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A chromatographic method to analyze products from photo-oxidation of anthropogenic and biogenic mixtures of volatile organic compounds in smog chambers

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ABSTRACT

A method for quantifying secondary organic aerosol compounds (SOA) and water soluble secondary organic aerosol compounds (WSOA) produced from photo-oxidation of complex mixtures of volatile organic compounds (VOCs) in smog chambers by gas chromatography/mass spectrometry (GC/MS) has been developed. This method employs a double extraction with water and methanol jointly to a double derivatization with N,O-bis (trimethylsilil) trifluoroacetamide (BSTFA) and O-(2,3,4,5,6)-pentafluorobenzyl-hydroxylamine hydrochloride (PFBHA) followed by an analysis performed by GC/MS. The analytical procedure complements other methodologies because it can analyze SOA and WSOA compounds simultaneously at trace levels. As application, the methodology was employed to quantify the organic composition of aerosols formed in a smog chamber as a result of photo-oxidation of two different mixtures of volatile organic compounds: an anthropogenic mixture and a biogenic mixture. The analytical method allowed us to quantify up to 17 SOA compounds at levels higher than 20 ng m^{-3} with reasonable recovery and a precision below 11%. Values found for applicability, selectivity, linearity, precision, recovery, detection limit, quantification limit and sensitivity demonstrated that the methodology can be satisfactorily applied to quantify SOA and WSOA.

1. Introduction

The presence of some chemical compounds in air can produce a deterioration of the optimal conditions for life, for instance exposure to fine particulates air pollution is associated with damaging effects on the respiratory and cardiovascular systems [1,2]. Besides their effect on human health, particles also contribute to the radiative balance by dispersing and/or absorbing light of certain wavelengths [3] and thus, the knowledge of air particle levels presents a high interest for different scientific areas [4]. The group of organic particles that are formed in the atmosphere is known as secondary organic aerosols (SOA). They are formed from the oxidation of certain organic gases leading to the production of low-volatility compounds than can partition into the aerosol phase. It is well known that SOA are composed of species containing multiple functional groups of carbonyl, carboxyl and hydroxyl groups [5,6].

Much progress has been made in recent years concerning SOA formation, particularly due to experiments performed in chambers. This kind of experiments offers a framework to reproduce chemical reactions under controlled conditions, and thus these studies constitute a very useful tool to investigate which specific processes are involved in SOA formation. In most of the previous experiments, one single volatile organic compound (VOC) or simple mixtures were investigated. [5,7,8]. However, there are few studies investigating complex VOC mixtures in smog chamber [9–11]. Vivanco and Santiago have presented a recent set of experiments performed in the EUPHORE outdoor chamber (CEAM, Spain) [12–14]. In those experiments, atmospheric oxidation of more complex mixtures of anthropogenic and biogenic organic gases was analyzed. Despite the extensive efforts over recent years, through a combination of smog chamber experiments and measurements of atmospheric aerosols, many aspects of SOA formation and composition are not well understood yet.

Gas chromatography/mass spectrometry (GC/MS) is a sensitive and selective analytical method which has been employed worldwide to measure SOA components. Despite its analytical capability to resolve many products, detecting and identifying SOA compounds is still an analytical challenge due to the large number of species with different functional groups that are present at low concentrations.

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Different analytical procedures have been used to find out SOA composition. Generally, all analytical strategies involve a sample extraction using solvents followed by derivatization and chromatographic separation [15–21]. By the end of the 1990s, some studies have shown measures of SOA compounds. One of the first methodologies to analyze SOA compounds was developed by Yu et al. [20–22] in 1997. They provided an analytical method to identify compounds containing one or more functional groups from atmospheric oxidation of α-pinene and Δ^3-carene. Simultaneously, Forstner et al. [23] performed smog chamber aromatic-NO_x photooxidations and summarized SOA species identified by extraction using supercritical CO_2 followed by a GC/MS analysis. Later, Jang et al. [5] have shown an extraction with dichloromethane followed by derivatization with pentafluorobenzyl bromide (PFBBr), PFBHA and BSTFA and analyzed by GC/MS and FTIR to identify products from photooxidation of toluene. Also Kleindienst et al. [17] have described a treatment using PFBHA and BSTFA with a positive chemical ionization gas chromatography ion trap mass spectroscopy (GC-ITMS) for oxidation products of toluene propylene mixtures. Chiappini et al. [24] have developed a SPE/GC/MS method which is able to identify and quantify 7 SOA compounds. Bateman et al., [25] have analyzed water-soluble organic aerosol compounds by high-resolution electrospray ionization mass spectrometry (HR-ESI-MS). Admittedly, the combination of these procedures offers a capability to reveal the formation of several SOA particles. However, it should be pointed out that none of these analytical methods are able to analyze simultaneously SOA and WSOA compounds. Consequently, it is noteworthy that to analyze them simultaneously, it would be necessary to carry out at least two different methods, with the necessity of splitting the sample and thus, some disadvantages, such as compounds at trace level could not be detected, the time consumption, and also higher cost, are larger.

For these reasons, this work has the aim of developing an analytical methodology able to quantify simultaneously, as sensible as possible, a higher number of SOA and WSOA compounds formed in the photo-oxidation of complex mixtures of VOCs. Emphasis has been placed in developing a soft extraction to minimize losses of volatiles and a multi-step derivatization technique to quantify even some compounds at trace level. Due to the high number of compounds that comprise SOA, the authors have chosen 20 species (major and minor SOA and WSOA compounds) which are products of the oxidation of octane, toluene, 1,3,5-thrimethylbenzene, o-xylene, α-pinene, limonene and isoprene [5,15,19,20,22,26,27]. Furthermore, to demonstrate the ability of the method to achieve applicability of developed methodology, the authors have analyzed two samples performed within a set of experiments carried out at the EUPHORE smog chamber to analyze several of the compounds formed.

2. Experimental

2.1. Chemicals

1,4-methyl benzoquinone (> 98%), 4-etoxyphenol (> 99%), benzoic acid (> 99.5%), glyoxylic acid (98%, monohydrate), malonic acid (99%), trans-norpinonic acid (98%), pinic acid (98%), cis-pinonic acid (98%), pyruvic acid (98%), citraconic anhydride (98%), maleic anhydride (99%), glycolaldehyde (crystal dimmer), glyoxal (40% water solution), hydroxyacetone (90%), phenol (> 99.5%) and methyl glyoxal (40% water solution) were purchased from Sigma-Aldrich. 2,3-butanedione (> 99.4%), adipic acid (> 99.5%), oxalic acid (> 99%) and succinic acid (> 99.5%) were obtained from Fluka.

