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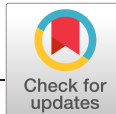
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RESEARCH ARTICLE

New application of direct analysis in real time high-resolution mass spectrometry for the untargeted analysis of fresh and aged secondary organic aerosols generated from monoterpenes

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Rationale: Secondary organic aerosols (SOAs) represent a significant portion of total atmospheric aerosols. They are generated by the oxidation of volatile organic compounds (VOCs), and particularly biogenic VOCs (BVOCs). The analysis of such samples is usually performed by targeted methods that often require time-consuming preparation steps that can induce loss of compounds and/or sample contaminations.

Methods: Recently, untargeted methods using high-resolution mass spectrometry (HRMS) have been successfully employed for a broad characterization of chemicals in SOAs. Herein we propose a new application of the direct analysis in real time (DART) ionization method combined with HRMS to quickly detect several hundred chemicals in SOAs collected on a quartz filter without sample preparation or separation techniques.

Results: The reproducibility of measurements was good, with several hundred elemental compositions common to three different replicates. The relative standard deviations of the intensities of the chemical families ranged from 6% to 35%, with sufficient sensitivity to allow the unambiguous detection of 4 ng/mm² of pinic acid. The presence of oligomers and specific tracers was highlighted by MSⁿ ($n \leq 4$) experiments, an achievement that is difficult to attain with other ultrahigh-resolution mass spectrometers. Contributions of this untargeted DART-HRMS method were illustrated by the analysis of fresh and aged SOAs from different gaseous precursors such as limonene, a β -pinene/limonene mixture or scots pines emissions.

Conclusions: The results show that it is possible to use DART-HRMS for the identification of tracers of specific aging reactions, or for the identification of aerosols from specific biogenic precursors.

1 | INTRODUCTION

Atmospheric particulate matter (PM) is generated by both human and natural sources. It adversely affects human health, air quality and climate change.¹⁻⁴ Whereas the inorganic fraction is well described in the literature today, atmospheric organic aerosols (OAs) are poorly known because of the high number of individual compounds present.

A significant portion of OAs originates from the oxidation of biogenic volatile organic compounds (BVOCs).⁵⁻⁷ Due to their high reactivity, they have a very short lifetime in the atmosphere, from several minutes to a few hours, and react quickly with various oxidants.⁸ β -Pinene and limonene, for example, have well-known biogenic sources, and their oxidation rates under ozone action are well determined. Thanks to these measurements, their lifetimes have been

calculated as 0.19 h and 1.9 h, respectively, in a urban atmosphere.⁹ This oxidation leads to numerous highly functionalized compounds that finally generate secondary organic aerosols (SOAs) by gas-to-particle conversion processes.¹⁰ This fraction of atmospheric OA is known to represent up to 90% of the total atmospheric particulate matter in tropical forest areas;³ for this reason, it should be accurately described. The in-depth investigation of SOAs remains an analytical challenge: on one hand, a considerable diversity of compounds is created during SOA formation, and, on the other hand, the dynamic character of environmental samples can induce additional transformations after SOA formation.¹¹ Sample analysis is usually performed by targeted techniques such as gas chromatography,¹² liquid chromatography,¹³ aerosol mass spectrometry,¹⁴ electrospray mass spectrometry,¹⁵ proton transfer mass spectrometry (PTRMS)¹⁶ and matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS).¹⁷ These techniques provide good sensitivity and specificity for targeted molecules, but the number of compounds analyzed is limited and a large proportion of the SOAs is neglected.

To obtain a wide overview of chemicals present in a complex mixture, untargeted methods can be used. The aim is to analyze samples with the minimum of selective experimental steps combined with an analysis of the whole mixture simultaneously. This methodology has the advantages that it can give a global description of samples and can be used to study the effect on samples of chemical reactions,¹⁸ the efficiency of industrial processes,¹⁹ or to characterize and compare natural substances.²⁰

For several years, high-resolution mass spectrometry (HRMS) has been employed as a powerful tool for the chemical speciation of extremely complex mixtures.^{21,22} It involves the use of an ionization method such as electrospray ionization (ESI) to generate mainly protonated or deprotonated molecules with a limited number of fragments without the use of chromatography. In addition, the mass accuracy of HRMS makes it possible to attribute an individual elemental composition to each mass peak. Several hundred compounds have thus been identified in SOAs from BVOCs, greatly increasing our overall knowledge about this kind of sample.²³⁻²⁵ In most cases, this approach requires the extraction of particles sampled on a filter into an organic solvent compatible with ESI although this procedure may alter the sample.²⁶ This step can induce some compound loss and often imposes an additional filtration step to eliminate from the sample any solid residues that could disturb the ionization. New technologies based on ambient ionization techniques can be used to avoid sample preparation by the direct ionization of chemicals at the surface of a sample. One of them is desorption electrospray ionization (DESI), which has been successfully employed in a wide range of applications.²⁷ This method is based on the formation of ions during the collision of charged droplets on a substrate. DESI leads to similar ions to ESI and does not require sample preparation. Nevertheless, the use of an adequate solvent remains essential. In addition, the ionization is strongly affected by the charges available, including anions or cations dissolved in solvents, present in ambient air or present in the samples. This can considerably affect the complexity of mass spectra, because several different adduct ions may appear, leading to a decrease in the intensity of protonated or deprotonated molecules.

