Development of a parallel sampling and analysis method for the elucidation of gas/particle partitioning of oxygenated semi-volatile organics: a limonene ozonolysis study

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Abstract

The gas/particle partitioning behaviour of the semi-volatile fraction of secondary organic matter and the associated multiphase chemistry are key features to accurately evaluate climate and health impacts of secondary organic aerosol (SOA). However, today, the partitioning of oxygenated secondary species is rarely assessed in experimental SOA studies and SOA modelling is still largely based on estimated partitioning data. This paper describes a new analytical approach, solvent-free and easy to use, to explore the chemical composition of secondary organic matter at a molecular scale in both gas and particulate phases. The method is based on thermal desorption (TD) of gas and particulate samples, coupled with gas chromatography (GC) and mass spectrometry (MS), with derivatisation on sampling supports. Gaseous compounds were trapped on Tenax TA adsorbent tubes pre-coated with pentafluorobenzylhydroxylamine (PFBHA) or N-Methyl-N-(*t*-butyldimethylsilyl)trifluoroacetamide (MTBSTFA). Particulate samples were collected onto quartz or Teflon-quartz filters and subsequently subjected to derivatisation with PFBHA or MTBSTFA before TD/GC/MS analysis. Method development and validation are presented for an atmospherically relevant range of organic acids and carbonyl and hydroxyl compounds. Application of the method to a limonene ozonolysis experiment, conducted in the EUPHORE chamber under simulated atmospheric conditions of low concentrations of limonene precursor and relative humidity, provides an overview of the method capabilities. 25 compounds were positively or tentatively identified, 9 being in both gaseous and particulate phases, and 11, among them tricarboxylic acids, hydroxyl dicarboxylic acids and oxodicarboxylic acids, being detected for the first time.

1 Introduction

Atmospheric formation of particulate matter from the gas-to-particle transfer of organics during their atmospheric oxidation is now considered as one of the main phenomena involved in both air quality and climate issues (IPCC, 2007; Hallquist et al., 2009). A better understanding of the interrelated processes

and a better representation in models are still required (Kanakidou et al., 2005). Secondary Organic Aerosol (SOA) formation is commonly described by gas-to-particle conversion of semi- and non-volatile secondary species formed in the gas phase by atmospheric oxidation of Volatile Organic Compound (VOC) precursors (e.g. Odum et al., 1996, Seinfeld and Pankow, 2003; Asher and Pankow, 2006;). However, for SOA formation and evolution pathways, in addition to the initial gas-phase oxidation processes, a significant number of studies in the last decade has pointed out the role of multiphase chemical processes in the particle phase (e.g. Graber and Rudich, 2006; Kroll et al., 2007; Healy et al., 2008; Monks et al., 2009) or at the gas-particle interface (e.g. Rudich, 2003; Rudich et al., 2007). These processes involve continuous modification of the chemical composition of SOA and its physicochemical properties, and interdependently influence the partitioning of semi-volatile organic species (SVOCs) between gaseous and aerosol phases, thereby consuming or forming SVOCs (Healy et al., 2008). Hence, understanding multiphase chemical processes is today a key issue to assess both aerosol climate impacts and health effects. It can improve climate impact evaluation through modelling enhancement of formation and evolution pathways and characterisation of aerosol physical properties. In terms of health issues, knowledge of SOA formation pathways and fine particle composition in different outdoor/indoor conditions is required for toxicological evaluation.

In spite of large progress made in recent years (e.g. Donahue et al., 2006; Camredon et al., 2010; Parikh et al., 2011), current SOA formation and evolution modelling, often suffers from discrepancies between modelling results and observations (e.g. Volkamer et al., 2007; Chan et al., 2009; Pankow, 2011) that notably reveal gaps in our knowledge of SOA formation and aging pathways. Atmospheric chemistry models integrating SOA formation are usually based on the parameterisation of $SVOC_i$ gas-particle partitioning proposed by Pankow (2006). This parameterisation is based on the definition of an equilibrium partitioning coefficient $K_{p,i}$ (m^3 µg^{-1}):

where P_i is the mass concentration (ng m^{-3} air) of the $SVOC_i$ in the particle phase, G_i is the mass concentration (ng m^{-3} air) of the $SVOC_i$ in the gas phase and M is the mass concentration (µg m^{-3} air) of the total sorbing particle phase. While Eq. (1) is independent of the nature of the sorption process — i.e. adsorption or absorption (Lazaridis, 1999) – most of the models assume an absorptive gas/liquid partitioning of SVOCs as this mechanism is expected to be predominant in SOA formation (Pankow, 1994; Odum et al., 1996) and links $K_{p,i}$ with the saturation vapour pressure of the $SVOC_i$ through the where R (m^3 atm mol^{-1} K^{-1}) is the ideal gas constant, T (K) is temperature, MW_{om} (g mol^{-1}) is the average molecular weight of the absorbing particulate material, γ is the activity coefficient of compound i in the particulate phase, and $P^o_{L,i}$ (Torr) is the vapour pressure of compound i as a pure liquid (subcooled, if necessary).

SOA modelling based on chemical oxidation schemes (e.g. Jenkin, 2004; Camredon et al., 2007; Bessagnet et al., 2008; Chan et al., 2009; Valorso et al., 2011) generally estimate theoretical $P_{oL,i}$ using group contribution methods (e.g. Arp and Goss, 2009; Barley and McFiggans, 2010) and usually sets i to unity, due to experimental determination difficulties. This can lead to uncertainties that are suspected to account for observed discrepancies between models and ambient observations in SOA yields. Another likely major source of discrepancies could be the poor consideration of multiphase chemical processes as a sink or source of SVOCs (Chan et al., 2009). An alternative modelling approach to the mechanistic description of SOA is the Volatility Basis Set (VBS) (Donahue et al., 2006, 2009; Farina et al., 2010; Tsimpidi et al., 2010; Cappa and Jimenez, 2010), which is based on distribution of the considered organic matter mass into volatility classes according to their saturation mass concentration $C_{partitioning_i}$ (corresponding to the inverse of the Pankow type partitioning coefficient). In this case, the dilution process and the evolution of particulate mass are the driving features. While the VBS scheme does not directly integrate chemical mechanisms, it takes reactivity into account considering a redistribution of the organic mass from one volatility bin to another. VBS consequently requires data to link atmospherically relevant partitioning behaviour to the origin of the organic aerosol and its composition. This context highlights the requirement in improving our comprehension of multiphase chemical mechanisms, especially those driving the formation of SVOCs and their consumption, and providing atmospherically relevant data on the partitioning behaviour of SVOCs. There is therefore a strong need to simultaneously explore the molecular composition of both gas and particulate phases in SOA studies, and to systematically determine the observed partitioning of SVOCs. The related experimental data have to be evaluated not only with low-concentration simulation chamber experiments but also using ambient atmospheres to assess the relevance of the obtained results.

However, since atmospheric secondary organic matter results from complex and successive oxidation processes, it is highly functionalised and reactive. It contains oxygenated moieties such as aldehyde, keto, hydroxyl, and carboxylic acid groups. Exploring SOA chemical composition and the associated gas phase at a molecular scale is consequently a true analytical challenge (Prather et al., 2008). This is emphasised when the atmospherically relevant constraints of low concentration levels and relative humidity are taken into account.

Until today, only a few studies have assessed the partitioning of secondary organic compounds through determination of partitioning coefficients K_p for individual secondary species. Some papers report the use of a thermodenuder (de Gouw and Warneke, 2007; Grieshop et al., 2009; Lee et al., 2011) in order to evaluate the volatility of SOA formed from different precursors without information on the chemical

composition. In these studies, SOA formed in simulated atmospheres flows through and evaporates in a temperature-controlled tube, previously calibrated with compounds with a known vapour pressure. By this method SOA mass is divided into volatility classes with known vapour pressure ranges, providing a volatility distribution. This method is very useful to provide atmospheric relevant constraints for modelling based on the Volatility Basis Set (Grieshop et al., 2009) and evaluate the semi-volatile and non-volatile fractions of SOA. Nevertheless, it remains incomplete as it provides no insights into chemical processes. Studies aiming at elucidating chemical processes focus on the characterisation of the chemical composition of secondary organic matter at a molecular scale. However, while the aerosol phase is most often analysed by chromatographic off-line methods in order to explore its highly complex molecular composition, the gas-phase products are most often monitored by an on-line method providing limited insights into the molecular composition. Today, Proton Transfer Reaction - Mass Spectrometry (PTR-MS) is the most widely employed on-line technique for assessing the chemical composition of the gas phase (e.g. Blake et al., 2004; Kroll et al., 2006) as it provides continuous molecular information and quantification of gas-phase compounds at very low concentration levels, around 10 ppt, especially for small molecules (Warscheid et al., 2003) without interference of water, so that it can be used in the ambient atmosphere. Nevertheless, PTR-MS is not specific as it does not provide detailed structural information.