N,O-bis (trimethylsilil) trifluoroacetamide (BSTFA) and O-(2,3,4,5,6)-pentafluorobenzyl-hydroxylamine hydrochloride (PFBHA) were used in derivatization reactions. BSTFA and PFBHA were acquired from Supelco and Aldrich, respectively.

Deuterated phenantrene (Dr. Ehrenstorfer GmbH) was used as internal standard. Acetone, acetonitrile, dichloromethane, isooctane, methanol and pyridine of GC grade were supplied by Aldrich.

All standards prepared from stock solutions were placed in sealed flasks and refrigerated at 4 °C until their use.

The VOCs employed in the smog chamber experiments were both anthropogenic and biogenic. The aromatic compounds 1,3,5-trimethylbenzene, o-xylene, and toluene, as well as the alkane octane, were selected as representative anthropogenic VOCs of an urban environment, while isoprene (2-methyl-1,3-butadiene) and the monoterpenes α-pinene and limonene were introduced as the biogenic VOCs mixture. Nitrous acid (HONO) was synthesized by the addition of sodium nitrite to a sulfuric acid solution and was used as photochemical oxidant.

2.2. Analytical method

2.2.1. Preparation of the calibration mixtures

Stock solutions were prepared by dissolving the objective compounds into a given volume of suitable solvents such as water, acetonitrile, dichloromethane or methanol in each case. Using liquid phase standards was due to the impossibility of using gas phase standards for all studied compounds. However, latest studies have revealed a bias due to matrix effects. This mismatch when analyzing real field samples using liquid phase standard is more significant for heavy compounds [28–31]. Be that as it may, this mismatch is inherent and admittedly, it will take time to solve.

In spite of this issue, the authors have performed an adequate calibration procedure. Briefly, six calibration solutions, at concentrations ranging from 0.1 to 30 μg mL^{-1}, were prepared by serial dilutions of the stock solution. Next, these solutions were derivatized with 150 μL of PFBHA (24 h; darkness) and later with 50 μL of BSTFA (40 min, 80 °C) according to the analytical procedure. Finally, the six derivatized solutions were injected in the gas chromatograph by triplicate.

2.2.2. Procedures of extraction and derivatization

The methodology was optimized by recovery studies of baked quartz filters spiked with a standard solution of objective compounds at a concentration of 10 μg mL^{-1} each.

The methodology begins as follows: the filters were treated with 5 mL water and 750 μL of PFBHA (2000 μg mL^{-1}) was subsequently added. The first extraction was performed by shaking the mixture for 1 min and storing at room temperature and darkness for 24 h in order to derivatize WSOA completely. The water extracts were separated by decantation. The following step included the addition of 5 mL MeOH to the sample, shaking it for 1 min and keeping it in the darkness at ambient temperature for 24 h. Subsequently the mixture was extracted by ultrasound for 10 min.

Aqueous and methanolic extracts were mixed and concentrated to 100 μL in a nitrogen stream. After adding 150 μL of PFBHA (2000 μg mL^{-1}) and 500 μL of acetonitrile, the mixture was stored for 24 h at room temperature and darkness in order to derivatize remainder compounds.

The extract was subsequently concentrated to dryness in a nitrogen stream and 50 μL of BSTFA and 50 μL pyridine were added. The mixture was shaken and introduced into the oven for 40 min at 80 °C. Finally, the extract was concentrated to dryness under nitrogen stream and re-dissolved in 100 μL of dichloromethane. Fig. 1 shows a schematic of the developed methodology.

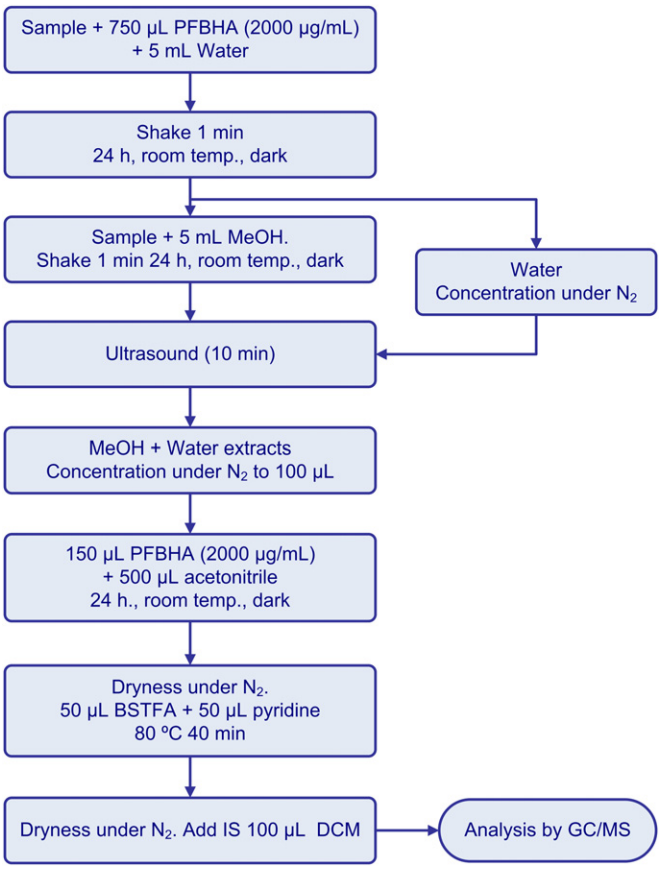

Fig. 1. Scheme of the analytical procedure to quantify simultaneously components of SOA and WSOA.

2.2.3. GC–MS conditions

A Fisons 8000 chromatograph with automatic injector equipped with a capillary column Zebron ZB-5MS of 30 m × 0.25 mm i.d. × 0.25 µm film thickness (crosslinked 5% phenylarylene 95% dimethylpolysiloxane) and coupled to a Fisons MD 800 mass spectrometer was used.