This paper proposes a new application of another soft ionization method: direct analysis in real time (DART). This ambient ionization technique was first presented by Cody in 2005 for the chemical analysis of organic compounds present on surfaces or in the gas phase.²⁸ It is based on a metastable helium stream allowing both desorption and ionization of organic molecules. Like the DESI method, DART does not require a time-consuming preparation step and presents the advantages of limited matrix effect, no solvent or additive use, and low adduct formation.²⁹ Although this method has been used successfully in numerous applications such as forensics,^{30,31} water analysis,³² petroleomic analysis³³ or online aerosol analysis,^{34,35} to our knowledge, no communication has yet been published about the analysis of filter-collected SOAs by DART-HRMS using an untargeted approach. Herein we present a description and characterization of DART ionization combined with HRMS and an untargeted approach for the chemical characterization of SOAs. The method was then applied to SOA samples from different precursors and for the study of their aging under irradiation or after a nitrogen oxide exposition.

2 | EXPERIMENTAL

2.1 | SOA sample collection

2.1.1 | SAPHIR chamber experiment

BVOCs were generated at the SAPHIR atmospheric simulation chamber in Forschungszentrum Juelich (Germany) during the PISA (PIMMS at SAPHIR) campaign (July 2015). The SAPHIR chamber is made of Teflon FEP (fluorinated ethylene propylene) foil and has a volume of 270 m³. During the experiments, synthetic air (Linde, Munich, Germany; purity 6.0) was constantly supplied, with a flush-out flow rate of <350 m³/h. Before the injection of any gas, the chamber was humidified by heating up high-purity water and adding it to the flush-out flow. The humidification stage lasted approximately 1 h, to reach a relative humidity of 60%. The reactive atmosphere was adjusted to 20 ppm of carbon dioxide, and to a controlled amount of reactive gases as described in Table 1.

Furthermore, SAPHIR has a shutter system, which permits the investigation of oxidation reactions initiated by the OH-radical (aging experiments). The SAPHIR-PLUS (plant chamber unit for simulations) is an environmentally controlled continuous-flow plant chamber installed next to SAPHIR that can be coupled to SAPHIR to simulate the atmospheric processes of BVOCs directly emitted by plants. All important environmental parameters, such as temperature, relative humidity, and photosynthetic active radiation (PAR), are monitored in PLUS. All chamber surfaces, including the film separating the stem and the leaves from the plants soil, are made out of fluorinated ethylene propylene (FEP, Teflon), in order to minimize potential losses of BVOCs.

The SOA from a unique precursor (limonene) was first analyzed. Then, a mixture of limonene/ β -pinene and finally a scots pines emission were used as precursors to increase the complexity of the SOAs produced. Aging of the SOAs was then performed under irradiation or in the dark after their creation to determine if the DART-HRMS method could be used for the study of aging processes.

TABLE 1 Experimental conditions of SOA creation and aging

Precursors	Precursor amount (ppbv)	Ozone amount (ppbv)	SOA amount in chamber ($\mu\text{g}/\text{m}^3$)	Aging conditions
limonene	25	150	40	NO 30 ppbv; dark; 18 h
β -pinene/limonene	60/12	300	50	Light; 4 h
Scot pines emissions		300	40	Light; 4 h

2.1.2 | Sampling system for the offline detection of SOAs

SOAs generated in the SAPHIR chamber were collected onto preheated (800°C for 24 h) Pall quartz filters (diameter 47 mm), at a flow rate of 14 sL/min, for 6.25 h from the ozone injection, by using particle samplers installed underneath the chamber. Field background filters were collected using the same method while the chamber was empty, during the chamber humidification process (for 1 h before the start of each experiment). Blank samples were collected by placing an empty filter in the samplers. The filters were transferred from the samplers to cleaned holders placed in sealed bags, kept at room temperature for some minutes to prevent particle condensation, then stored in a refrigerator at 4°C and transported cooled. The filters were then stored at 4°C for 4 weeks prior to analysis.

2.2 | Mass spectrometry parameters

2.2.1 | DART-HRMS

All mass spectra presented in this study were acquired from only one filter, in negative detection mode with a DART-SVP ion source (IonSense, Saugus, MA, USA). High-purity helium (99.998%) heated at 300°C was used as ionization gas at a pressure of 80 psi. A slight vacuum was applied with a small membrane pump working at a flow of approximately 11 L/min (Vacuubrand, Wertheim, Germany) and connected to a Vapur® interface (IonSense) located between the DART source and the mass spectrometer. The outlet of the DART source was placed in the axis of the ceramic tube leading to the Vapur interface before the inlet of the mass spectrometer. The distance between the outlet of the DART source and the ceramic tube was approximately 15 mm, and samples were placed in the middle of this gap for their analysis.

The DART ion source was interfaced to an LTQ-Orbitrap XL ion trap-Orbitrap mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA). The ion optics were optimized on background ions for the best transfer at m/z 255 and finally set as follows: capillary voltage: -35 V; tube lens voltage: -45 V; capillary temperature: 275°C; multiple 00 offset voltage: 3.25 V; multipole 0 offset voltage: 3.25 V; multiple 1 offset voltage: 45 V; lens 0 voltage: 9.5 V; lens 1 voltage: 12 V; gate lens voltage: 95.5 V; front lens voltage: 5.25 V. The mass range acquired was m/z 150–1000. The resolving power was set to 100,000 FWHM at m/z 400 with 1 microscan and a maximum injection time of 500 ms. Each mass spectrum was obtained from the average of 100 individual scans, corresponding to a total analysis time of 3.5 min. All fragmentation experiments were performed by collision-induced dissociation (CID) using helium as the collision gas. The collision energy was set to 30 eV for all experiments.