Chromatographic methods using an on- or off-line approach, often coupled with thermal desorption, are sometimes applied to elucidate the molecular composition of the gas phase. However, apart from a few approaches using derivatisation strategies (e.g. Ho and Yu, 2002, 2004; Temime et al., 2007; Pacolay et al., 2008), these techniques are limited to non-polar or mono-functionalised compounds (e.g. Wedel et al., 1998; Xu et al., 2003; Sinha et al., 2010) with limited applications to secondary chemistry studies. Studies aiming at elucidating the underlying mechanisms of SOA formation require a detailed knowledge of the chemical composition of the particle phase. For this purpose, a wider range of powerful analytical methods exists, mainly because of the chemical complexity of the aerosol and its diversity, which can be divided in on-line and off-line methods (Hallquist et al., 2009). Over the past decade, on-line real-time Aerosol Mass Spectrometry (AMS) has become a technique of choice to explore the chemical composition of the aerosol phase with a high time resolution (Sullivan and Prather, 2005; Canagaratna et al., 2007). Combining direct thermal extraction of sampled airborne aerosol (flash vaporisation upon impaction on a hot surface (600 °C), under high vacuum) with Electron Ionisation (EI) and mass spectrometry, the AMS technique provides data on the bulk chemical nature of particulate organic matter – sulphate, nitrate, ammonium and chloride contents, and oxidation state with function types identification (alcohols, carboxylic acids, and carbonyls) – and is consequently a powerful tool for the chemical and physical characterisation of SOA. It has been

successfully applied to both ambient (e.g. Zhang et al., 2011) and simulated atmospheres (e.g. Sato et al., 2010). However, complex EI mass spectra resulting from extensive fragmentation do not allow unambiguous identification of individual organic compounds, which limits the exploration of the composition at a molecular scale. Another interesting in-situ method is the TAG method, based on coupling thermal desorption of the aerosol with gas chromatography/mass spectrometry (GC/MS) or GC-flame ionisation detection (GC-FID) (Williams et al., 2006). Recently, improved by GCxGC separation (2D-TAG, Goldstein et al., 2008; Isaacman et al., 2011), TAG provides detailed data on the volatility distribution of particle components with a good time resolution (from 1 to 2 h). However, GC separation limits TAG detection and the identification range to non-polar and mono-functionalised compounds, so that it does not allow to obtain insights into SOA chemistry.

Off-line chromatographic methods are required to address the high complexity of SOA composition. The methods differ in a first instance by the extraction step. Hays and Lavrich (2007) provided an interesting review on Thermal Desorption/Gas Chromatography/Mass Spectrometry (TD/GC/MS) applied to fine aerosol, which has as main advantages that it can be fully automated and is inexpensive, sensitive, and solvent-free. However, like on-line TAG, this technique is limited by the polarity of the SOA compounds. To overcome this limitation, an in-situ derivatisation step can be introduced. A few recent studies have integrated this principle, exposing sample filters to a derivatisation reagent for methylation or trimethylsilylation during thermal desorption for the detection and quantification of mono- and di-carboxylic acids (Beiner et al., 2009; Sheesley et al., 2010; Orasche et al., 2011). Other extraction techniques, more scarcely used, have also been reported. As an example, Supercritical Fluid Extraction (SFE) couples the extraction step directly to the analytical process. Its efficiency for extracting organic compounds from complex matrices has been demonstrated by coupling SFE with GC/MS or Liquid Chromatography/GC/MS (LC/GC/MS) (Hansen et al., 1995; Forstner et al., 1997; Castells et al., 2003). The process has the advantage that it allows derivatisation of polar compounds during the static extraction step (Shimmo et

10 al., 2004; Chiappini et al., 2006). Nevertheless, the large majority of studies exploring the chemical composition of fine organic aerosol is based on a first solvent sample extraction step as it provides a huge range of possibilities for further analytical processes. Solvent extraction type and steps to be considered (solvents choice, ultrasonication, Soxhlet, pre-concentrations steps, derivatisation, etc.) are selected according to both the fraction of the organic mass studied (water-soluble organic compounds, PAHs, carbonyl, carboxyl and/or hydroxyl compounds, organosulphates, organonitrates, oligomers, humic-like substances, etc.) and the analytical technique employed (GC, LC, Ion Chromatography – IC, electrophoresis, etc.). Mass spectrometric analysis is largely used for identification and quantification.

Among the various possible combinations, those aiming at analysis of polar and functionalised compounds (compounds containing carbonyl, carboxyl, and hydroxyl groups) are mainly divided between derivatisation/ GC/MS analysis (e.g. Nolte et al., 2001; Claeys et al., 2004, 2007; Edney et al., 2005; Szmigielski et al., 2007; Chan et al.,2010; Vivanco et al., 2011) and direct LC-soft ionisation-MS analysis [electrospray ionisation (ESI-MS) or atmospheric pressure chemical ionisation (APCI-MS)] (Kitanovski et al., 2011). These techniques are constantly improved and made more complex in order improve detection limits, enlarge the range of separable species (GC×GC, LC×LC), or increase the structural characterisation capability through higher-order MS (MS^n) or high-resolution MS (e.g. ion trap – ITMS, Time of Flight – ToFMS, Fourier Transform Ion Cyclotron Resonance Mass Spectrometry – FTICR-MS) (e.g. Hamilton et al., 2005; Pol et al., 2006; Claeys et al., 2009; Yasmeen et al., 2011; Hamilton et al., 2011). Nevertheless, while solvent extraction has proven useful for subsequent quantification and precise molecular structure identification, related protocols are time-consuming, and are prone to contamination and losses, especially for the semi-volatile fraction during the different extraction steps.

Global approaches considering gas and particulate phases simultaneously are required to elucidate secondary organic matter at a molecular scale for both phases and to provide partitioning data for relevant SVOCs. Most works aiming at studying the partitioning of SVOCs are based on off-line chromatographic techniques coupled to mass spectrometry, for both phases. This approach involves simultaneous sampling of both gas and particulate phases. One of the most common sampling methods is to trap gas-phase compounds on one or more annular glass denuders (XAD-4 coated) placed in series with a filter collecting the aerosol phase. This sampling technique has been applied without any derivatisation step prior to gas GC/MS analysis in order to investigate gas/particle partitioning of non-polar compounds – alkanes, PAHs (Volckens and Leith, 2003), or small carbonyls in diesel exhaust (Lee et al., 2004; Jakober et al., 2008). In more specific SOA studies targeting poly-functionalised and reactive compounds (carbonyls, hydroxyls, carboxyls), a derivatisation step has been introduced prior to the chromatographic separation. After solvent extraction of both denuder and filter, each sample is derivatised, in the liquid phase, by oximation with pentafluorobenzylhydroxylamine (PFBHA). Extracts are reduced in volume and blown to dryness before reconstitution in a suitable solvent. Double derivatisation is then achieved by trimethylsilylation with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and heating. Subsequently, aliquots of the doubly-derivatised extracts are injected into the GC/MS instrument (e.g. Woo and Kim, 1999; Kalberer et al., 2000; Jaoui et al., 2003). Alternative derivatisation reagents have occasionally been employed, such as the BF$_3$-methanol reagent (Jaoui and Kamens, 2003). In spite of its powerful capacity to identify and quantify individual species in complex mixtures of poly-functionalised compounds, this procedure presents the disadvantage

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of solvent extraction. More recently, the same simultaneous sampling technique of both gas and particulate phases onto a denuder/filter pack has been improved for carbonyl measurements, where PFBHA is used prior to sampling to coat the XAD-4 denuder and impregnate the filter(s) (Temime et al., 2007; Healy et al., 2008, 2009; Ortiz et al., 2009). The sample treatment is thus reduced to a simple extraction of the sampling supports, denuders and filters, possibly followed by a solvent reduction step and/or a filtering step. However, this method is reserved to carbonyls and solvent extraction is still required.

In this study, we present a new analytical approach to explore, simultaneously and in parallel, the chemical composition of both gas and particulate phases, and to quantify the partitioning of individual and poly-functionalised SVOCs. Reducing both solvent use and time-consuming sample treatment steps, the new method is based on thermal desorption of both gas and particulate phases sampling supports, coupled to GC/MS. It involves on-sorbent derivatisation of gas-phase compounds and on-filter derivatisation of particulate-phase compounds. The validation of the method is presented as well as its application to smog chamber experiments. As to the latter experiments, two series of simulated atmosphere experiments were performed in the EUPHORE European reactor. A first series focuses on the limonene ozonolysis chemical system, while a second one focuses on the isoprene photo-oxidation chemical system. Results from these experiments are used here to illustrate the capability of the method to explore the chemical composition of secondary organic matter in both gas and particulate phases.

2 Materials

2.1 Chemical

2.1.1 Standards

The standards used for the method development were chosen in order to fulfil the following purposes: (i) represent a wide range of functionalised semi-volatile secondary organic compounds and (ii) aid the identification and quantification of secondary products that are expected from limonene ozonolysis (as this system has been chosen as a model system). Each series of compounds used for the different method characterisation tests is chosen in order to meet both experimental requirements and objectives. All chemicals were purchased from Sigma-Aldrich Co. (St. Louis, USA) with the exception of 4-oxopentanal, available from Diverchim SA (Montataire, France). Given the large number of compounds used for both analytical development and application of the method to limonene ozonolysis, a complete list is provided in the Supplement.

