often observed in particulate phase as artefacts or owing to their gas/particle partitioning [12]. Methyl-butenediols are major gaseous products reported at low concentrations in particle phase from the degradation of isoprene in the absence of NOx [8,13,26]. Although, they have not been identified in our samples, two C4-polyhydroxyl compounds (MW 112) have been registered at 11.64 and 12.25 min. Neither, C5-alkenetriol compound or hydroperoxide compounds (which require other analytical conditions to be detected but have been identified previously [10,13]) have not been identified in our samples; however, other more oxidised compounds, C5-hydroxyl carboxylic acids have been detected. Methacrolein, methyl vinyl ketone, glycolaldehyde and hydroxyacetone have been also detected.

Moreover, the use of our optimised derivatisation process has allowed us to determine new condensed products consistent with isoprene degradation mechanisms [22,26,35]. The identification of dicarboxylic acids with short retention times – oxalic, malonic, butenedioic and succinic acids – has been supported from standards. Under conditions of absence of NO_x, SO_2 and seed particles, their formation can be justified by the oxidation of intermediate 1,2 diols, described in isoprene – H_2O_2 photo-oxidation [20]. Moreover, malic acid has been identified using a standard ($t_r = 13.35$ min). Although described in field samples and proposed as late products of forest vegetation emissions [20], malic acid is first reported here in a chamber study. Several unknown compounds have been observed, but we cannot propose any specific structure owing to their low response or undefined MS spectra. Finally, the following tentative compounds have been identified based on their EI and CH_4-CI mass spectra, which appear in Appendix A. Supplementary data 1.

2-Methyl-propene-1,3-diol. The mass spectrum of the derivative showed fragments at m/z 232 $[M]^+$, 217 $[M\text{-}15]^+$, 189 $[M\text{-}43]^+$, 159 $[M\text{-}73]^+$ and 147, corresponding to the fragment $[(CH_3)_3Si\text{-}O\text{-}Si(CH_3)_2]^+$. Ion fragment 143 $[M\text{-}89]^+$ presents high intensity owing to the fact that it can be originated from both parts of the molecule. We also observed ions at m/z 132 $[M\text{-}100]^+$, attributed to the loss of $[CH\text{-}O\text{-}Si(CH_3)_3]^+$, 103 $[CH_2\text{-}O\text{-}Si(CH_3)_3]^+$ and 73 $[Si(CH_3)_3]^+$. Moreover, the fragments at m/z 132 and 103 strongly suggested the presence of a double carbon bond and a primary alcohol proposed by Little [25]. The CI-spectrum confirmed its molecular weight with a high intensity of [M+1] fragment. The detection of this diol agrees with the fact that the degradation of isoprene in the absence of NO_x follows the mechanism of peroxy radicals proposed by [22,26].

2-Hydroxy-2-methylpropionic acid. The derivative fragments were m/z 246 $[M]^+$, 231 $[M\text{-}15]^+$, 155 $[M\text{-}89]^+$ and 147. Moreover, we detected the characteristic ion of carboxylic acids and hydroxyl group (m/z 117 and 73). The ion at m/z 143 $[M\text{-}103]^+$, is the base peak in the EI mass spectra, explained by the loss of $[(CH_2\text{-}O\text{-}Si(CH_3)_3]^+$. The fragments observed were consistent with the presence of a compound with both a primary alcohol and a carboxylic group. These assumptions of a double oxidised C4-isoprene product were confirmed by its high polarity - retention time of 7.12 min – and the presence of ions at m/z 103 and 117.