2.2.2 | Calibration and data processing

Prior to acquisition, the instrument was first externally calibrated as instructed by the manufacturer's manual using the provided mixture consisting of sodium dodecyl sulfate (SDS), sodium taurocholate and Ultramark 1621. During acquisition, each individual spectrum was recalibrated online, using an internal lock mass consisting of a background ion previously identified by isotopic distribution, mass accuracy and MS/MS analysis. Typically, the $[\text{M} - \text{H}]^-$ ion of palmitic acid at m/z 255 was used as the lock mass, and other identified background signals, such as that of oleic acid, were used to check the mass accuracy. Blank filters from the PISA experiments were first analyzed to verify the absence of chemical contamination that could be adsorbed. The quartz filter did not contribute to blank analysis. The main part of the peak observed was attributed to the instrumental background. All data were acquired using Thermo Xcalibur™ software.

All peaks detected with a signal-to-noise (S/N) ratio higher than 3 were processed using Composer software (Sierra Analytics, Pasadena, CA, USA). Before processing, the mass accuracy was checked by the attribution of the elemental composition of a known background compound (oleic acid). The error observed on the elemental composition assignments for these compounds before recalibration was systematically lower than 2 ppm. The post-acquisition recalibration was then based on a fifth-degree polynomial equation. Internal reference masses used for the calibration were based on the CH_2 series computed from different formulae to calibrate the mass spectrum over the entire mass range. The error of internal reference masses was systematically lower than 2 ppm before recalibration. The second possibility for the elemental composition was checked for each spectrum and at three different reference masses: at low mass, in the middle of the mass range and at high mass. For all mass spectra, the error corresponding to the second possibility was higher than 5 ppm. The calibration was then validated by the verification of the average error of the reference mass, which must be lower than 1 ppm. After the removal of background ions, the elemental compositions were assigned, with an error lower than 3 ppm. The elemental compositions authorized were C_{5-30} ; H_{5-70} ; O_{0-30} ; and N_{0-5} ; they followed the rules for hydrocarbons. The assignments were validated by checking the error distribution, which had to be between -3 and +3 ppm and equitably distributed around 0 ppm. Moreover, the Shapiro-Wilk test was performed on residual errors using Statistica software to validate the normality of the distribution. Elemental compositions were exploited using the double-bond equivalent (DBE) value, its ratio to the number of carbon atoms (DBE/C), and several graphical representations such as classification by chemical families, the Kendrick plot and the Van Krevelen diagram, whose construction is described in numerous other papers.³⁶⁻³⁸

3 | RESULTS AND DISCUSSION

3.1 | Method performances

3.1.1 | Full scan analysis

Methods sensitivity, the reproducibility of elemental composition assignment and chemical families intensities are presented only for the SOA sample generated from the β -pinene/limonene mixture for which the analysis was performed in triplicate.

The mass spectrum represented in supplementary data 1 (supporting information) shows several distributions from m/z 150 to 280, 280 to 480 and 480 to 650 which are here described as areas 1, 2 and 3, respectively. The presence of these distributions is in agreement with data available in the literature and the distributions are usually assigned to primary oxidation products for area 1, and to oligomers from the primary oxidized compounds for areas 2 and 3.

The sensitivity was estimated by quantifying the pinic acid collected on the filter. It was determined by LC/ESI-MS/MS as described in other papers³⁹ and estimated at 7 $\mu\text{g}/\text{filter}$, corresponding to 4 ng/mm^2 . This quantity of pinic acid was unambiguously detected by DART(-)-Orbitrap at m/z 185 with a S/N ratio of close to 12,000 that indicated good sensitivity.

To estimate the reproducibility of assignments, DART(-)-HRMS analysis was performed in full-scan mode at three times over three different days. For each mass spectrum obtained, the elemental composition assignment was performed as described in section 2. The mass spectra of the three replicates are displayed in supplementary data 1 a, 1b and 1c (supporting information). They show similar distributions from m/z 150 to 750 with similar relative intensities. For each replicate, 91–93% of the assignable peaks were successfully attributed, whereas 7–9% of the residual signals correspond mainly to artefacts linked to the deformation of very