2.1.2 Derivatisation reagents

Derivatisation of oxygenated species blocks the reactive functions, reduces their polarity and consequently enhances GC/MS response factors. Two derivatisation reagents were employed in order to derivatise

either carbonyl compounds or carboxyl and hydroxyl compounds. O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA, purchased from Sigma-Aldrich: PFBHA hydrochloride, puriss. p.a., derivatisation grade for GC, 99.0 %) was used to derivatise carbonyl compounds (aldehydes, ketones). The PFBHA derivatisation reaction (Fig. 1) forms oximes that provide characteristic fragmentation in MS and enhance detection limits. It is the most frequently used reagent in SOA studies to derivatise carbonyl groups (e.g. Wu and Hee, 1995; Jaoui et al., 2006; Carrasco et al., 2007; Healy et al., 2008; Ortiz et al., 2009). The reaction is commonly achieved in aqueous or water-containing solution (Cancilla and Que Hee, 1992). N-Methyl-N-(*t*-butyldimethylsilyl)trifluoroacetamide (MTBSTFA, purchased from Regis® Technologies Inc., MTBSTFA+1% *t*-BDMCS) was used to derivatise carboxyl and hydroxyl compounds. MTBSTFA converts hydroxyl groups (Fig. 2) to form *t*-butyldimethylsilyl (TBDMS) esters with increased volatility compared to the parent compounds, and consequently extends the range of semi- and non-volatile compounds observable in GC analysis. BSTFA is more largely employed in SOA studies for derivatisation of hydroxyl and carboxyl groups than MTBSTFA (e.g. Kleindienst et al., 2004; Jaoui et al., 2006; Pietrogrande and Bacco, 2011); nevertheless, MTBSTFA was chosen since *t*-butyldimethylsilyl derivatives formed with MTBSTFA provide similar fragmentation pathways as trimethylsilyl derivatives formed with BSTFA but are less sensitive to hydrolysis.

2.1.3 Adsorbent

Gas-phase sampling is achieved on adsorbent support. Tenax TA was chosen based on three criteria: (1) its chemical inertness, (2) its capacity to trap compounds with a large range of volatility, and (3) its highly hydrophobic nature. Commercial Tenax TA sorbent tubes were purchased from PerkinElmer, Inc. (Waltham, USA, stainless steel ATD Prepacked Sample Tubes, Sorbent: Tenax TA mesh 60/80). Before first use and after use, adsorbent tubes are conditioned overnight under heated helium flow (295 ℃). Adsorbent purity is checked before use by TD/GC/MS analysis.

2.1.4 Filters

Particulate phase sampling was achieved on two types of filters. To trap, derivatise with PFBHA and analyse the carbonyl-containing fraction of the aerosol phase, high-purity quartz microfibre filters (QM-A grade, 47 mm, Whatman™, Whatman International Ltd. Maidstone, UK) were used since quartz is the most thermal-resisting filter type commercially available. To trap, derivatise with MTBSTFA and analyse the hydroxyl- and carboxyl-containing fraction of the aerosol phase, pure borosilicate glass fibres with fluorocarbon (tetrafluoroethylene, TFE) coating (Fiberfilm™, 47 mm, PallFlex®, Pall Life Sciences, Port Washington, USA) were used since TFE coating reduces reactivity of the filter surface and moisture loading during sampling. Thereafter, Fiberfilm™ filters are referred to as Teflon-quartz filters. Before use,

quartz fibre filters were conditioned by heating at 450 °C for 5 h and Teflon-quartz filters by heating at 300 °C for 5 h. To trap particles upstream the Tenax TA sorbent tubes, Teflon filter (Zefluor PTFE membrane filters, Pall Life Sciences, not analysed) were used.

2.2 Analytical systems

Two analytical systems were used to perform analytical development owing to the large number of samples to be treated. The TD/GC/MS system was used for constructing calibration curves, evaluating detection limits, and analysing simulation chamber samples, while the TD-GC-FID system was preferred above the other system as FID response stability over time does not require system recalibration and facilitates comparison of the results. Both systems were used with the same analytical conditions. It goes without saying that only the TD/GC/MS system was used to apply the developed method.

2.2.1 Thermal desorption/gas chromatography/mass spectrometry system and procedures

The thermal desorption (TD) system was composed of: (1) an Ultra 50:50 (Markes International, Llantrisant, UK) multi-tubes auto-sampler equipped with an injected sample split flow automated re-collection system, (2) an Unity 1 (Markes International) platform desorber for single tubes, and (3) an Air Server (Markes International) used in the mass flow controller mode. Samples were desorbed at 300 °C for 15 min at a flow rate of 50 ml min^{-1} and were cryogenically trapped on Tenax TA (mesh 60/80) adsorbent at −10 °C. The trap was desorbed for GC injection at 300 °C, for 15 min in order to clean the trap, with a split ratio of 1:9. The split flow from the injected sample was systematically re-collected, onto the same tube in the case of the gas-phase samples and onto a cleaned Tenax TA tube in the case of the aerosol-phase filter samples. The gas chromatography system was a 6890A type instrument from Agilent Technologies equipped with an Rxi®-5Sil MS column (60 m, 0,25mmi.d., film thickness: 0.1 µm, Restek Corporation, Bellefonte, USA). Samples were chromatographically separated with the following temperature program: from 40 to 305 °C with a thermal ramp of 10 °C min^{-1}. The mass spectrometry system was a 5973 type instrument from Agilent Technologies. It was equipped either with an Electron Ionisation (EI) source (operated at an energy of 70 eV), used in the case of the first injections of samples for structural identification and quantification, or a Chemical Ionisation source (CI in positive mode, methane as reagent gas), used in the case of the injection of the re-collected samples to provide complementary structural information.

2.2.2 Thermal desorption/gas chromatography/flame ionisation detection

The TD/GC-FID system was composed of a thermal desorber (TurboMatrix 650, Perkin Elmer, Inc.) coupled to a gas chromatograph (Clarus 500, Perkin Elmer, Inc.) and equipped with an Rxi®-5Sil MS column (60 m, 0,25mmi.d., film thickness: 0.1 µm, Restek Corporation, Bellefonte, USA) and a flame ionisation detector. The system was also coupled to a mass spectrometer (Clarus 500, Perkin Elmer, Inc.).

The analytical method was the same as that used on the Markes-Agilent TD/GC/MS system. No recollection was performed for analytical development. The separation of the compounds was achieved with the following temperature program: from 40 to 305 $^{\circ}$C with a thermal ramp of 10 $^{\circ}$C min^{-1}.

2.3 Simulation chambers

2.3.1 INERIS dynamic simulation chamber

The INERIS dynamic simulation chamber consists on a borosilicate glass loop (200 l volume) which has been described elsewhere (Martin et al., 2003; Gonzalez-Flesca and Frezier, 2005). It has been especially designed to generate single or multicomponent gaseous species atmospheres at known and stable concentrations (from hours to weeks). Clean and dry air was generated by a zero air generator (Claind, AZ Air purifier 2010) and atmospheres were generated by continuous dilution of a concentrated mixture (typically, standard pollutants gas tanks). The dilution process was controlled and monitored by mass flow meters. If required, relative humidity was generated from a pressurised bulb containing ultrapure water (18.2MÒ, ElgaPureLab Flex, Veolia water) connected to a heated liquid mass flow controller system. Temperature was maintained around 22 $^{\circ}$C into the chamber by the circulation into the chamber double walls of a temperature-conditioned mixture of water/ethylene glycol. Temperature, pressure and relative humidity were continuously monitored.

2.3.2 CESAM atmospheric simulation chamber

The CESAM atmospheric simulation chamber was used to perform determination of breakthrough volumes presented Sect. 3.2.4. It has been described in detail elsewhere (Wang et al., 2011). Briefly, this facility consists of a cylindrical 4.2 m^3 stainless steel chamber. The chamber is evacuable using a powerful pumping system consisting of a root pump, a rotary pump and a turbomolecular pump, which allows the evacuation down to 8×10^{-4} mbar between each experiment to minimise the memory effect. Both temperature and relative humidity were measured with a HMP234 Vaisala® humidity and temperature transmitter equipped with a capacitive thin-film polymer sensor Humicap®. Compound injection was performed by introducing a precisely known pressure (in the range 0.1 mbar) via a vacuum ramp from a frozen pure standard solution into a bulb of known volume (V =1.0832 l). The bulb content was then immediately flushed into the chamber. Hydrocarbon products were monitored using a Fourier Transform InfraRed spectrometry (FTIR) instrument from Bruker GmbH. The total optical path length for the in-situ FTIR measurement was set to 192 m.

2.3.3 EUPHORE simulation chamber

Simulation chamber experiments on limonene ozonolysis (cf. Sect. 4) and isoprene photo-oxidation (cf. Sect. 3.3.4) were conducted in chamber B of the EUphore PHOtoREactor (EUPHORE) facility in Valencia

(Spain), consisting of 200 m³ outdoor hemispheric Fluorinated Ethane/Propene (FEP) bags mixed with high power fans. For limonene ozonolysis experiments the chamber was protected from outdoor conditions (irradiation) by a retractable steel cover to achieve dark conditions. Before the experiment, the chamber was flushed overnight and then filled with clean air from an air purification system including an absorption dryer with molecular sieve. Air volume losses due to sampling were compensated by introduction of clean air. Prior to every experiment, an aliquot of SF₆ was introduced in the chamber as an inert tracer to determine the dilution rate. Limonene or isoprene was introduced using a heated clean air stream. Relative humidity was generated by water introduction through a sprayer. Humidity and temperature were monitored by a hygrometer model TS-2 (Waltz, Effeltrich, Germany). Pressure was monitored by a barometer model Air DB-VOC (Sirsa, Madrid, Spain). Ozone was produced by passing clean air (Linde, purity of 99.999 %) through a bulb equipped with a mercury UV lamp. This home-made system was previously calibrated as producing ozone with a typical rate of 20 ppb min⁻¹. The terpene concentration was monitored by an on-line gas chromatograph coupled with a photoionisation detector (Fisons GC-8160, Thermo-Fisher, Waltham, MA, USA equipped with a DB-624 cyano-propylphenylpolysiloxane fused silica capillary column, J &W Scientific, 30m, 0.32mmi.d., 1.8 µm film) programmed isothermally at 160 ₃C with a total run time of 10 min. The total aerosol mass was continuously monitored by a TEOM microbalance (model 1400a, Ruppert and Patashnick Co. Inc, Albany, USA) with a one minute averaging time step.