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

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

3.3 *Photochemical oxidation of isoprene: quantitative results*

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

The most abundant compounds were threitol, erythritol, 2-methylthreitol and 2-methylerythritol. The concentrations obtained from the methyl-tetrols - 2-methylthreitol and 2-methylerythritol – are quite consistent with previously reported product yields [13,20]. The main newly identified products were 2-hydroxy-3-methylsuccinic, 2-methyl-propene-1,3-diol and 2-hydroxy2-methylpropionic acid, indicating that these compounds can serve as suitable tracers for low-NO_x isoprene photo-oxidation but additional confirmation should be accomplished with further experimentation. In comparison with previous studies, the total contribution of alcohols, aldehydes and ketones is reduced, while the amount of dicarboxylic and hydroxyl-carboxylic acids is increased. Therefore, the photo-oxidation of isoprene in the absence of NO_x, performed in our high-volume smog chamber and induced by natural sunlight, seems to promote the formation of more oxidised products. The percentage of identified SOA fraction was 12% using authentic standards. These values could increase to ~55% if the isoprene degradation tentative products are confirmed.– unknown compounds were not taken into account -, increasing the identified SOA fraction. Previous reported values were ranged between 12–34% [10].

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

Peak n°	Identified compounds	MW	MF	t_r (min)	µg m^{-3}
1	C5-hydroxycarboxylic acid(b)	148	$C_5H_8O_5$	6.06	1.61
2	2-Methylpropene-l,3-diol(b)	88	$C_4H_8O_2$	6.51	2.80
3	2-Hydroxy-2-methylpropionic acid(b)	102	$C_4H_6O_3$	7.12	2.42
4	Oxalic acid[a]	90	$C_2H_2O_4$	7.49	0 06
U1	Unknown-1	–	–	7.73	–
U144	Unknown-144	142	$C_5H_4O_5$	7.94	–
5	Malonic acid(a)	104	$C_3H_4O_4$	8.21	0.34
6	2-Methylbuta-l,3-diene-1,3-diol(b)	100	$C_5H_8O_2$	8.37	0.04
U2	Unknown-2	–	–	8.58	–
7	Butenedioic acid(a)	116	$C_4H_4O_4$	8.68	0.03
U3	Unknown-3	–	–	8.95	–
8	Methacrolein(a)	70	C_4H_6O	8.99	trace
9	Threitol(b)	122	$C_4H_{10}O_4$	9.05	2.37
10	Methyl vinyl ketone(a)	70	C_4H_6O	9.15	trace
11	C5-hydroxy-dicarboxylic acid(b)	148	$C_5H_8O_5$	9.50	0.60
12	Succinic acid(a)	118	$C_4H_6O_4$	9.93	1.44
13	Erythritol(b)	122	$C_4H_{10}O_4$	10.11	1.52
14	2-Methylen-butandioic acid or 2-Methylbutenedioic acid (b)	130	$C_5H_6O_4$	10.48	0.05
U4	Unknown-4	–	–	11.01	–
15	2-Methylbutandioic acid or 2-Methylbutanedioic acid(b)	132	$C_5H_8O_4$	11.11	0.04
U162	Unknown-162	162	$C_4H_6O_6$	11.15	–
16	Glycoladehyde(a)	60	$C_2H_4O_2$	11.29	0.74
17	2-Methylglyceric acid(b)	120	$C_4H_8O_4$	11.39	0.04
18	C4-polyhydroxyl compound(b)	122	$C_4H_{10}O_4$	11.64	0.07
19	Hydroxyacetone	74	$C_3H_6O_2$	11.84	0.52
20	C4-polyhydroxyl compound(b)	122	$C_4H_{10}O_4$	12.25	0.03
U5	Unknown-5	–	–	12.41	–
21	2-Methylthreitol(b)	136	$C_5H_{12}O_4$	12.91	1.51
U6	Unknown-6	–	–	12.99	–
22	2-Methylerythritol(b)	136	$C_5H_{12}O_4$	13.12	2.07
U7	Unknown-7	–	–	13.28	–
23	Malic acid(a)	134	$C_4H_6O_5$	13.35	0.02
24	C5-polyhydroxycarboxylic acid(b)	148	$C_5H_8O_5$	13.73	0.02
U128	Unknown-128	128	$C_5H_4O_4$	14.05	–
Ul56	Unknown-156	156	$C_4H_{10}O_6$	16.13	–
U8	Unknown-8	–	–	16.61	–
25	lst peak Glyoxal(a)	58	$C_2H_2O_2$	16.82	0.56
	2nd peak Glyoxal	58	$C_2H_2O_2$	16.92	
26	1st peak Methylglyoxal(a)	74	$C_3H_4O_2$	16.98	0.05
	2nd peak Methylglyoxal	74	$C_3H_4O_2$	17.27	
U136	1st peak Unknown-136	136	$C_4H_8O_5$	18.96	–
	2nd peak Unknown-136	136	$C_4H_8O_5$	19.12	
U9	Unknown-9	–	–	19.62	–