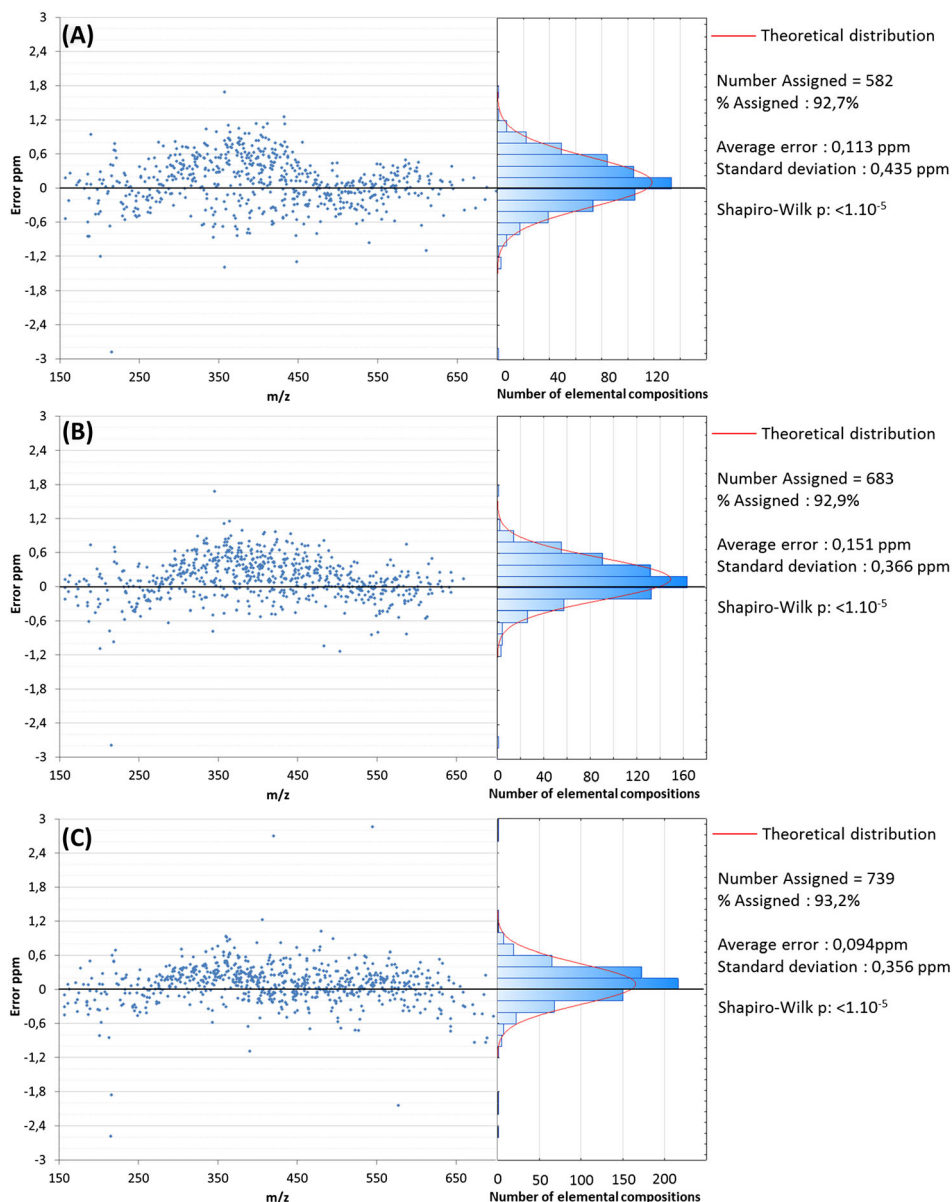


FIGURE 1 Error distribution and Shapiro–Wilk tests for A, first analysis, B, second analysis and C, third analysis of SOAs from the ozonolysis of the β -pinene/limonene mixture

intense peaks. The intensity of signals common to each replicate represents 90–99% of the total ion current (TIC), meaning that the elemental compositions assigned to only one or two of the three replicates correspond to low-intensity peaks. For each analysis, 647–739 elemental compositions were assigned, and among them, 580 were common to the three samples, indicating good reproducibility for the attribution. The error committed on the elemental composition assignment is displayed in Figures 1A, 1B and 1C for the three replicates. It shows a regular distribution around the 0 value with an average error from 0.094 ppm to 0.15 ppm. The normality of the distribution is graphically represented in Figure 1, and shows good agreement with the theoretical Gaussian function. Moreover,

a Shapiro–Wilk test at an alpha value of 5% was performed. The p-value calculated was systematically lower than 1.10^{-5} , confirming the distribution normality hypothesis and validating the mass calibration.

Elemental compositions were grouped into different chemical families according to their numbers of oxygen and nitrogen atoms. The relative intensities of each family and their respective standard deviation are shown in Figure 2A; the reproducibility of the intensities is good, and the RSD values are situated between 6% and 35% for all families with abundance higher than 2%. Figure 2B displays the Kendrick plot corresponding to a typical mass spectrum of the SOA from the β -pinene/limonene mixture and clearly shows the three distributions defined before.