3 Analytical development

3.1 Method overview

The method development was based on the simultaneous sampling of the gaseous phase on Tenax TA sorbent tubes pre-coated with the derivatisation agents and the particulate phase on filters (derivatised after sampling). The global sampling and analytical method is summarised in Fig. 3. The method allows the use of common VOC denuders upstream of aerosol collection filters. Nevertheless, in the present analytical development no denuder was tested.

3.2 Carbonyl functions derivatisation in gas phase samples

For the analysis of carbonyl-bearing molecules in the gas phase, the collection of air samples was achieved on Tenax TA sorbent tubes pre-coated with PFBHA. As the derivatisation reaction occurs onto the sorbent of the cartridges, which is not a classical medium for oximation with PFBHA, one of the key parts of this work was the optimisation of this process and its characterisation.

3.2.1 Sorbent coating and derivatisation

Tenax TA coating was achieved in 20 min, without using any solvent by sublimation of PFBHA: a nitrogen stream (100 ml min⁻¹ tube⁻¹) was passed through a glass bulb, which contained solid PFBHA and was

connected to one or more Tenax TA sorbent tubes (max. 8 tubes, Fig. 4). A PFBHA mass of 330 µg (1.3 µmol) per tube connected was introduced. For a 12 l sample volume (corresponding to a sampling flow rate of 100 ml min^{-1} for 2 h), this PFBHA mass is sufficient to derivatise (i.e. is 10 times higher than) a carbonyl compound at a concentration of around 1 mg m^{-3} (for an average molecular weight of 100). The glass bulb and sorbent tubes were kept at 110 °C in an oven during the coating. As reported by Ho and Yu (2002), after sampling, closed samples were stored at room temperature for a minimum of five days before TD/GC/MS analysis to allow full derivatisation.

3.2.2 Humidity influence

3.2.3 Derivatisation yield and standardisation

The derivatisation yield was estimated by comparing in-solution derivatisation and on-Tenax TA derivatisation. Standard solutions were prepared in a 5/95 water/acetonitrile mixture at a concentration of 80 ng µl^{-1} with 19 carbonyl compounds (eleven aldehydes: methacrolein, valeraldehyde, 2-ethylbutyraldehyde, benzaldehyde, nonanal, ethyl-3-methyl-4-oxocrotonate, citronellal, citral, glyoxal, perillaldehyde, and glutaraldehyde; seven ketones: butanone, 3-buten-2-one, 4-heptanone, carvone, 2,3-butadione, 3-methyl-2,4-pentadione, and camphor; and one keto-aldehyde: methylglyoxal). For in-solution derivatisation, a molar excess of PFBHA corresponding to ten times the molar concentration of derivatisable functions was added to 1 ml of each solution. The solutions were kept at room temperature (around 22 °C) for 24 h. One µl of each of the five derivatised solutions was subsequently vaporised under a heated helium stream (270 °C) and trapped onto five clean Tenax TA tubes just before TD/GC/FID analysis. For on-sorbent derivatisation, one µl of the non-derivatised solutions was injected onto PFBHA-coated Tenax TA tubes by the same procedure. In order to expose the tubes to humidity, clean and wet (50%RH) zero air was sampled onto the tubes during 30 min at a flow rate of 100 ml min^{-1}. Samples were kept at room temperature for 5 days before TD/GC/FID analysis. Two on-Tenax TA derivatisations per solution were performed. The comparison of the results is shown in Fig. 7. For aldehydes (Fig. 7a), on-Tenax TA derivatisation results in close to 100% or higher yields (from 102% to 205%) compared to in-solution derivatisation, except for methacrolein (9%). For ketones (Fig. 7b), on-Tenax TA derivatisation results in lower yields (from 12% to 41 %) compared to in-solution derivatisation (derivatised camphor was not observed in both derivatisation processes).

Based on this experiment and previous ones (see Sect. 2.2.2), the repeatability was estimated from the standard deviation/mean ratio and determined to be equal to or lower than 10% for compounds with more than 4 carbons and lower than 20% for compounds with 4 carbons or less (except for the 80%RH

experiment). Thus, despite the low derivatisation yield for some compounds, a satisfactory on-Tenax TA derivatisation repeatability was observed, allowing quantification.

Consequently, a calibration curve for quantification cannot be based on standards prepared from in-solution derivatisation but has to be made by preparing standards that reproduce real sampling conditions with the method described above and used for estimating the on-sorbent derivatisation yield (by injecting non-derivatised standard solutions onto PFBHA-coated Tenax TA tubes and exposing them to a wet zero air stream to adjust humidity).

3.2.4 Breakthrough volumes

Experiments to determine breakthrough volumes were performed in the CESAM smog chamber. The relative humidity was maintained between 65 and 80% as it was assumed to be unfavourable for breakthrough which may lead to the determination of a lower limit. A temperature of 23 °C remained constant during the experiment. Samplings were achieved on five sampling trains equipped with two in series identical PFBHA-coated sorbent tubes and operated at a flow rate of 100 ml min^{-1}. The experiment was performed within five hours. One sampling was stopped each hour in order to test five sampling volumes.

The breakthrough volume is defined as the air volume required to completely elute a compound through an adsorbent tube (Baltussen et al., 2002). It defines a limit beyond which the trapping is no longer fully efficient and where losses may be encountered. It is defined for a given compound on a given mass of adsorbent and in given environmental conditions of temperature and relative humidity (CEN, 2005). Breakthrough volumes for PFBHA-coated Tenax TA sorbent tubes were evaluated for a series of five carbonyl compounds. A mixture of methacrolein, hydroxyacetone, octanal, benzaldehyde, carvone and perillaldehyde was injected in the CESAM simulation chamber with respective concentrations of 71, 78, 121, 101, 137 and 152 µg m^{-3}. Absolute quantification of these species was achieved by the method used for their injection: for each one of them, a precisely known pressure (in the range 0.1 mbar) was applied via a vacuum ramp from a frozen pure standard solution into a bulb of known volume (V =1.0832 l). The bulb content was then immediately flushed into the chamber. For a given compound, the breakthrough volume is reached when measurable quantities of it are found in the second coated tube (back-up tube). Results are shown in Fig. 8. For most of the compounds the breakthrough was found to be satisfactory as it fell in the range needed to sample organics in air. For methacrolein, the breakthrough volume was reached within the first hour, corresponding to a sampling volume smaller than 6 l. It was reached between the first and the second hour for hydroxyacetone, corresponding to a breakthrough volume between 6 and 12 l. Nevertheless, for the others compounds, octanal, benzaldehyde, carvone and perillaldehyde, the

breakthrough volumes were not reached within five hours, corresponding to a breakthrough volume higher

than 30 l (results are only shown for perillaldehyde, Fig. 8c). Consequently, when the method was applied,

a sampling time between one and five hours was used depending on the atmosphere concentrations but

keeping in mind that carbonyls with a number of carbon inferior to five are subjected to breakthrough, i.e.

keeping back-up tubes if C_4-C_4 carbonyl compounds require quantification.

3.2.5 Linearity and detection limits

Both linearity and detection limits were evaluated from calibration curves. A dilution series of five carbonyl

compounds solutions (9 aldehydes and 8 ketones) from 5 to 320 ng µl^{-1} was used. Calibration curves were

performed from standards reproducing real on-Tenax TA sampling conditions (see Sect. 3.2.3). Results are

shown Table 1, where calibration curve slopes, good correlation coefficient (ranging from 0.9883 to

0.9999) and satisfactory detection limits are given. The response linearity was evaluated from a specific

m/z ion extraction for each compound and was statistically validated (Student's t-test). For the negative

intercepts obtained for two compounds (citronellal and citral), no explanation could be found. Uncertainties

(corresponding to ±2 standard errors) are given for a 95% confidence level. Detection limits (corresponding

to 3 times the area noise) are given in absolute mass per sample tube and in concentration units for a

sampling volume of 12 l (i.e. 100 ml min^{-1} for 2 h). They range from 0.07 to 6 ng per tube corresponding to

concentrations ranging from 6 to 500 ng m^{-3} (or 1.3 to 81 ppt). These detection limits are in the same order

of magnitude or better than those obtained by Ho and Yu (2004) and Li et al. (2009), who propose

sampling of aldehydes onto PFPH (pentafuorophenylhydrazine)-coated Tenax TA tubes and obtained

detection limits ranging from 0.07 to 6 ng sampled per tube (corresponding to atmospheric concentrations

ranging from 6 to 500 ng m^{-3} for a 12 l sample volume). Compared to the classical DNPH method, involving

collection of carbonyls onto DNPH-coated silica cartridges before elution and analysis by HPLC-UV, the

detection limits obtained in the present study correspond to a gain of around one order of magnitude (Ho

and Yu, 2004). The detection limits in the ppt range provided by the method are more than satisfactory

considering the concentration levels of carbonyls which can be reached in the atmosphere. As an example,

Müller et al. (2006) found concentrations of biogenic carbonyl compounds in a forest region to be about

hundreds of ppt.