(a)Standard identified compounds
(b)Tentative identified compounds
n.q: note quantified
standard error $< 10\%$

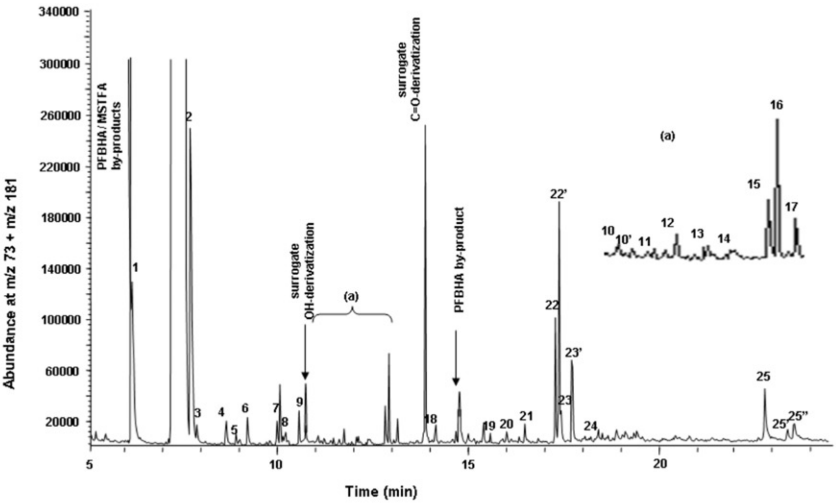

Figure 2. Chromatogram of the m/z 73+181 for an aerosol sample obtained from toluene photo-oxidation (see code Table 3).

This improvement is the result of using our PFBHA/MSTFA optimised protocol, which facilitated the determination of more oxidised multifunctionalised compounds ($t_r < 9$ min).

3.4 *Photochemical oxidation of toluene: qualitative results*

SOA compounds were obtained from the toluene photo-oxidation reaction under constant low NO_x concentrations, simulating traffic emissions in an urban zone. The maximum mass concentration of aerosol formation, obtained 7 hours after the reaction start, was $1050\,\mu g\,m^{-3}$ with an aerosol yield of 33%. A typical extracted ion chromatogram of PFBHA/MSTFA derivatives in EI-mode is shown in Figure 2. Some of the ring-retaining products and ring-opening products have been previously detected [14–16]. The p-cresol was formed from an initial OH attack; meanwhile, the addition of NO_2 to the oxidised aromatic ring leads to the formation of 4-nitrophenol, 2-methyl-5-nitrophenol, 3-methyl-4-nitrophenol and 2-methyl-4-nitrophenol. Moreover, the small amount of benzaldehyde and the high concentration of benzoic acid registered are attributed to the fact that benzaldehyde further reacts with the OH radical, forming a benzoylperoxy radical and leading to benzoic acid. As the photo-oxidation reaction advances, oxygenated ring-opening products are also generated, such as glycolaldehyde, hydroxyacetone, n-oxopentenoic acid, glyoxylic acid and methyl-glyoxylic acid. Compounds such as glyoxylic and n-oxopentanoic acid were previously identified [17]. The detection of glyoxal and methylglyoxal in the particle phase was interpreted as the result of the cleavage process of condensed polymeric or oligomeric compounds [37]. However, polyketones and hydroxyl polyketones, expected at lower NO_x initial conditions [36], were not present. This absence could be due to our experimental conditions (constant NO_x addition, lower toluene concentrations and natural sunlight).