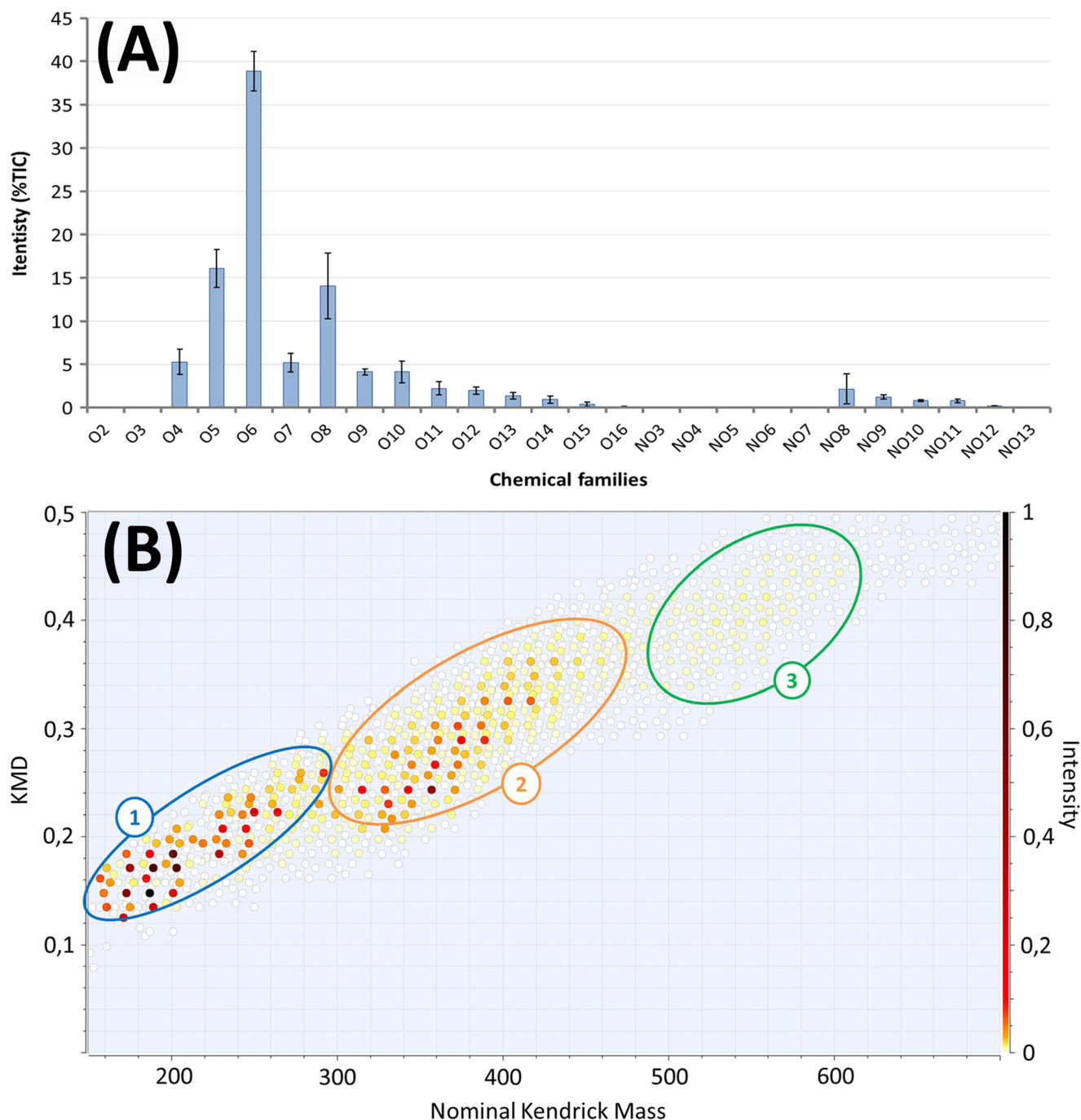


FIGURE 2 A, Chemical families with the standard deviation as error bars. B, Kendrick plots obtained after the analysis by DART(-)HRMS of SOAs from the ozonolysis of the β -pinene/limonene mixture

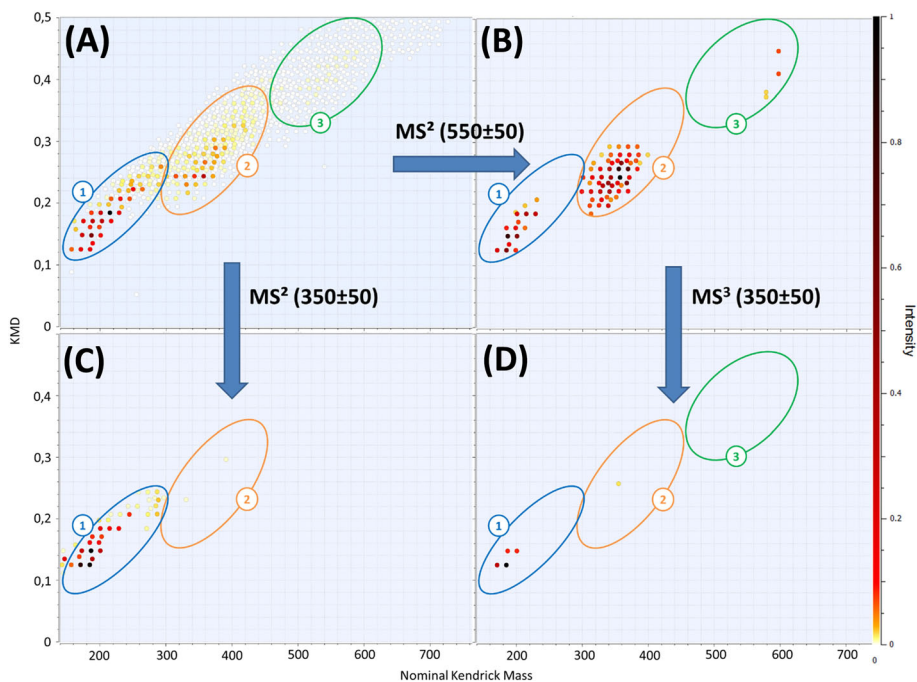


FIGURE 3 DART(-)HRMS Kendrick plots of A, full scan analysis of SOA, B, MS^2 experiment from area 3, C, MS^2 experiment from area 2 and D, MS^3 experiment from area 2 in B,