3.3 Derivatisation of carboxylic and hydroxyl functions in gas-phase samples

For the analysis of hydroxyl-bearing gaseous molecules, collection of the gas phase was performed on

Tenax TA sorbent tubes pre-coated with MTBSTFA reagent in order to analyse the carboxyl and hydroxyl

containing fraction of the gaseous organic matter. This reaction requires significantly different experimental

conditions compared to derivatisation with PFBHA and is known to be sensitive to different parameters. In particular, it is sensitive to humidity, and, hence, required the development of a specific protocol.

3.3.1 Sorbent coating and post-sampling derivatisation protocol

Similarly to the PFBHA procedure, Tenax TA coating with MTBSTFA was achieved without any solvent by vaporisation of 0.3 µl pure MTBSTFA (+1% TDBMCS) under a heated helium stream (270 °C, 30 ml min^{-1}) for only 8 min. A dry purge of 2 min was applied before injection of MTBSTFA to remove traces of water on the sorbent tube. However, as previously mentioned, MTBSTFA-derivatised compounds are subjected to hydrolysis, especially during sampling of humid ambient or simulated atmospheres. Consequently, in order to promote derivatisation, and considering the hydrophobic nature of Tenax TA, samples were re-exposed to MTBSTFA after sampling: samples were opened, 0.3 µl of pure MTBSTFA (+1% TDBMCS) was spiked at each end of the sampling tubes and the re-closed samples were left in a furnace at 60 °C for 5 h. After cooling to room temperature, the samples had to be rapidly analysed by TD/GC/MS within 5 h to prevent decomposition of the derivatives.

3.3.2 Derivatisation yield and standards preparation

Derivatisation yields were estimated comparing in-solution derivatisation and on-Tenax TA derivatisation. In-solution derivatisation was achieved at room temperature within two hours by adding a molar excess of MTBSTFA (corresponding to ten times the molar concentration of derivatisable functions) to the non-derivatised solution in acetonitrile (80 ng µl^{-1}). Derivatised solutions were then evaporated under a heated helium stream and trapped onto clean Tenax TA tubes before TD/GC-FID analysis. On-Tenax TA derivatisation was achieved by preparing standard Tenax TA tubes. Clean Tenax TA tubes were spiked with the non-derivatised solution directly onto the Tenax TA adsorbent with a micro-syringe. Spiked tubes were placed 3 min under a heated helium stream (270 °C, 30 ml min^{-1}) in order to elute compounds on the Tenax surface and better represent a real sampling. Tubes, thereafter referred as carboxyls/hydroxyls standard tubes, were then derivatised as previously presented for samples (see Sect. 3.3.1) and analysed by TD/GC-FID. The comparison of the results is shown in Fig. 9. A good agreement was found between in-solution and on-Tenax TA derivatisation yields for the acids while significant discrepancies were observed for hydroxyl-bearing species. This is especially true for some alcohols such as phenol, *t*-butyl-4-hydroxy-butyrate, 1-nonanol, 4-methoxyphenol - for which decreases larger than 45% in the derivatisation yield were observed. Thus, despite the low derivatisation yields for some compounds, satisfactory on-Tenax TA derivatisation repeatability was observed, allowing quantification. Consequently, calibration curves for quantification cannot be based on standards prepared from in-solution derivatisation but have to be

constructed by preparing standards reproducing real sampling conditions with the method described above and used for estimating the on-sorbent derivatisation yield.

3.3.3 Humidity influence

The ability of the post-sampling derivatisation process to overcome the influence of humidity on the derivatisation process was evaluated by humidifying carboxyl/hydroxyl standard tubes before the post-derivatisation process. Two series of three carboxyls/hydroxyls standard tubes were prepared by spiking one µL of a non-derivatised solution at a concentration of 80 ng µL^{-1}. Wet zero air (50%RH) was sampled for thirty minutes at a flow rate of 100 ml min^{-1} on the first series while the second series remained closed, in dry conditions. After the post-derivatisation process, both series were analysed by TD/GC-FID. The results are shown in Fig. 10, revealing no significant discrepancies between wet and dry standards (except for nonanol and phenol) despite a lower repeatability for some compounds in wet conditions. Consequently, the post-derivatisation process is assumed to overcome the influence of humidity on the analytical protocol and the calibration can be performed using dry carboxyls/hydroxyls standard tubes. From the humidified series of three standards, an estimation of the method repeatability can be given. The mean standard deviation/mean ratio was 25% for all compounds, ranging from 12 (*t*-butyl 4-hydroxybutyrate) to 55% (ethyleneglycol) for alcohols and from 1 (crotonic acid) to 79% (caffeic acid) for carboxylic acids.

3.3.4 Breakthrough volumes

Given the difficulty to generate stable atmospheres of low vapour pressure hydroxyl and carboxyl compounds, precise breakthrough volumes could not be determined. An evaluation of the breakthrough of MTBSTFA-coated sorbent tubes is given here as breakthrough data for a series of carboxyl and hydroxyl compounds generated in an isoprene photo-oxidation experiment. This experiment was selected because it produced a wider range of volatile oxygenated species compared to the limonene ozonolysis experiment and was conducted in the EUPHORE chamber. The initial isoprene concentration was 55 ppb for an initial H$_2$O$_2$ concentration of 4 ppm. The relative humidity and temperature were 25% and 303 K, respectively, during sampling time, after exposing the chamber to sunlight and system stabilisation. Sampling was achieved onto two in series MTBSTFA pre-coated Tenax TA sorbent tubes at a flow rate of 100 ml min^{-1} during two hours (sampled volume: 12 l). The second tube (following air flux) is considered as a "back-up tube" to collect the compounds that were not completely trapped onto the first one. The results are shown in Table 2, which gives an evaluation of the breakthrough in %, corresponding to the ratio between the amount of compound measured in the back-up tube and that measured in the sample tube, for each examined compound. No breakthrough could be observed for most examined compounds, especially for those bearing several functionalities and/or displaying a carbon skeleton with more than five carbons. It

must be pointed out, to explain the measurement of compounds with more than five carbons when running an isoprene photo-oxidation experiment, that the smog chamber blanks were contaminated. Since the purpose of this experiment was to determine the breakthrough volume and not to explain isoprene oxidation pathways, all the detected compounds were taken into account for the evaluation of the breakthrough. Significant breakthrough was only observed for mono-functionalised compounds with a carbon number less than seven. If these compounds are targeted, the use of back-up tubes is thus required. Poly-functionalised compounds, even with only two carbons, do not seem to be affected by breakthrough under our experimental conditions. Their breakthrough volumes are consequently estimated to be greater than 12 l. When performing measurements in the same sampling conditions of sample volume, sampling flow rate, humidity, and temperature, the use of back-up tubes is thus not required. When performing measurements in different conditions, the determination of breakthrough volumes or the use of back-up tubes is recommended.

3.3.5 Linearity and detection limits

Both linearity and detection limits were evaluated from calibration curves. A dilution series of five hydroxyl compounds and organic acid solutions (6 alcohols and 14 organic acids) from 5 to 320 ng μl^{-1} was used. Calibration curves were performed from standards reproducing real on-Tenax TA sampling conditions (see Sect. 3.3.2). 1 µl of carbonyl compound standard solutions were spiked onto Tenax TA tubes and subsequently derivatised with MTBSTFA at 60 °C for 5 h. Results are shown in Table 3. Response linearity for all compounds was statistically validated (Student's t-test) and uncertainties (corresponding to ±2 standard errors) are given for a 95% confidence level. Detection limits (corresponding to 3 times the area noise) are given in absolute mass per sample tube and in concentration units for a sampling volume of 12 l (i.e. 100 ml min^{-1} for 2 h). They range from 0.05 to 10 ng per tube and from 5 to 830 ng m^{-3}. These detection limits are lower than those obtained by Wu et al. (2008) for the analysis of volatile fatty acids without derivatisation and in the same order of magnitude or lower than those obtained by Chiappini et al. (2006) or Pietrogrande et al. (2010). The detection limits in the latter study ranged from 1.2 to 6.8 ng per GC/MS injection for mono- and di-carboxylic acids in the aerosol phase with prior derivatisation in CO_2 super-critical fluid or in solution. The detection limits obtained in the present study, ranging from 1 to 232 ppt, are more than satisfactory to measure hydroxyl and carboxyl compounds at lower ambient concentration levels. As an example, the concentration levels of dicarboxylic acids measured by Legrand et al. (2005) at altitude sites in France are a few tens of ppb.