Gas chromatograph was programmed at 80 °C for 5 min, then ramped at a rate of 10 °C min^{-1} to 210 °C, held for 3 min, and finally increased at rate of 10 °C min^{-1} to 250 °C. Injector port was held at 250 °C and 1 µL of sample was injected in the GC–MS in splitless mode (1 min), using helium as carrier gas (column flow 1 ml min^{-1}).

Mass spectrometry analysis was performed in electronic impact (EI) ionization mode with electron energy of 70 eV and mass range *m/z* 40–550 was scanned. Ion source temperature was 200 °C and solvent delay was 5 min. Qualitative analysis was based on matching mass spectra to standards reference mass spectra of the National Institute of Standards and Technology (NIST) library, where available, and confirmation was performed by comparison with reference compounds.

2.3. Smog chamber experiments

The photo-oxidation experiments were carried out in the EUPHORE (EUropean PHOto-REactor) smog chamber at CEAM (Centro de Estudios Ambientales del Mediterráneo, Valencia, Spain). The chamber is a 200 m^3 half-spherical Teflon outdoor chamber which has been previously described in detail [32].

Two sets of experiments were conducted (Table 1). The anthropogenic VOCs mixture experiment (AE) was conducted with 1,3,5-TMB, toluene, o-xylene and octane. In addition, the biogenic VOCs mixture experiment (BE) was carried out for isoprene, α-pinene and limonene. The aim of the experiments was to study the SOA formation potential of two different VOC mixtures in the presence of natural sunlight and using HONO as the oxidant agent. A description about the chemical processes that lead to SOA formation can be seen elsewhere [33].

No seed aerosol was used in these experiments, being the background particle levels of 2–5 µg m^{-3}, which were measured using a Tapered Element Oscillating Monitor (TEOM). Also, multiple measurement techniques, such as gas chromatography coupled with mass spectrometer (GC–MS), Fourier Transform Infrared Spectrometry (FTIR), High Pressure Liquid Chromatography (HPLC), Gas Chromatography (GC-ECD and GC-FID/PID), Absorptive Sampling Solid Phase Microextraction (SPME) and different monitors were used to measure the gas concentration of reactants and products. Table 2 shows the compounds measured by the different techniques.

Table 1
Initial concentrations of VOCs and experimental conditions for smog chamber experiments.

	Anthropogeic mixture experiment (AE)	Biogenic mixture experiment (BE)
1,3,5-trimethylbenzene ([ppb])	131	
Toluene [ppb]	87	
o-xylene [ppb]	22	
Octane [ppb]	87	
Isoprene [ppb]		107
α-pinene [ppb]		66
Limonene [ppb]		58
Nitrous acid [ppb]	122	99
NO [ppb]	59	34
NO_2 [ppb]		128
VOC/NO_x [ppbC/ppb]	15	7
Temperature [K]	302–308	302–307
RH [%]	1.7–4	0.5–3

Table 2
Compounds measured by the different techniques used in the photooxidation experiments.

	Compounds measured
GC/MS	**Reactive VOCs:** • Anthropogenic (octane, toluene, o-xylene and 1,3,5-TMB) • Biogenic (isoprene, α-pinene and limonene) **Organic oxidation products** (pentanal, acetic acid, benzaldehyde, methacroleine, metilvinylketone, and acetone)
GC	**Reactive VOCs:** • Anthropogenic (octane, toluene, o-xylene and 1,3,5-TMB) • Biogenic (isoprene, α-pinene and limonene) **Organic oxidation products** (peroxyacetylnitrate, methacroleine and metilvinylketone)
FTIR	**Reactive VOCs:** • Anthropogenic (octane, toluene, o-xylene and 1,3,5-TMB) • Biogenic (isoprene, α-pinene and limonene) **Initial oxidant** (nitrous acid) **Organic oxidation products** (peroxyacetylnitrate, formic acid, acetic acid, methyl-glyoxal, formaldehyde, methanol, pinonaldehyde, glyoxal, acetone, methacroleine and metilvinylketone) **Inorganic oxidation products** (ozone, nitric acid)
HPLC	**Organic oxidation products** (hydroxyacetone, propanal, methyl-glyoxal, glyoxal, methacroleine and metilvinylketone)
SPME	**Organic oxidation products** (glycolaldehyde, hexanal, glyoxal and methyl-glyoxal)
MONITORS	**Inorganic oxidation products** (CO, ozone, NO_x)

In order to analyze SOA composition, a filter system is installed in a laboratory below the chamber. The samplings were performed by driving an air flow from the chamber through a tube to the filter at 10 L min^{-1} during 1 h. While the chamber is opened to the sunlight, three-low volume samplings were taken for each experiment at a flow rate of 10 L min^{-1} during 1 h. Once the chamber is closed, an additional high-volume sampling was carried out in each experiment during 1–2 h at a flow rate of 70.5 L min^{-1} [13]. The filters used in this paper are low volume samplings, with a total sampling volume of 0.6 m^3 for each of them.

3. Results and discussion

3.1. Identification of compounds by mass spectra

The total ion chromatogram (TIC) for a calibration solution of the derivatized standards is shown in Fig. 2. All the compounds were well separated in less than 25 min, exhibiting good peak shapes. Several compounds were identified through their mass spectra by comparing it, when possible, with reference mass spectra of NIST. SOA products detected and identified by this methodology are listed in Table 2. Also, the molecular weights of both derivates and original compounds are shown.

As indicated in Table 3, after the double derivatization, there could be five types such as BSTFA, bis-BSTFA, PFBHA, bis-PFBHA and PFBHA+BSTFA derivatizations in terms of the structure and functional groups of the SOA compounds. Fig. 3 displays the mass spectra of four compounds and the main fragmentations are explained in Fig. 4. The mass spectra and main fragmentations of the rest of the compounds are in the Supporting material.

Derivates share several common ion fragments. Thus, compounds containing hydroxyl groups substituted the active H atom with $Si(CH_3)_3$. The major fragments include *m/z* 73 $[Si(CH_3)_3]^+$ and 75 $[HO{=}Si(CH_3)_3]^+$. As can be seen in Fig. 3, these fragments are the base peak in the mass spectra of BSTFA derivate of 4-etoxyphenol and in the mass spectra of BSTFA+PFBHA derivate of hydroxyacetone. Compounds with two active H atoms show a strong fragment *m/z* 147 $[(CH_3)_2Si{=}OSi(CH_3)_3]^+$, as it can be seen in the mass spectrum of succinic acid. For linear diacids M-15 (loss of $-CH_3$) and M-89 (loss of $-OSi(CH_3)_3$) fragments are generally the dominant peaks in the mass spectrum [21,34–36].