Other multifunctional products have been newly determined in this study. The ring-retaining products were two dihydroxynitrotoluene isomers from the OH and NO_2

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

Peak n°	Identified compounds	MW	MF	t_r (min)	μg m^{-3}
U102	Unknown-102	102	$C_4H_6O_3$	5.12	–
1	Formaldehyde[(a)]	30	CH_2O	6.13	trace
2	C5-polyhydroxycarboxylic acid[(b)]	148	$C_5H_8O_5$	7.40	67.9
3	n-Oxopentanoic acid[(c)]	116	$C_6H_{12}O_2$	7.93	0.6
4	n-Oxopentenoic acid[(c)]	114	$C_6H_{14}O_2$	8.60	1.71
U1	Unknown-1	–	–	8.70	–
5	p-cresol[(a)]	108	$C_7H_8O_4$	8.83	0.7
6	Malonic acid[(a)]	104	$C_3H_4O_4$	9.20	0.6
7	Benzoic acid[(a)]	122	$C_7H_6O_2$	9.90	4.9
U2	Unknown-2	–	–	9.95	–
8	Succinic acid[(a)]	118	$C_4H_6O_4$	10.05	8.9
9	Butenedioic acid[(a)]	116	$C_4H_4O_4$	10.32	7.9
10	1st peak Glycoladehyde[(a)]	60	$C_2H_4O_2$	11.29	1.5
	2nd peak Glycoladehyde	60	$C_2H_4O_2$	11.40	
11	Hydroxyacetone[(a)]	72	$C_3H_6O_2$	11.69	1.0
12	Glyoxylic acid[(a)]	74	$C_2H_2O_3$	12.14	trace
13	4-Nitrophenol[(a)]	139	$C_6H_5NO_3$	12.38	0.9
14	Methyl-glyoxylic acid[(a)]	88	$C_3H_4O_3$	12.49	trace
15	2-Methyl-5-nitrophenol[(a)]	153	$C_7H_7NO_3$	12.65	0.7
16	3-Methyl-4-nitrophenol[(a)]	153	$C_7H_7NO_3$	13.04	4.8
17	2-Methyl-4-nitrophenol[(a)]	153	$C_7H_7NO_3$	13.54	11.5
18	Benzaldehyde[(a)]	106	C_7H_6O	14.28	0.2
U3	Unknown-3	–	–	15.26	–
19	Methylmuconaldehyde[(b)]	116	$C_7H_8O_2$	15.84	trace
20	Dihydroxynitrotoluene[(c)]	169	$C_7H_7NO_4$	16.19	0.9
21	Dihydroxynitrotoluene[(c)]	169	$C_7H_7NO_4$	16.56	1.0
22	1st peak Glyoxal[(a)]	58	$C_2H_2O_2$	16.85	11.2
	2nd peak Glyoxal	58	$C_2H_2O_2$	16.95	
23	1st peak Methylglyoxal[(a)]	74	$C_3H_4O_2$	17.00	1.5
	2nd peak Methylglyoxal	74	$C_3H_4O_2$	17.30	
24	4-Hydroxybenzaldehyde[(a)]	122	$C_7H_6O_2$	18.04	0.6
25	1st peak 2-methylbutendial[(b)]	98	$C_5H_6O_2$	22.68	0.9
	2nd peak 2-methylbutendial	98	$C_5H_6O_2$	23.26	
	3rd peak 2-methylbutendial	98	$C_5H_6O_2$	23.48	

[(a)] Standard identified compounds
[(b)] Tentative identified compounds
[(c)] or structural isomer
n.q: not quantified
standard error < 10%

attack, and 4-hydroxybenzaldehyde, from the OH ring addition at the para-position in benzaldehyde, which eluted at 16.19, 16.56 and 18.04 min, respectively. In addition, reactions leading to the formation of ring-opening compounds can be deduced from the mechanisms described in [14,15]. Thus, 2-methylbutendial - identified using a laboratory synthesised standard- came from the direct oxidative ring cleavage, malonic acid from the oxidation of ring-opening carbonyl products and succinic acid from the oxidation of 4-oxo-2-butenoic acid. Although, several additional products were observed, only a few tentative compounds were identified from EI and CH_4-CI mass spectra (Appendix B. Supplementary data 2).