For general purposes, PFBHA derivatisation is usually performed in aqueous or water containing solutions (Cancilla and Que Hee, 1992) and a molecule of water is formed for each derivatised compound (Fig. 5). A

positive influence of the humidity contained in the sampled air is consequently expected on the derivatisation process. On the other hand, humidity can disturb the collection of compounds, reducing the adsorption efficiency (Harper, 1993; Loedwyckx and Vansant, 2000). In order to evaluate this humidity influence a series of aldehydes was sampled from a dry (0%RH) and wet (50%RH) simulated atmosphere. The experiment was carried out in the INERIS dynamic simulation chamber. The system was adjusted to generate crotonaldehyde, benzaldehyde, butanal, pentanal and hexanal at concentrations of 11.7, 17.7, 12.0, 14.3, and 16.7 µg m^{-3}, respectively. Sampling was performed during four hours at a sampling flow rate of 150 ml min^{-1}, connecting coated sorbent tubes to the chamber through a sampling cane. Five and six replicates were collected for a complementary experiment that was performed in order to evaluate bias linked with humidity variations within a realistic relative humidity range. Three sampling series of three replicates were collected at 30, 50, and 80%RH. Sampling was performed during one hour at a sampling flow rate of 100 ml min^{-1}. The results are shown in Fig. 6, revealing no significant bias linked to humidity variations within this realistic relative humidity range. A relative humidity of 30% appears to be sufficient to reach a maximum derivatisation yield in these conditions. However, a slight repeatability decrease is observed at 80% RH, probably due to competition between water and adsorbed organic molecules on adsorbent surface sites. Nevertheless, this observation is consistent with the fact that high humidity levels are known to affect sampling on classic adsorbents, decreasing breakthrough volumes (Harper, 1993; Loedwyckx and Vansant, 2000). The developed method to trap and derivatise gaseous carbonyl compounds can thus be considered as suitable under realistic sampling conditions.

3.4 Derivatisation of carbonyl functions in particulate phase samples

Collection of the particulate phase for the analysis of carbonyl compounds was achieved on 47 mm quartz fibre filters (see Sect. 2.1.4) at a typical flow rate of 1 m^3 h^{-1} (16.7 l min^{-1}) and was done simultaneously with sampling of the gas phase. The PFBHA post-sampling derivatisation was performed by sample introduction into stainless-steel tubes that are suitable for thermal desorption and derivatisation by the in-solution PFBHA procedure. The humidity influence on the particulate-phase derivatisation process is expected to be similar to that observed for gas-phase derivatisation (cf. Sect. 3.2.2).

3.4.1 Post-sampling derivatisation protocol

The 47mm sample filter was cut in four parts and one part was introduced into a clean stainless steel thermal desorption tube. After introduction, 2 µl of a saturated PFBHA solution (27 mg ml^{-1}, 90/10 acetonitrile/ultrapure water mixture) is applied onto the filter part. A glass bulb with eight outlets is then used to expose in-tube samples to a saturated PFBHA aqueous solution for 40 h. This duration is

expected to be sufficient to impregnate a rolled filter with PFBHA and is convenient for protocol organisation. From one end, the filter sample tubes are connected to the bulb outlets while the other end is maintained closed.1 mL of ultrapure water is introduced in the bulb and stirred (500 rounds per min). 90mg of pure and solid PFBHA is then added to the water. The bulb is closed and the system is kept at room temperature. After 20 h, the filter sample tubes are disconnected, reversed, reconnected by the other end and let for 20 h again. Filter sample tubes are then definitely disconnected, closed and kept at room temperature for a minimum of 5 days before analysis.

3.4.2 Standard preparation, linearity, and detection limits

Standards used to construct calibration curves were prepared and derivatised in the same way as sample filters. Clean quartz fibre filters were introduced into empty stainless steel desorption tube with application of a PFBHA-saturated solution, spiked with 1 µl of standard carbonyl compound solutions (5 points from 5 to 320 ng µl^{-1}) and left for 40 h connected to a stirred glass bulb containing 1 ml of a PFBHA-saturated aqueous solution (with tube reversion after 20 h) at room temperature. Both linearity and detection limits were evaluated. Results are shown in Table 4, giving for each compound the calibration curve slopes, the correlation coefficients, which are generally good (most are ranging from 0.9131 and 0.9999, except for three compounds displaying an R_2 value ranging from 0.7846 to 0.8890), and the detection limits, which are satisfactory.

Response linearity for all compounds was statistically validated (Student's t-test) and uncertainties (corresponding to ±2 standard errors) are given for a 95% confidence level. Detection limits (corresponding to 3 times the area noise) are given in absolute mass per filter and in concentration units for a sampling volume of 2 m^3 (i.e. 16.7 l min^{-1} for 2 h). These detection limits ranging from 0.04 to 120 ng per filter (corresponding to an atmospheric concentration of 0.02 and 60 ng m^{-3} for a 2 m^3 sample volume) are more than sufficient to measure carbonyl compounds in the atmosphere, where their concentrations are in the same order of magnitude (Liggio and McLaren, 2003).

3.5 Derivatisation of carboxylic and hydroxyl functions in particulate-phase samples

Collection of the particulate phase for the analysis of carboxyl and hydroxyl compounds was performed on 47mm Teflon-quartz fibres filters (see Sect. 2.1.4.) at a typical flow rate of 1 m^3 h^{-1} (16.7 l min^{-1}), simultaneously with gas-phase sampling. The MTBSTFA post-sampling derivatisation procedure was performed after sample introduction into stainless-steel tubes that are suitable for thermal desorption by sample exposure to pure MTBSTFA (+1% TDBMCS).

3.5.1 Post-sampling derivatisation protocol

The 47 mm sample filter was divided in four parts and one part was introduced into a clean stainless-steel thermal desorption tube. MTBSTFA was not spiked directly onto the filter: 10 µl of pure MTBSTFA (+1% TDBMCS) was applied on the bottom of one tube cap and the sample filter tube was closed in vertical position above the MTBSTFA (cf. Fig. 11). The filter was exposed to MTBSTFA at room temperature during 24 h. The filter sample tube was then directly analysed by TD/GC/MS within 5 h.

3.5.2 Humidity influence and standard preparation

As for gaseous compounds, derivatisation on Tenax TA tubes, humidity is expected to influence the on-filter MTBSTFA derivatisation process; therefore, Teflon-quartz filters were chosen to reduce moisture loading during wet air sampling. Nevertheless, in order to evaluate the influence of this moisture loading on the derivatisation process, response factors of a series of standard compounds were compared for dry and prehumidified Teflon-quartz filters. Five point calibration curves (from 5 to 320 ng µl^{-1}) were constructed using filters spiked with standards and prepared and derivatised in the same way as sample filters. Wet Teflon-quartz filters were humidified by sampling wet zero air (50%RH) at a flow rate of 7 l min^{-1} for 2 h. Clean and dry or wet filters were introduced into empty stainless-steel desorption tubes and spiked with standard solutions. They were subsequently derivatised by exposition to MTBSTFA for 24 h at room temperature. The comparison results for compound response factors are given in Fig. 12. Surprisingly, the response factors were significantly higher onto humidified filters for 15 standard compounds on 18. Moreover, for keto-acids (6-oxoheptanoic acid and cis-pinonic acid), di-acids (succinic acid and pinic acid) and malic acid, the compound responses became linear compared to their responses on dry filters (not mentioned in Fig. 12). The reason why humidity positively influences on-filter derivatisation is not clear. It might be explained by competition phenomena between water and polar compounds to form bonds with the quartz surface. In this case, moisture loading may positively affect both the derivatisation reaction and the desorption capacity, limiting the adsorption of polar compounds on the filter surface. Anyway, the positive influence of moisture loading onto filters has two main consequences on the method: it is not necessary to dry sample filters before derivatisation with MTBSTFA and calibration curves can be constructed using humidified Teflon-quartz filters.

3.5.3 Linearity and detection limits

Both linearity and detection limits were evaluated from calibration curves that were previously used for the evaluation of the humidity influence. The results are shown Table 5, giving for each compound the calibration curve slopes, correlation coefficients, which are satisfactory and range from 0.9433 to 0.9999, and detection limits, which are low. Response linearity was statistically validated (Student's t-test) and uncertainties (corresponding to ±2 standard errors) are given for a 95% confidence level. Detection limits

(corresponding to 3 times the area noise) are given in absolute mass per filter and in concentration units for a sampling volume of 2 m^3 (i.e. 16.7 l min^{-1} for 2 h). The linearity was not validated for two standard compounds, i.e. 4-oxoheptanedioic acid (keto-diacid) and 3-carboxyhexanedioic acid (tri-acid). Nevertheless, these compounds were detected above an absolute mass of 100 ng spiked onto standard filters and their responses were linear derivatisation with MTBSTFA onto Tenax TA tube, meaning that ketodi-acids and tri-acids cannot be quantified but can be detected in the particulate phase. Improvement of the developed particulate-phase MTBSTFA derivatisation protocol is required to specifically quantify keto-di-acids and tri-acids. Detection limits for all other compounds range from 0.04 to 1.0 ng per filter. These detection limits are significantly better than those obtained by Chiappini et al. (2006), which range from 1 to 7 ng for an analogous series of acids, keto-acids and di-acids, using derivatisation with BSTFA during supercritical fluid extraction coupled to GC/MS analysis. The detection limits are more than satisfactory to measure carboxylic acids in atmospheric particles since their concentration levels are about a few tens of ng m^{-3} as measured by Sun and Ariya (2006).

4 Method application to limonene ozonolysis in a simulated atmosphere

Limonene is a significant contributor to monoterpene emissions that accounts for around 11% of global VOC emissions (Guenther et al., 1995). Moreover, with two double bonds, it is more reactive and has a higher SOA yield (around twice, Griffin et al., 1999) compared to mono-unsaturated monoterpenes, such as α- and β-pinene, which are emitted in larger amounts at a global scale. Limonene is consequently supposed to be a significant contributor to SOA at global scale. Furthermore, limonene is also widely present in indoor environments as it is largely employed in household cleaning products, air fresheners, or essential oils, for example (Singer et al., 2006). Limonene oxidation in indoor environments, especially through ozonolysis, has been demonstrated by many studies in the last years, pointing out strong airway irritants and ultrafine particle formation (Clausen et al., 2001; Sarwar and Corsi, 2007; Langer et al., 2008; Coleman et al., 2008; Forester and Wells, 2009; Jardine et al., 2011). Therefore, limonene ozonolysis was chosen as a relevant system to assess the potential of the developed method to explore the chemical composition of oxygenated secondary organic matter simultaneously in gaseous and particulate phases. Moreover, this chemical system is sufficiently well characterised, allowing us to compare our results to the literature for method validation purposes (e.g. Leungsakul et al., 2005a,b; Jaoui et al., 2006; Walser et al., 2007; Forester and Wells, 2009; Yasmeen et al., 2011).

