



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(trimethylsilyl) 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.

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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 photo-oxidations and summarized SOA species identified by extraction using supercritical CO₂ 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-trimethylbenzene, 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%), cispinonic 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 (trimethylsilyl) 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 $\mu\text{g mL}^{-1}$, 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 $\mu\text{g mL}^{-1}$ each.

The methodology begins as follows: the filters were treated with 5 mL water and 750 μL of PFBHA (2000 $\mu\text{g mL}^{-1}$) 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 $\mu\text{g mL}^{-1}$) 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.

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