On the other hand, derivatization of carbonyl groups by PFBHA produces an addition of a pentafluorobenzyl group to the

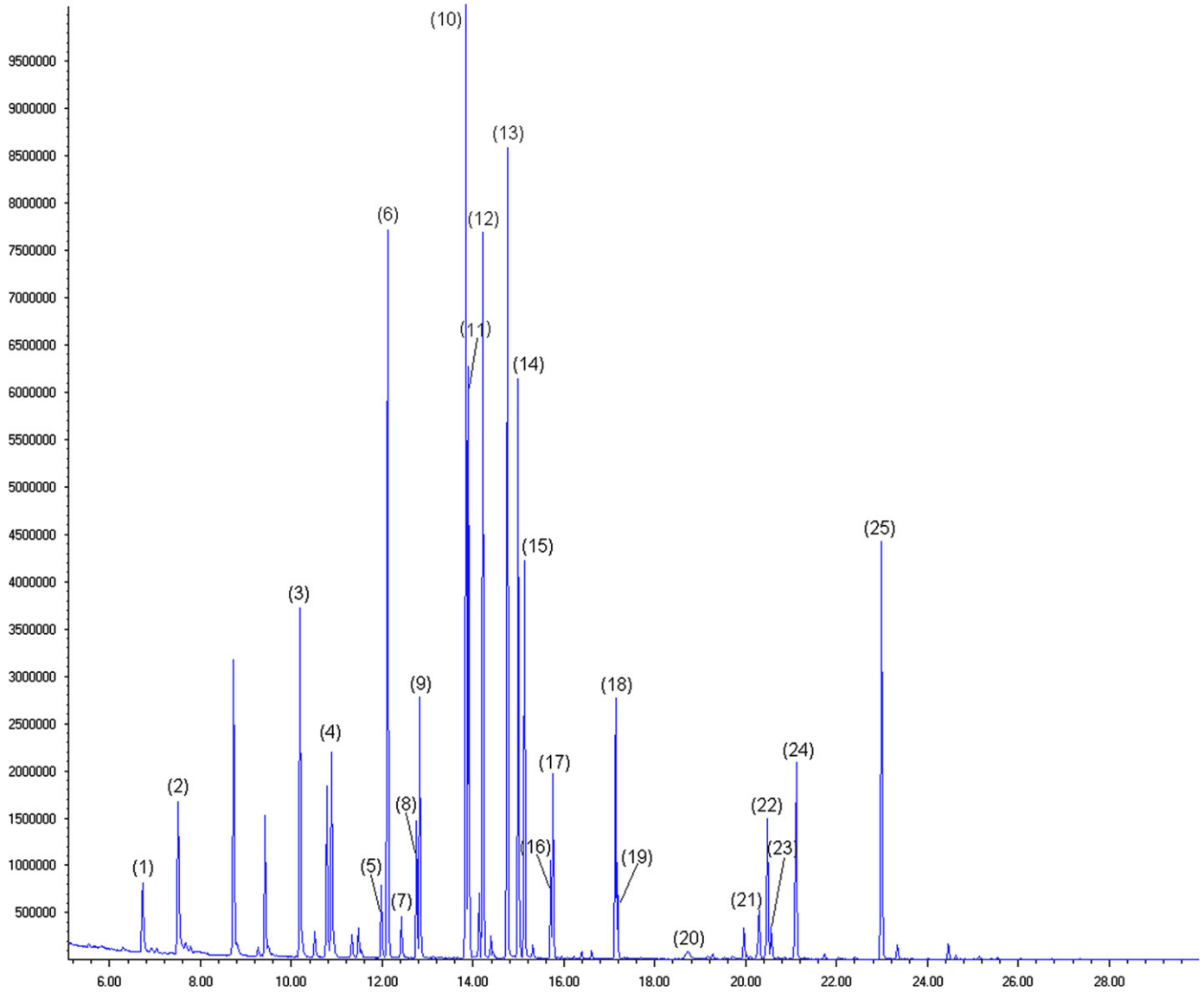

Fig. 2. Total ion chromatogram of the calibration solution (10 μg mL^{-1}) of the mixture of SOA and WSOA standards.

Table 3
Molecular weights of SOA and WSOA products detected by this methodology.

Peak	RT ($_{min}$)*	Compound	Derivate	MW[a]	FW[b]
1	6.724	Phenol	BSTFA	166	94
2	8.729	Oxalic acid	Double BSTFA	234	90
3	10.190	Malonic acid	Double BSTFA	248	104
4	10.884	Benzoic acid	BSTFA	194	122
5	11.981	Maleic anhydride	Double BSTFA	260	116
6	12.118	Succinic acid	Double BSTFA	262	118
7	12.417	2,3-butanedione	PFBHA	281	86
8	12.756	Citraconic anhydride	Double BSTFA	273	129
9	12.825	4-etoxyphenol	BSTFA	320	138
10	13.846	Glycolaldheyde	PFBHA+BSTFA	327	60
11	13.900	Glycolaldheyde	PFBHA+BSTFA	327	60
12	14.214	Hidroxyacetone	PFBHA+BSTFA	341	74
13	14.757	Glyoxylic acid	PFBHA+BSTFA	341	74
14	14.993	Adipic acid	Double BSTFA	290	146
15	15.132	Pyruvic acid	PFBHA+BSTFA	355	88
16	15.711	Norpinonic acid	Double BSTFA	316	172
17	15.761	Norpinonic acid	Double BSTFA	316	172
18	17.132	Pinic acid	Double BSTFA	330	186
19	17.178	Pinic acid	Double BSTFA	330	186
20	19.230	Methyl benzoquinone	PFBHA	317	122
21	20.296	Glyoxal	Double PFBHA	448	58
22	20.479	Glyoxal	Double PFBHA	448	58
23	20.563	Methyl glyoxal	Double PFBHA	462	72
24	21.107	2,3 butanedione	Double PFBHA	476	86
25	22.995	Pinonic acid	PFBHA+BSTFA	451	184