4.1 Experimental protocol

Limonene ozonolysis experiment was conducted in the EUPHORE simulation chamber (cf. Sect. 2.3.3) in order to approach real indoor or outdoor atmospheric conditions. Limonene was first injected in the

chamber at an initial concentration level of 100 ppb. Non-acidified sulphate ammonium seeds were introduced by nebulisation of a 0.02M solution at a concentration of 12.5 µg m^{-3}. Water was then introduced until an initial relative humidity of 50% was reached. Ozone was finally injected during 5 min 16 s, corresponding to an initial concentration of 105 ppb (see Sect. 2.3.3). The average temperature during the experiment was 300±1 K. No hydroxyl radical scavenger was introduced as this would stray the experiment from realistic indoor conditions (Docherty and Ziemann, 2003; Jonsson et al., 2008). Main parameter variations as monitored during the course of the experiment are given in Fig. 13. In order to evaluate the fraction of the oxidative chemistry initiated by hydroxyl radicals on limonene – originating from Criegee intermediate decomposition after ozone addition onto double bonds – a simulation was run using the Master Chemical Mechanism, MCM v3.2 (Jenkin et al., 1997; Saunders et al., 2003). Initialising the MCM with our experimental conditions, it was found that around two-thirds of the initial limonene amount reacts with ozone while one-third is expected to react with hydroxyl radicals. As a result, both ozonolysis and photo-oxidation products of limonene are likely to be detected and are thus consequently specifically investigated. Blanks were sampled just before ozone introduction during 120 min. Gas-phase blanks were sampled on one PFBHA- and one MTBSTFA-coated Tenax TA tubes at a flow rate of 100 ml min^{-1} downstream a Teflon filter (Zefluor, 47 mm, Pall Life Sciences).

Particulate-phase blanks were sampled in parallel on one quartz filter and one Teflon-quartz filter at a flow rate of 16.7 l min^{-1}. Sampling was performed during 160 min after ozone introduction and system stabilisation (aerosol maximum mass reached within one hour). The gas phase was sampled onto three PFBHA- and three MTBSTFA-coated Tenax TA tubes at a flow rate of 100 ml min^{-1} downstream a Teflon filter. For each derivatisation reagent one tube was equipped with a back-up tube (see Sect. 3.2.4), which was coated in the same way to observe possible breakthrough of the sample tubes. The particulate phase was sampled onto one Teflon-quartz and two quartz filters at a flow rate of 16.7 l min^{-1}. No VOC denuder was used in this method testing experiment. It is important to note that no specific set-up was used to minimise sampling artifact for these experiments, since the main objective of the experiments here was the application of the methodology presented and characterised in the previous section. All samples were analysed by TD/GC/MS, in both EI and CI modes, as previously described (see Sect. 2.2.).

4.2 Results

4.2.1 Aerosol mass yield

The secondary aerosol growth curve for the limonene ozonolysis experiment is given in Fig. 14. The aerosol mass yield corresponds to the time-dependant aerosol mass yield Y calculated from TEOM measurements and is defined as:

$Y = \acute{E}M_0 \acute{E}HC$

where $\acute{E}M_0$ is the aerosol mass loading (µg m^3) and $\acute{E}HC$ is the total reacted limonene (µg m^3), both corrected for dilution and wall losses. The final aerosol mass yield was around 20%. Higher values are usually observed in the same experimental conditions (_50% by Jaoui et al., 2006; Northcross and Jang, 2007; Sun et al., 2011, _65% by Saathoff et al., 2009). The lower value measured here can be explained by the elevated temperature of 300 K achieved in the chamber during our experiment, as demonstrated by Saathoff et al. (2009) who examined the influence of temperature on SOA yields from limonene ozonolysis.

4.2.2 Product detection and identification

Compound detection and identification were based on characteristic fragmentation patterns of PFBHA and MTBSTFA derivatives (cf. Table 6) in EI and CI modes. As much as possible, the mass spectra of derivatised compounds and their retention time were compared to available standard data. Compounds were positively identified in the case where standards are available. Otherwise, a tentative assignment is proposed based on the comparison of the fragmentation pattern and the retention time comparison with surrogate standards. Compounds detected in chamber blanks in the same order of magnitude than in samples were removed from the product list. Around 30 compounds could be detected in the gas phase as PFBHA or MTBSTFA derivative products (20 PFBHA derivatives and 10 MTBSTFA derivatives) and around 65 in the particulate phases (30 PFBHA derivatives and 35 MTBSTFA derivatives). These products range from C_{8} to C_{10} compounds and from mono- to tri-functionalised species. Compounds detected in the gas phase range from C_3 mono-carbonyl, C_5 mono-hydroxyl or C_6 mono-acid to C_{10} di-carbonyl and C_8 di-hydroxyl or di-acids. In the particulate phase tri-functionalised compounds are observed in the C_8–C_{10} range. Among all these detected products, 25 have been positively (based on standard mass spectra comparison) or tentatively identified (based on surrogate standard and/or mass spectra). An overview of the limonene oxidation products detected and tentatively or positively identified in both gas and particulate phases is presented in Table 7. Fourteen products previously identified from limonene oxidation experiments (Leungsakul et al., 2005a; Jaoui et al., 2006; Forester and Wells, 2009) or expected from theoretical oxidation schemes (Leungsakul et al., 2005b) were observed (P2, P3, P5, P6, P8, P9, M1, M2, M4, M6, M7, M9, and M10). In addition to these species, eleven other products were, to the best of our knowledge, detected for the first time (P1, P7, M4, M6, M9, M12, M13, M14, M15, M16, and M17). This provides certainly the most comprehensive list of detected compounds in a single experiment for limonene ozonolysis in both gaseous and particulate phases. This new information shows the potential of the method to explore the chemical composition of the secondary organic matter in a relevant range of semi-volatile

compounds, and, hence, opens the way to new chemical scheme building for the production of semi-volatile organic species in the limonene ozonolysis system. An example of chromatograms is given for the analysis of carbonyl compounds in both phases (Fig. 15). Recollection is a useful option provided by some commercial thermal desorbers, which provides a way to easily obtain complementary data for compound identification by re-injection of the same sample. We used this option to confirm peak identification by re-analysing samples in the chemical ionisation mode. It must be indicated here that this approach is affected by elevated detection limits obtained in CI mode for recollected samples, especially for MTBSTFA-derivatised samples. The approach was not validated for quantification as further experiments revealed that recollected MTBSTFA samples have to be analysed as soon as possible after first injection. Unfortunately, this was not possible in this study. Other attempts showed that a 24 h delay seems to significantly improve detection limits compared to the presented results for recollected sample, analysed in the CI mode within 7 days.

4.2.3 Quantification and estimation of partitioning coefficients

Among the 30 compounds detected in the gas phase and the 65 compounds detected in the particulate only those for which a relevant standard calibration in the gas and/or particulate phases (see Tables 1, 3, 4 and 5) could be obtained were quantified. This has led to the quantification of 18 detected compounds, which are given Table 8. For compounds quantified in both the gas and particulate phases, it was possible to calculate their experimental partitioning coefficient (Table 9), considering a total aerosol concentration of 45±12 µg m^{-3} that corresponds to the average real aerosol concentration during sampling, not corrected for aerosol losses in the chamber. Uncertainties were calculated on the basis of gas phase, particulate phase and aerosol mass quantification uncertainties (calibration curves and TEOM uncertainty). Experimental partitioning coefficients were compared to values calculated from theoretical vapour pressure data estimated for three group contribution methods (Myrdal and Yalkowsky, 1997; Nannoolal et al., 2008; Pankow and Asher, 2008). The following parameters were used for these calculations: an experimental temperature of 300 K, an average molecular weight in the particulate phase (MW_{om}) of 142 and an activity coefficient (i) of 1.27. These two last values were taken from simulation results reported by Leungsakul et al. (2005a). When available, experimental partitioning coefficients were also compared with other experimental values.

The total quantified products represent around 16% in carbon mass of the reacted limonene. The remaining non-quantified mass can be divided in three main groups: (1) non-identified compounds that were detected here but not quantified, (2) non-derivatisable species, and (3) high molecular weight compounds such as oligomers.

Limononaldehyde (P6) was the most abundant product in the gas phase, as observed by Leungsakul et al. (2005a) for limonene ozonolysis experiments. However, contrary to this previous study, limononaldehyde was also the most abundant product observed in the particulate phase instead of keto-limononaldehyde. The experimental partitioning coefficient for limononaldehyde obtained in the present study is 3.5×10^{-3} m^3 µg^{-1}, a value which is three orders of magnitude higher than estimation calculation and two orders of magnitude higher than the limononaldehyde experimental partitioning coefficients estimated by Leungsakul et al. (2005a) (around 6×10^{-5} m^3 µg^{-1}). The second most abundant products in the gas phase were methylglyoxal and dimethylglyoxal, methylglyoxal being also the second most abundant compound in the particulate phase. The experimental partitioning coefficient for methylglyoxal is also three orders of magnitude higher than estimated coefficients. However, it is similar to experimental values determined by Ortiz et al. (2010) during field (3.4×10^{-2} m^3 µg^{-1}) and toluene oxidation smog chamber (1×10^{-4} m^3 µg^{-1}) experiments.