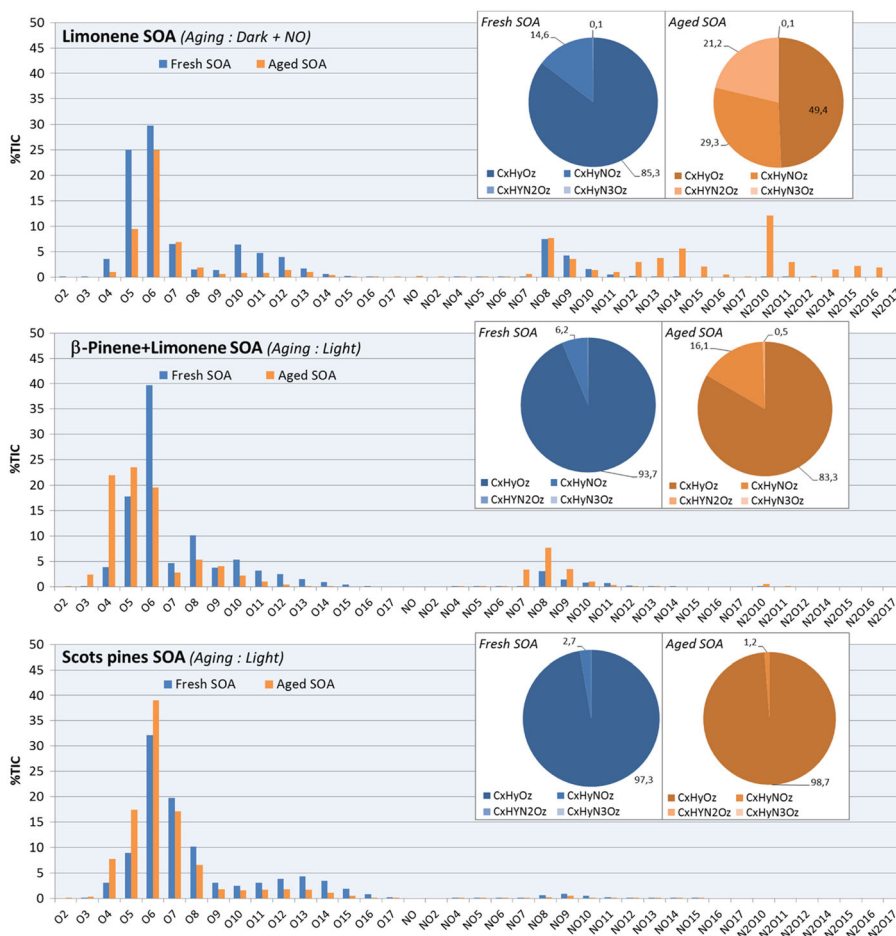


FIGURE 4 Chemical families detected by DART(-)HRMS for fresh (blue bars) and aged (orange bars) SOA created from limonene, the β -pinene/limonene mixture and scots pines emissions

These results obtained in full scan detection mode by DART-HRMS are in accordance with other studies of SOAs from monoterpene using ESI-HRMS, DESI-HRMS or nanoDESI-HRMS,^{23,27,40,41} revealing the reliability of the description for a typical sample. The main advantage of the method presented here is the absence of solvent for extraction or ionization allowing us to limit sample manipulation and contamination.

3.1.2 | MSⁿ experiments

In an attempt to explore the possibility of structural studies, MSⁿ experiments were conducted. Due to the complexity of the mass spectra, it was impossible to specifically isolate one ion. The methodology used therefore consists in a selection of *m/z* 100 ranges to isolate areas 1, 2 or 3. Kendrick maps corresponding to product ion mass spectra (Figures 3B, 3C and 3D) show that the product ions from area 2 are very similar to those present in area 1 (Figure 3C). The presence of ions at *m/z* 185 and *m/z* 171 that could correspond to pinic acid and norpinic acid, respectively, can be noted.

The fragmentation of area 3 (Figure 3B) reveals the presence of two distinct distributions close to areas 1 and 2. An MS³ experiment was then conducted by isolating the distribution from *m/z* 300 to 400; this led to the appearance of four peaks located in area 1, among

them peaks corresponding to pinic acid at *m/z* 185 and norpinic acid at *m/z* 171 were observed. Finally, *m/z* 185 was isolated from the MS³ experiment and fragmented at 30 eV (MS⁴) before being compared with the spectrum obtained from the MS² experiment with pure pinic acid. The two product ion spectra are displayed in supplementary data 2 (supporting information). Product ions obtained from pure pinic acid correspond to the loss of CO₂, H₂O and CO₂ + H₂O, in agreement with other studies.^{39,42,43} The MS⁴ spectrum clearly shows two common peaks with a relative distribution close to the pinic acid MS² spectrum, allowing its unambiguous identification. This allows a reliable identification of pinic acid after several stage of fragmentation, and shows its importance in the oligomerization processes as described in the literature.¹⁷

In order to reject the possibility of dimerization in the DART ionization region, 500 ng (~ 40 ng/mm²) of pure pinic acid was deposited on a grid prior to analysis. No dimers or trimers were observed in this case, confirming that all dimers and trimers detected originated from the sample and were not generated by DART ionization.