* Retention time.
[a] Molecular weight of PFBHA/BSTFA derivate.
[b] Molecular weight of original compounds.

molecule. A strong fragment ion at m/z 181 $[C_6F_5CH_2]^+$ is shown in Fig. 3 for the mass spectra of 2,3-butadione as well as for the mass spectra of hydroxyacetone. The presence of m/z 181 as the base peak in the 2,3-butadione mass spectrum is consistent with the expected fragmentation patterns. Other characteristic fragments ions included M-181 (loss of $[-C_6F_5CH_2]^+$), M-197 (loss of $[-C_6F_5CH_2O]^+$), M-211 (loss of $[-C_6F_5CH_2ON]^+$), M-167 (loss of $[-C_6F_5]^+$) and M-30 [loss of –NO]. As can be seen in the mass spectra of 2,3-butadione, the additional fragment at m/z 99 corresponds to (M^+-181).

It is remarkable that some PFBHA derivates have shown double peaks. This is the case of glycolaldehyde and glyoxal. It is because PFBHA forms geometric isomers due to the nitrogen–carbon double bond, which can be resolved by a GC column [20]. Double peaks for trimethylsilil derivates of norpinonic and pinic acids because were also identified two isomers were formed.

It is significant that 2,3-butanedione has shown the mono- and di-PFBHA derivates. The first one has shown a higher sensitivity due to the lower steric impediment to form it. Another specie that could form a mono- and di-PFBHA derivates was 1,4-methylbenzoquinone. In this case, only the mono PFBHA derivate has been formed and there is no sign of di-PFBHA derivate.

On the other hand, it has been shown that anhydrides were hydrated by the extraction methodology there by converting to their respective dicarboxylic acids.

3.2. Validation of analytical methodology

It is well known that validation of an analytical methodology can involve evaluating up to 14 parameters, among which trueness, linearity, limit of detection (sensitivity), limit of quantification, precision, valid range, selectivity and accuracy are the most important [37,38]. The method has been optimized and validated according to Eurachem [39,40]. The results of validation of analytical methodology are summarized in Table 4.

The trueness is related to systematic errors and is measured by a bias or recovery. Taking into account the lack of a certified reference material encompassing all compounds involved in this work, trueness was demonstrated by spiking blank matrices (10 μg mL^{-1}).

Linearity was checked by the calculation of a six-point linear plot based on linear regression. Results, expressed as squared correlation coefficients (r^2), denoted good linearity in the range from 0.1 to 30 μg mL^{-1} as it can be seen in Table 4. The smallest and highest calibration standards of the calibration have defined the valid range 0.01–3 μg. These ranges of mass are within the mass measured for several organic compounds formed in smog chamber by others authors. Chiappini et al. [24] determined values of SOA formed from ozonolysis ranged from 0.01 to 0.44 μg. Hamilton et al. [15] have shown that several SOA products from photooxidation were observed at levels ranged from 5 to 2000 ng m^{-3} (approximately 0.2–9 μg). Therefore, since our calibration is in the ranges reported, the authors have considered this range valid to analyze secondary compounds produced in smog chambers.

Limit of detection (LOD) and limit of quantification (LOQ) were calculated as three and ten times the standard deviation of four samples at a concentration of 0.1 mg L^{-1} respectively. Results are summarized in Table 4. These concentrations were calculated assuming a sample volume of 0.6 m^3. Concentrations obtained were low enough to enable this methodology suitable to analyze SOA generated in smog chambers.

Sensitivity can be defined as the slope of calibration curve. Some compounds have shown quite high sensitivities as it can be seen in Table 4. Specifically, sensitivity for pinic, pinonic and norpinonic acids was comparable to those published by Chiappinni et al. [24].

Repeatability was evaluated by determining the RDS of the analytical signal obtained from a spiked aliquot at a concentration of 10 μg mL^{-1} ($n=6$). Results obtained (Table 3) showed that precision was not above 11%.

The authors also compared GC/MS results for different storage times during the extraction and derivatization procedure (12–48 h). It is remarkable that analytical signals decreased dramatically with time. Thus 48 h after derivatization reactions, peak areas were at least 35% lower; therefore samples cannot be stored and must be injected immediately after derivatization (Fig. 5).

3.2.1. Recovery study

Nowadays, there are no certified reference materials for SOA and WSOA components. That is why a spiking/recovery test has been performed to investigate the bias of the method, and thus to estimate accuracy. To sum up, a small bias indicates a great trueness [37]. The recovery test is aimed to analyze a sample after addition of a known mass of analytes. Therefore, recoveries significantly different from 100% is a clear indication of a lack of trueness. At any rate, good recoveries do not fully guarantee trueness but are considered an indication of the closeness to trueness.

It should be noted that the recovery study was conducted to investigate accuracy of analytical procedure to analyze SOA and WSOA components, not to evaluate efficiencies from sampling, because this is not the objective of this study. In that case, a different test should be performed, for instance, injecting known amounts of compounds in the chamber and analyze it there.

In order to perform the recovery test, eight spiked samples at a concentration of 10 μg mL^{-1} have been analyzed. Table 5 shows the results obtained.

Results have shown recoveries higher than 50%, being close to 100% for several compounds. However, the lowest recoveries were found for phenol. This is why phenol is the most volatile compound (vapor pressure 47 Pa at 20 °C) and losses could have