n-Oxopentanoic acid. The fragmentation pattern of the derivative provided at m/z 188, 173, 129, 117 and 73 corresponded to $[M]^+$, $[M\text{-}15]^+$, $[M\text{-}59]^+$, $[COO\text{-}Si(CH_3)_3]^+$, and $[Si(CH_3)_3]^+$. The carbonyl group of this ring-opening oxocarboxylic acid (MW 116) should be in the C2 or C3 position since its MS spectrum is similar to the reference compound of 4-oxopentanoic acid; however, it appeared at a different retention time. Moreover, the unsaturated homologue n-oxopentenoic acid was observed at 8.10 min.

Butenedioic acid. The mass spectrum of the derivative showed fragments at m/z 260 $[M]^+$, 245 $[M\text{-}15]^+$, 217 $[M\text{-}43]^+$, 201 $[M\text{-}59]^+$, 117 $[COO\text{-}Si(CH_3)_3]^+$, and 73 $[Si(CH_3)_3]^+$. The structure of double-derivatised dicarboxylic acid agrees with an elution at 0.4 minutes later to the succinic acid (saturated homologue). The CI mass spectrum reinforces this identified C4-carboxylic acid, probably formed from the oxidative ring opening of toluene.

Methylmuconaldehyde. The mass spectrum of the derivative showed the fragments at m/z 311 $[M]^+$ and the characteristic fragments of the PFBHA derivatisation m/z 195, 181 and 116 $[M\text{-}181]^+$. For benzene photo-oxidation reactions muconaldehyde, has been proposed as an intermediate SOA precursor [27]. However, this is the first time that it has been experimentally determined in toluene photo-oxidation.

3.5 *Photochemical oxidation of toluene: quantitative results*

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

The percentage of identified SOA fraction was 5.5% using authentic standards. These values could increase to ~15% if the toluene degradation tentative products are confirmed, improving previous studies – although the experimental conditions are not exactly the same [12,17]. The constant low NO_x concentrations in our experiment, which simulate traffic emissions in an urban zone – instead of a high initial NO_x concentration of a short-term emission-, promote more extensively oxidised pathways. Under our photo-oxidation conditions, 80% of the identified products are associated with multifunctional ring-opening products (oxo-carboxylic acids and dicarboxylic acids).

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

4. Conclusion

A better understanding of the atmospheric degradation of biogenic and anthropogenic pollutants involves the development of high throughput analytical protocols. Our optimised derivatisation, based on PFBHA/MSTFA, has improved the detection and quantification of multi-oxygenated photochemical products by GC-MS. The interpretation of chromatograms has been easier, since enhanced features have been achieved for small molecules, containing hydroxyl, carbonyl and/or carboxylic groups. These advantages have allowed us to obtain satisfactory results in the application of this methodology to high-volume photoreactor samples. The number of secondary organic compounds identified has been extended, increasing the SOA fraction quantified from isoprene and toluene photo-oxidations. Similar results using our proposed derivatisation protocol are also expected for other aerosol samples.

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Appendix A. Supplementary data 1

Mass spectra obtained for derivative products from isoprene photo-oxidation. (a) 2-Methylpropene-1,3-diol in EI, (b) 2-Methylpropene-1,3-diol in CI, (c) 2-Hydroxy-2methylpropionic acid in EI, (d) 2-Methylbuta-1,3-diene-1,3-diol in EI, (e) 2-Methylen-butandioic acid or 2-methylbutenedioic acid in EI.

Appendix B. Supplementary data 2

Mass spectra obtained for derivative products from toluene photo-oxidation. (a) n-Oxopentanoic acid in EI, (b) Oxopentenoic acid in EI, (c) Butenedioic acid in EI, (d) Butenedioic acid in CI, (e) Methylmuconaldehyde.

Supplementary material is available via the Supplementary Content tab on the article's online page at http://dx.doi.org/10.1080/03067319.2011.572164.