3.2 | Fresh SOA analysis

When a fresh SOA is analyzed, the number of elemental compositions assigned varies between 893 for limonene precursors and 1198 for

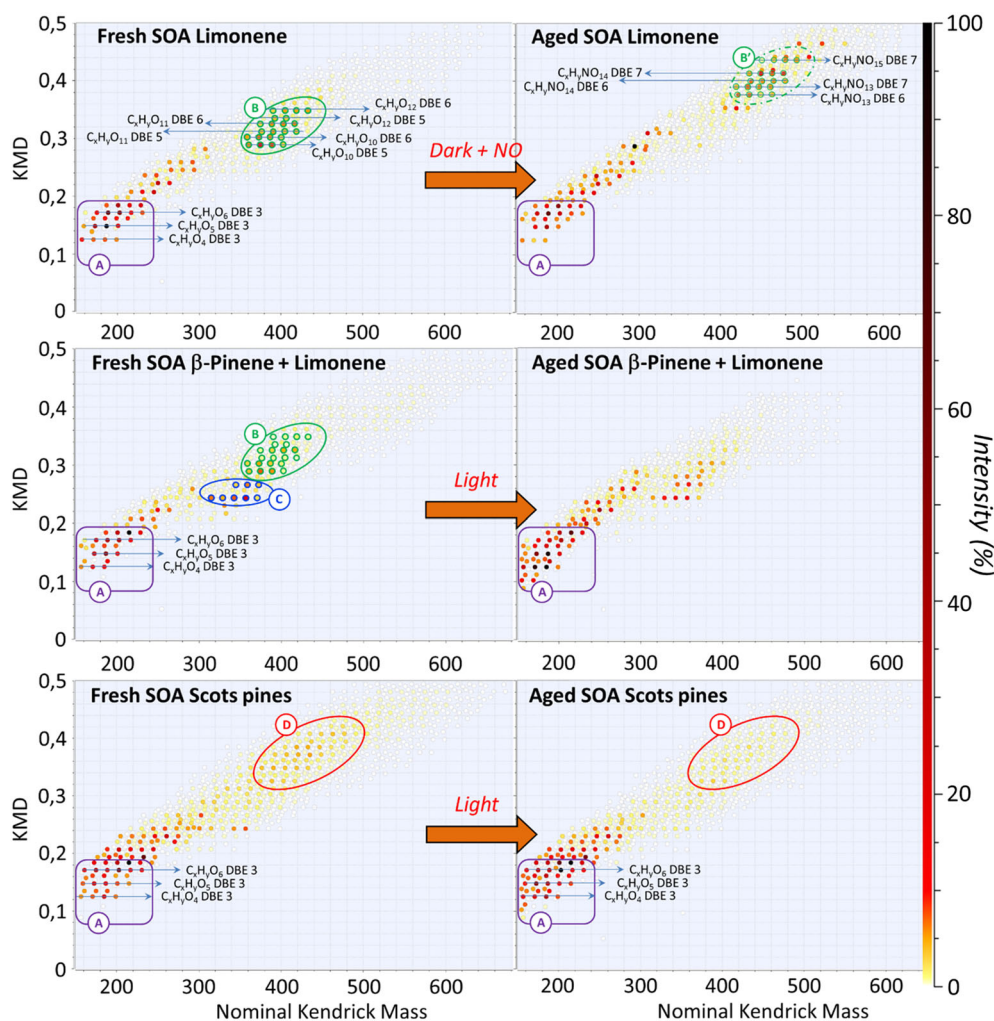


FIGURE 5 Kendrick plots for fresh (right-hand side) and aged SOA (left-hand side) created from limonene, the β -pinene/limonene mixture and scots pines emissions

scots pine precursors, with most of these corresponding to oxygenated families. Figure 4 shows that 85–97% of the intensity of the total ion current (TIC) is assigned to $C_xH_yO_z$ compounds and 5.6–29.3% to $C_xH_yNO_z$ compounds. More precisely, three distributions of chemical families can be observed for the limonene fresh SOA depending on the number of oxygen atoms. The first corresponds to $C_xH_yO_{4-7}$, a second is associated to $C_xH_yO_{10-14}$ and the last is identified as nitrogenated compounds $C_xH_yNO_{8-11}$.

The distribution of chemical families for the SOA generated from the mixture of β -pinene and limonene is slightly different from that of the limonene SOA. The $C_xH_yO_{4-7}$ and $C_xH_yO_{10-13}$ distributions seem close to the homologous distributions of limonene SOA. The $C_xH_yO_{8-9}$ classes are clearly seen in the mixture, whereas they had a low intensity in the lone limonene SOA sample. Their formation could be explained by a specific oxidation pathway from β -pinene.

Particles generated from scots pines present a first intense distribution of chemical families corresponding to $C_xH_yO_{4-9}$, a second distribution from 10 to 17 oxygen atoms and the lowest intensities were assigned to $C_xH_yNO_{8-11}$ compounds.

It has been noted that nitrogenated families containing a high number of oxygen atoms were observed. One explanation is the possibility that the nitrate ions created from the ambient atmosphere could lead nitrate adducts.