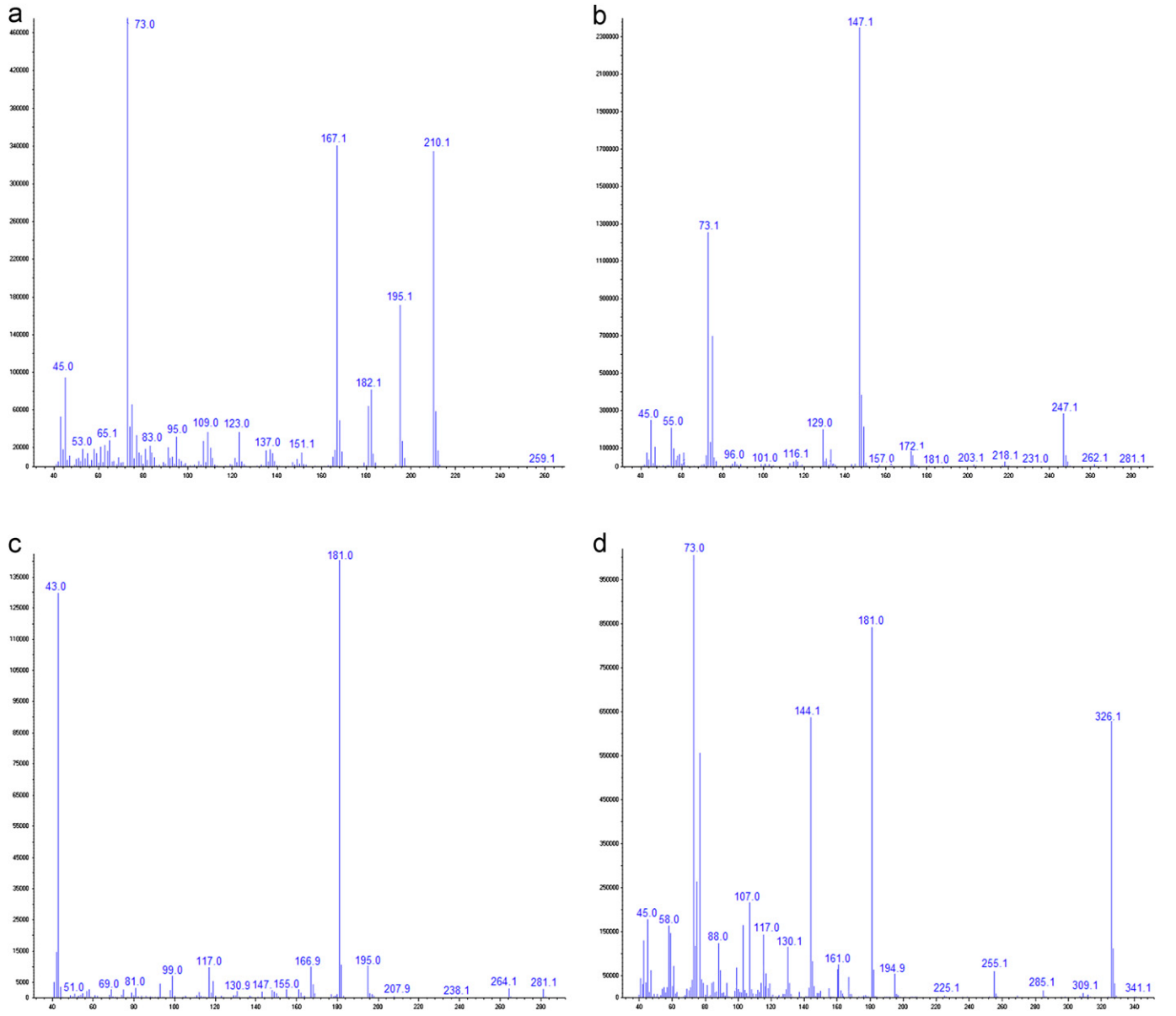

Fig. 3. Mass spectra obtained for PFBHA/BSTFA derivates of (a) 4-etoxyphenol, (b) succinic acid, (c) 2,3-butanedione and (d) hydroxyacetone.

been occurred along concentration under N_2. Also, phenol has the lowest sensitivity, so higher amounts are necessary to be detected by GC/MS. This problem can be solved by detecting in SIM mode. On the other hand, citraconic and maleic anhydrides were hydrated along the process and citraconic and maleic acids were formed. As a result, the compounds analyzed were the trimethylsilil derivates of these dicarboxylic acids. Consequently, when analyzing real field samples, it would be impossible to discern between anhydrides formed and their respective dicarboxylic acids. For this reason the developed methodology is not suitable to analyze anhydrides.

3.3. Analysis of two smog chamber experiments by the developed methodology

In the last stage of this study, the developed methodology was carried out to quantify several SOA and WSOA components produced as a result of the photo-oxidation of two different experiments performed in a smog chamber. These two experiments were part of a set of experiments performed in the EUPHORE smog chamber. Experimental conditions of the smog chamber, also in-depth analysis of experiments have been already published [12–14]. The first experiment comprised the oxidation of an anthropogenic mixture of volatile organic compounds (toluene, 1,3,5-trimethylbenzene, o-xylene and octane) meanwhile the second one comprised the oxidation of a biogenic mixture of volatile organic compounds (α-pinene, limonene and isoprene). A single sample, collected into quartz filters, was taken from each of the two environmental chamber experiments. Table 6 summarizes the concentrations of identified compounds in both experiments.

As shown in Table 6, the experiment with the anthropogenic mixture of VOCs produced compounds at concentrations in the range of 0.2–7.7 $\mu g\ m^{-3}$. The most abundant specie is 2,3-butanedione. This carbonyl compound has been already detected as a main oxidation product of o-xylene [20]. Other compounds detected are glycolaldehyde and hydroxyacetone, which are the products of oxidation of isoprene [27], glyoxylic acid and pyruvic acid, that have been detected by the other authors as products of