Another important product detected in both gas and particulate phases was 4-oxopentanal (P5). This compound was previously detected as a limonene oxidation product only by Forester and Wells (2009). It was also observed at high levels in a forestal atmosphere (180–1570 ng m^3 in the gas phase and 25–207 ngm^3 in the particulate phase (Matsunaga et al., 2004), indicating that 4-oxopentanal could be an important SOA contributor. However, its major source is assumed by these authors to be the oxidation of 6-methyl-5-heptene-2-one (6-MHO), which originates from squalene oxidation). However, 6-MHO was not observed in the present study, suggesting another pathway for 4-oxopentanal formation, which will not be discussed here.

Experimental partitioning coefficient estimation for 4-oxopentanal provides a value five orders of magnitude higher than estimation calculation. Dioxohexanal (P7), 3,6-dioxoheptanal (P8) and keto-limononaldehyde (P9) were only quantified in the particulate phase although their estimated partitioning coefficients predict gas phase concentration higher than 100 000 µg m^{-3}. More realistically, Leungsakul et al. (2005a) provide experimental partitioning coefficients of keto-limononaldehyde in the range of 1.41–1.76×10^{-3} m^3 µg^{-1}. From these values and the keto-limononaldehyde particulate phase concentration estimated in the present study, a gas phase concentration of around 1×400 ng m^{-3} could be expected, which is still largely above detection limits achieved for di-carbonyls compounds in the gas phase. From this observation, three hypotheses could be advanced. Firstly, tri-carbonyl compounds may not exist significantly in the gas phase under the experimental conditions of this work and the keto-limononaldehyde gas phase concentration quantified by Leungsakul and co-workers was either mainly a positive artifact due to volatilisation from the particulate phase or linked to different experimental conditions. Secondly, these compounds are more

subjected to a negative artifact upon quantification in the gas phase than dicarbonyl compounds due to adsorption onto the Teflon filter placed upstream the adsorbent tubes, this negative artifact increasing as expected when decreasing compound volatility (Volckens and Leith, 2003). Thirdly, tricarbonyl compounds may not be detectable when sampled onto gas collection Tenax TA tubes due to either derivatisation which may not be complete or a limited desorption. Further experiments based on tricarbonyl standards are required to support or invalidate this last hypothesis.

Levulinic acid (M1) was the most important acid observed in the gas phase. Li and Yu (2005) proposed that levulinic acid is an oxidation product of 4-oxopentanal. Limonic acid (M9) was the major acid that could be precisely quantified in the particulate phase with a concentration of 70±10 ng m^{-3}. A keto-diacid (M10: ketolimonic acid) and two tridicarboxylic acid (M15 and M16) were also identified in the particulate phase. However, since their standard or surrogate standard calibration curves were not linear, their concentration was estimated on the basis of pinic acid for M10 (160 µg m^{-3}) and malic acid for M15 and M16 (100 µg m^{-3} and 80 µg m^{-3}). The experimental partitioning coefficient of limonic acid is of the same order of magnitude than estimation calculation from MY and SIM. However, it is an order of magnitude higher than NAN estimation calculation and experimental values provided by Yu et al. (1999) for other biogenic di-acids: pinic acid, caric acid, and sabinic acid, 2.8–3.5×10-2 µgm-3, 3.3×10-2 µgm-3 and 2.7×10-2 µgm-3, respectively, at 306–308 K. Experimental partitioning coefficients of hexanedioic acid (M6) and pentanedioic acid (M4) were also consistent with theoretical calculations. The experimental partitioning coefficient of succinic acid (M2) was one or two orders of magnitude higher than theoretical calculations. To conclude, using quantification of compounds in both gaseous and particulate phases, partitioning coefficients have been calculated. Differences can be observed in comparison with estimated and other experimental coefficients. Some hypotheses can be proposed to explain these discrepancies: (i) the estimated partitioning coefficient are calculated on the basis of estimations that may be wrong, which is one of the objectives of the present study; providing partitioning coefficient obtained under real atmospheric conditions, (ii) reactions occurring in the particulate phase can disturb the equilibrium leading to different partitioning coefficients than expected, which is another objective of our study; identifying unsuspected reaction pathways, and (iii) sampling positive artifacts upon particulate phase quantification since no denuder has been used for particulate phase sampling.

Artifacts seem to be less important for di-acids than for carbonyl compounds. This is consistent with: (i) the Teflon-quartz nature of the filter media that is expected to reduce adsorption artifacts compared to quartz filters, even if this feature is not confirmed by Arp et al. (2007) and (ii) the artifact tendency expected to

decrease decreasing compound volatility, from carbonyl compounds to limonic acid (Volckens and Leith, 2003).

5 Conclusions and perspectives

This work has provided a useful new analytical method based thermal desorption coupled with GC/MS, to explore the secondary organic matter composition at a molecular scale from a global point of view, in both gas and particulate phases. Using separately but in parallel two derivatisation reagents, PFBHA and MTBSTFA, to analyse carbonyl compounds, and organic acids and hydroxylated compounds, respectively, the method allows to explore chemical composition up to tri-functionalised species. Furthermore, it combines the classical advantages of thermal desorption – solvent free, easy to use and fast – to the possibility to analyse the same sample in both EI and CI modes, providing complementary structural information, through the use of the recollection option of commercial thermal desorbers. The potential of the method to determine the partitioning behaviour of a wide range of semi-volatile compounds has been demonstrated. Quantification in both gas and particulate phases is indeed validated for mono- and di-functionalised species and for hydroxyl di-acids. This is a substantial progress compared to other techniques designed for compound partitioning studies. Compared to the TAG technique (Isaacman et al., 2011), whose main advantage is based on on-line measurements, the developed method widens the range of detectable species to polar and multi-functionalised compounds. Compared to denuder/filter techniques (e.g. Leungsakul et al., 2005a; Temime et al., 2007) it provides a simpler way to study the partitioning of the secondary organic matter, avoiding time-consuming sample workup procedures that are prone to sample losses during solvent extraction steps, with similar detection limits. It is an easy way to systematically assess, in simulation chamber experiments and in the field, the partitioning behaviour of semi-volatile compounds, providing a set of data in a wide range of environmental conditions able to support a relevant integration of partitioning in models.

Application of the method to the study of limonene ozonolysis demonstrates the potential of the method to explore the chemical composition of a complex mixture in both gas and particulate phases, detecting both compounds already known as limonene oxidation products and a range of products detected for the first time. In the present study, 25 limonene oxidation products were positively or tentatively identified, 9 being in both gaseous and particulate phases and 11, among them tricarboxylic acids, hydroxyl dicarboxylic acids and oxodicarboxylic acids, being detected for the first time.

Quantification and partitioning coefficient estimations were provided, although, as no precautions were taken to avoid or correct artifacts for the quantification of compounds in both gas and particulate phases, their relevance for atmospheric conclusions are limited here.

Nevertheless, decoupling gas and particulate sampling, the method allows testing a wide range of possibilities to limit (e.g. denuder use) or correct (e.g. backup filter use) artifacts. Furthermore, derivatisation protocols should be improved to extend the range of quantifiable species to tri-functionalised compounds. To improve the confidence in the experimental determination of partitioning coefficients for tri-carbonyl compounds, observed in limonene ozonolysis particulate phase samples, it appears necessary to assess detection limits in the gas phase and to provide more relevant calibration curves for the particulate phase. It is demonstrated that ketodiacids and triacids are quantifiable in the gas phase and can be detected in limonene ozonolysis particulate phase samples. An adjustment of the derivatisation protocol for the particulate phase, such as a small increase of the derivatisation temperature, is shown to provide relevant calibration curves.

In conclusion, the developed method allows to explore the chemical composition of the semi-volatile fraction of the oxygenated secondary organic matter and to assess its partitioning behaviour from mono- to difunctionalised carbonyl, hydroxyl and organic acids species. Further improvement could enlarge the quantifiable species in both gas and particulate phases to trifunctionalised compounds. The method is applicable to both simulation chamber experiments under realistic humidity conditions and field campaigns.

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experiment produced a wider range of volatile oxygenated species compared to the

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A complementary experiment was achieved in order to evaluate bias linked with humidityvariations

within a realistic relative humidity range. Three sampling series ofthree replicates were achieved at 30,

50 and 80 %RH. Sampling was performed duringone hour at a sampling flow rate of 100 ml min^{-1}.

Results are shown Fig. 6. Theyreveal no significant bias linked to humidity variations within this

realistic relative humidity

range. A relative humidity of 30% appears to be sufficient to reach maximumderivatisation yield in

these conditions. However, a slight repeatability decrease is observedat 80%RH, probably due to

competition between water and adsorbed organicmolecules on adsorbent surface sites. Nevertheless, this observation is consistent withthe fact that high humidity levels are known to affect sampling on classic adsorbents,

decreasing breakthrough volumes for example (Harper, 1993; Loedwyckx and Vansant,2000). The developed method to trap and derivatise gaseous carbonyl compounds isconsequently considered as suitable under realistic sampling conditions.

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Carbonyl functions derivatisation

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