Kendrick maps for all fresh samples are displayed in Figure 5. Each sample reveals several distributions assigned to primary oxidized products and their oligomers as described in the previous section. Nevertheless, the mixture of β -pinene and limonene clearly reveals a specific contribution (area C) at m/z ~320 to 380 with lower KMD from 0.24 to 0.28 than for the lone limonene precursor. This could indicate the possibility of specific oligomerization reactions when β -pinene is used as the SOA precursor despite the strong similarities of the primary oxidized products located in area A. Thus, one ion could represent different isomers, which are impossible to observe individually with our mass spectrometer. Nevertheless, the DART-MS method could be potentially used to identify SOAs created from specific precursors using their oligomer identifications.

For the scots pines SOA, the Kendrick plot shows a strong density of points revealing the high complexity of this sample with more than 1000 elemental compositions. The Kendrick plot presents specific peaks in the area named 'D' with high intensities, which appears specific to this mixture of precursors.

3.3 | Aged secondary organic aerosol analysis

3.3.1 | OH aging

Mixture of β -pinene and limonene SOA aging

The number of elemental compositions assigned was 893 before and 743 after aging of this mixture, indicating a slight decrease in the complexity on the mass spectrum. The intensity of highly oxygenated species ($O > 10$) as well as the $C_xH_yO_6$ family decreased after aging whereas the $C_xH_yO_4$ and $C_xH_yO_5$ families increased (Figure 4). Area A on the Kendrick map shows chemical families close to these before aging, but with a larger range of DBE values (Figure 5). The aging of the mixture of β -pinene and limonene reduces the molecular weights

of the molecules. Indeed, only a few compounds are observed with ions at m/z higher than 500 whereas a high number of compounds was observed in this mass range for fresh SOA.

Scots pines SOA aging

The aging of SOA from Scots pines reveals an increase in the intensity of $C_xH_yO_{4-6}$ families and a decrease of all families with more than 7 oxygen atoms (Figure 4). As for the mixture of β -pinene and limonene, the complexity of area A is increased after aging. On the contrary, compounds with masses higher than 500 all have a lower intensity after aging. This results in an increase in the number of compounds of low mass and a decrease in compounds with a high mass, as has been observed for the mixture of β -pinene and limonene.

3.3.2 | NO aging

The aging of the limonene SOA in the dark in the presence of NO drastically changes the chemical composition of the SOA. First, the intensity of nitrogen-containing families reaches 50.6% of the TIC (Figure 4). Among them, the $C_xH_yNO_z$ and $C_xH_yN_2O_z$ families represent 29.3% and 21.2% of the TIC, respectively, whereas the $C_xH_yN_wO_z$ family was associated with 14.6% of the TIC in fresh SOA. Even if the NO_{8-11} families which were already present before aging did not vary, the appearance of the $C_xH_yNO_{12-17}$ and $C_xH_yN_2O_{10-17}$ families with a relative abundance reaching 17% of the TIC can be noted. On the contrary, the intensities of the $C_xH_yO_{10-12}$ and $C_xH_yO_{4-5}$ families that are present at strong intensity in the fresh SOA are drastically decreased after aging.

The Kendrick maps (Figure 5) show different regions. Some similarities can be observed, such as area A, which contains the same species before and after aging. On the contrary, however, major differences can be observed particularly in area B from m/z 350 to 450. A large proportion of the compounds in this region is of low intensity or completely disappears after aging. The appearance of other compounds with higher mass can be noted after aging, and these are grouped in a same area named B' on the Kendrick map. This area contains intense peaks associated with $C_xH_yN_{1-2}O_{12-16}$ molecules with the same pattern as in area B before aging, but with differences of an increase of one DBE and an addition of NO_3 in the elemental composition. It is reasonable to suspect that this chemical transformation affects specifically a targeted class of compounds whereas the others stay unchanged.

4 | CONCLUSIONS

This paper presents a new application of DART-HRMS for the investigation of different secondary organic aerosols created from the ozonolysis of monoterpenes, and their aging under different conditions. Particles were collected on a quartz filter prior to their direct analysis without a preparation step in a run time lower than 4 min. The method described presents sufficient sensitivity for an unambiguous detection of pinic acid at a level of 4 ng/mm², and good reproducibility of the elemental composition assignments with several hundred compounds common to three different analyses. For all families with a relative abundance higher than 2% of the TIC, the relative standard deviation ranged from 6 to 35%. The

sensitivity and the signal stability allowed MSⁿ ($n \leq 4$) experiments that highlighted the oligomeric distribution of the sample and a reliable identification of pinic acid.

The DART-HRMS method was then applied for the analysis of SOAs coming from one precursor (limonene), a mixture of precursors (limonene+ β -pinene) and a real mixture (scots pines emissions). Each aerosol was then aged under irradiation or in the dark and in the presence of NO.

For fresh SOA, the DART-HRMS method allowed the distinction of probable specific tracers of β -pinene SOA by the study of the oligomeric compounds. For samples aged under irradiation, a global decrease in the mass of molecules was observed. Moreover, the distributions corresponding to oligomers of the primary oxidized compounds present a decrease in their intensity after aging. The DART-HRMS analysis of sample aged in the dark with NO oxidant allowed us to highlight a specific aging reaction on oligomeric compounds whereas primary oxidized molecules stay unchanged.

DART-HRMS could therefore be used as a rapid, easy-to-use, solvent-free and reliable method for the chemical study of atmospheric organic aerosols with the possibility to quickly identify specific tracers of SOAs created from different precursors. In addition, DART-HRMS was successfully applied to investigate the aging of different SOAs.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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