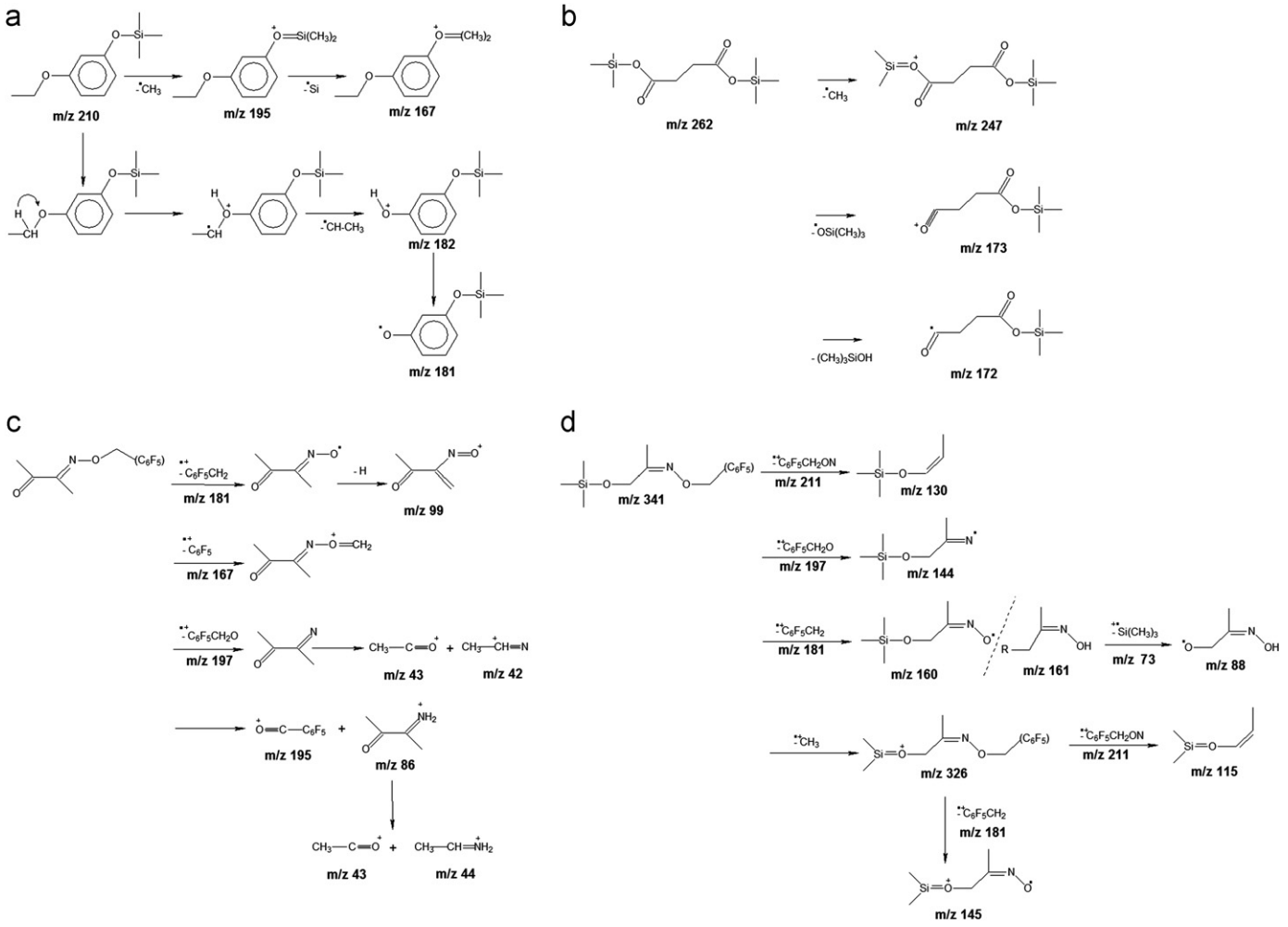

Fig. 4. Fragmentation for (a) BSTFA derivate of 4-etoxyphenol, (b) BSTFA derivate of succinic acid, (c) PFBHA derivate of 2,3-butadione and (d) PFBHA+BSTFA derivate of hydroxyacetone.

Table 4
Calibration parameters, LOD and LOQ*.

Compound	*m/z*	r^2	Linear range (mg L^{-1})	LOD[a] (μg m^{-3})	LOQ[a] (μg m^{-3})	Sens. (mg L^{-1})	RDS (%)
Phenol	151	0.98	0.09–18.84	0,17	0,57	0.021	11
Oxalic acid	147	0.98	0.11–21.20	0,20	0,68	0.153	10
Malonic acid	147	0.98	0.09–18.96	0,13	0,47	0.078	10
Benzoic acid	105	0.98	0.10–20.48	0,18	0,63	0.166	5
Maleic anhydride	147	0.995	1.26–37.86	0,17	0,57	0.072	8
Succinic acid	147	0.98	0.11–22.52	0,22	0,73	0.609	7
2,3-butanedione	181	0.98	0.09–18.00	0,13	0,42	0.114	8
Citraconic anhydride	147	0.992	1.03–30.78	0,33	1,08	0.497	6
4-etoxyphenol	210	0.98	0.10–19.44	0,18	0,63	0.137	8
Glycolaldheyde	181	0.98	0.10–20.00	0,20	0,67	0.423	8
Hidroxyacetone	181	0.96	0.10–28.68	0,27	0,92	0.657	5
Glyoxylic acid	181	0.98	0.11–21.60	0,12	0,40	1.973	7
Adipic acid	147	0.98	0.12–24.04	0,23	0,78	0.359	6
Pyruvic acid	181	0.992	0.10–29.40	0,05	0,18	1.088	5
Norpinonic acid	157	0.98	0.11–21.44	0,20	0,63	0.187	5
Pinic acid	171	0.99	0.10–19.48	0,15	0,52	0.097	7
Methyl benzoquinone	181	0.96	0.10–20.68	0,87	2,37	0.307	4
Glyoxal	181	0.998	0.11–22.00	0,07	0,20	2.998	4
Methyl glyoxal	181	0.998	0.12–23.96	0,02	0,05	1.904	5
Pinonic acid	181	0.991	0.10–19.68	0,15	0,47	0.126	5

*Squared correlation coefficient, 'r^2'; Limit of detection, 'LOD'; Limit of quantification, 'LOQ'; Sensitivity, 'Sens'; Deviation standard relative, 'RDS'.

[a] For a sampling volume of 0.6 m^3.

the oxidation of isoprene using different devices as ESI/MS [41]. Hamilton et al. also identified these compounds as the products of oxidation of toluene, by GC/MS–TOF/MS [15]. Finally glyoxal, an oxidation product of toluene and o-xylene, and methylglyoxal, a known product of oxidation of toluene, o-xylene and 1,3,5-TMB, have been detected [5,15,20,27].

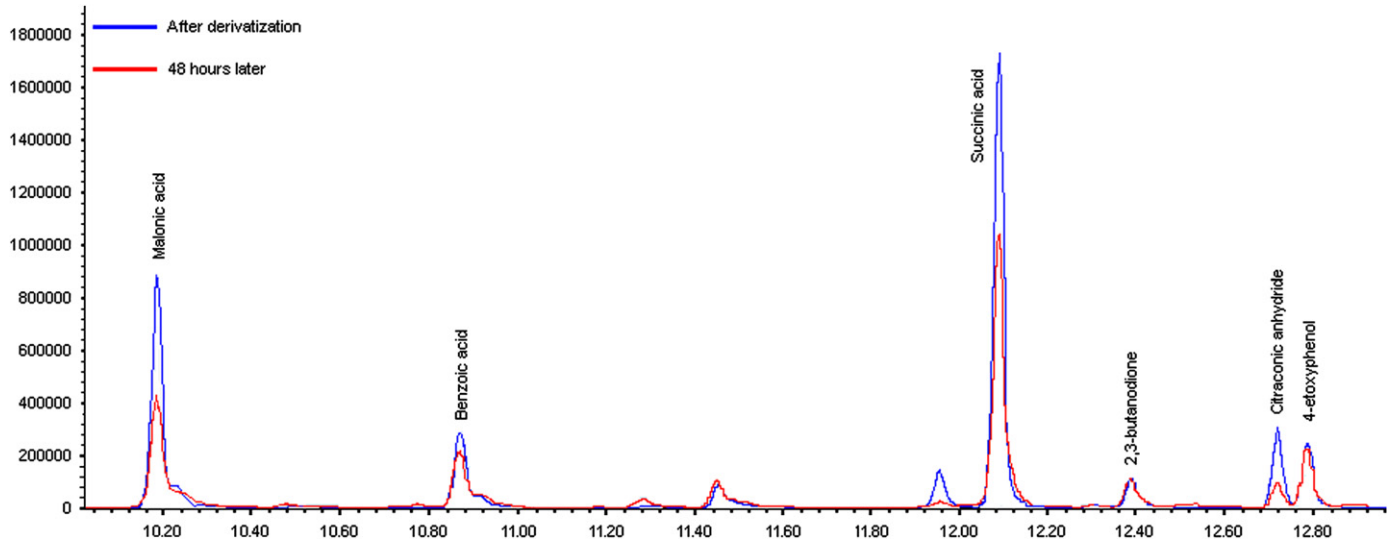

Fig. 5. Details of chromatogram of the standard solution: injected after derivatization (blue line) and after 48 h (red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 5
Results of recovery test for 20 compounds at a concentration of 10 μg mL^{-1}.

Compound	Rec. (%)	Bias (%)	Compound	Rec. (%)	Bias (%)
Phenol	12	4	Hydroxyacetone	48	14
Oxalic acid	74	12	Glyoxylic acid	76	16
Malonic acid	50	6	Adipic acid	90	18
Benzoic acid	58	11	Pyruvic acid	79	15
Maleic anhydride	80	20	Norpinonic acid	89	15
Succinic acid	81	21	Pinic acid	109	5
2,3-butanedione	81	21	Methyl benzoquinone	46	23
Citraconic anhydride	383	189	Glyoxal	61	14
4-etoxyphenol	53	8	Methyl glyoxal	71	24
Glycolaldheyde	55	10	Pinonic acid	105	10

Recovery, 'Rec'; Bias calculated as RDS.

Table 6
Concentration (μg m^{-3}) of the compounds identified in each experiment.

Compound	Antropogenic mixture experiment (μg m^{-3})	Biogenic mixture experiment (μg m^{-3})
Phenol	< 0.17	< 0.17
Oxalic acid	< 0.33	< 0.33
Malonic acid	< 0.13	< 0.13
Benzoic acid	0.90	< 0.18
Maleic anhydride	< 0.17	0.20
Succinic acid	0.25	0.22
2,3-butanedione	7.67	0.43
Citraconic anhydride	< 0.33	< 0.33
4-etoxyphenol	< 0.18	< 0.18
Glycolaldheyde	0.57	< 0.20
Hydroxyacetone	0.57	0.35
Glyoxylic acid	0.20	< 0.12
Adipic acid	< 0.23	< 0.23
Pyruvic acid	0.73	< 0.05
Norpinonic acid	< 0.20	< 0.20
Pinic acid	< 0.15	0.28
Methyl benzoquinone	< 0.02	< 0.02
Glyoxal	0.25	< 0.07
Methyl glyoxal	0.60	0.10
Pinonic acid	< 0.15	2.70

In relation with the experiment that comprised the oxidation of a biogenic mixture of VOCs, several compounds have been quantified at levels of 0.1–2.7 μg m^{-3}, of which pinonic acid is the most abundant. This compound has been identified as a product of the ozonolysis of α-pinene, the same as pinic acid and methylglyoxal [42]. Hydroxyacetone has been detected as a product of the photo-oxidation of isoprene [27] and succinic acid has been identified as a product of the photo-oxidation of d-limonene with NO_x [19].

The authors have estimated that compounds detected in both experiments account for approximately 1% and 8% of the total formed SOA for the biogenic and anthropogenic experiments, respectively. The SOA yield are consistent with other works, where the SOA yield ranged from 0.5% to 10.3% depending on the experimental conditions [9,43,44] in spite of the fact that SOA yield is slightly lower because no major SOA compounds from isoprene have been included in this study.

4. Conclusions

An analytical method suitable to analyze simultaneously several compounds of SOA and WSOA has been performed. The analytical protocol allowed us to quantify 17 compounds.

A combined extraction-derivatization step that was able to analyze WSOA joint to non-soluble compounds has been performed. The soft extraction has led to a minimization of losses of volatile compounds, meanwhile the double derivation led to an easy identification of a higher number of compounds. Thus, this method contributes to enhance the knowledge of SOA and WSOA composition.

The methodology showed adequate validation parameters such as applicability, selectivity, linearity, precision, recovery, detection limit, quantification limit and sensitivity. Results obtained suggest that this methodology can be applied to smog chamber experiments. LOD and LOQ are low enough to apply this method to samples generated in smog chambers with masses higher than 20 ng m^{-3} with satisfactory recoveries.

This methodology was successfully applied to analyze organic composition formed in two experiments that comprised the photo-oxidation of a mixture of toluene, 1,3,5-trimethylbenzene, o-xylene and octane (anthropogenic mixture) and a mixture of α-pinene, limonene and isoprene (biogenic mixture).

However the method was inadequate to identify anhydrides because these compounds were hydrated along extraction, forming their respective dicarboxylic acids.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.11.081.

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