



Functional group composition of organic aerosol from combustion emissions and secondary processes at two contrasted urban environments[☆]



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HIGHLIGHTS

- Tandem mass spectrometry is used to characterize functional groups in primary and secondary OA.
- Aging increases by one order of magnitude carboxylic and carbonyl functional groups.
- Biomass burning OA and SOA are associated with substantial amounts of alcohol functional groups.

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ABSTRACT

The quantification of major functional groups in atmospheric organic aerosol (OA) provides a constraint on the types of compounds emitted and formed in atmospheric conditions. This paper presents functional group composition of organic aerosol from two contrasted urban environments: Marseille during summer and Grenoble during winter. Functional groups were determined using a tandem mass spectrometry approach, enabling the quantification of carboxylic (RCOOH), carbonyl (RCOR'), and nitro (RNO₂) functional groups. Using a multiple regression analysis, absolute concentrations of functional groups were combined with those of organic carbon derived from different sources in order to infer the functional group contents of different organic aerosol fractions. These fractions include fossil fuel combustion emissions, biomass burning emissions and secondary organic aerosol (SOA). Results clearly highlight the differences between functional group fingerprints of primary and secondary OA fractions. OA emitted from primary sources is found to be moderately functionalized, as about 20 carbons per 1000 bear one of the functional groups determined here, whereas SOA is much more functionalized, as in average 94 carbons per 1000 bear a functional group under study. Aging processes appear to increase both RCOOH and RCOR' functional group contents by nearly one order of magnitude. Conversely, RNO₂ content is found to decrease with photochemical processes. Finally, our results also suggest that other functional groups significantly contribute to biomass smoke and SOA. In particular, for SOA, the overall oxygen content, assessed using aerosol mass spectrometer measurements by an O:C ratio of 0.63, is significantly higher than the apparent O:C* ratio of 0.17 estimated based on functional groups measured here. A thorough examination of our data suggests that this remaining unexplained oxygen content can be most probably assigned to alcohol (ROH), organic peroxides (ROOH), organonitrates (RONO₂) and/or organosulfates (ROSO₃H).

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1. Introduction

There has been strong interest of late in the organic fraction of the atmospheric aerosol (OA), particularly its complex composition, oxidation state, and reactivity (Hallquist et al., 2009 and reference therein), properties that govern its health and climate impacts. Recent developments of isotopic (^{14}C) and real-time aerosol mass spectrometry (e.g. Aerodyne Aerosol Mass Spectrometer, AMS), together with updated inventories of molecular markers, have markedly improved our ability to identify different components of OA including its primary fraction (POA) directly emitted from fossil fuel combustion (PFOA) or biomass burning (BBOA) and its secondary fraction (SOA) formed in-situ in the atmosphere (Hallquist et al., 2009). While it was shown that highly oxygenated organic aerosol (OOA) constitutes the overwhelming fraction of OA in nearly all environments (Jimenez et al., 2009), considerable uncertainties remain in identifying the most significant routes by which this fraction accumulates and evolves in the atmosphere (Kroll and Seinfeld, 2008).

A widespread source of OOA is SOA, whose formation implicates complex oxidative processes of a myriad of volatile organic compounds (VOC), processes that include both functionalisation and fragmentation of the parent carbon backbone. As a result, an immensely complex matrix of organic compounds is formed, which remain dynamic through reversible partitioning and ongoing photochemical aging (Donahue et al., 2009; Kroll et al., 2009). Despite the complexity of the detailed molecular mechanism of SOA formation and aging, a relatively small number of functional groups characterize the oxidized molecules constituting SOA. That is, given the carbon number and the set of functional groups (Kroll et al., 2009), the physicochemical properties of SOA components including their volatility and oxidation state can be estimated and used for the development of predictive models for SOA production rates, burden, sinks and interaction with climate (e.g. Valorso et al., 2011). Ambient AMS measurements suggest that the chemical composition of SOA is characterized amongst functional groups by both carbonyls (traced by the fragment at m/z 43) and carboxylic acids (traced by the fragment at m/z 44), the latter predominating in aged air masses (Ng et al., 2010). More recently, the application of Van Krevelen diagrams (H:C vs. O:C ratio) to HR-ToF-AMS data (High Resolution-Time of Flight-Aerosol Mass Spectrometer) points out that aging seems to be in line with the formation of carboxylic (Heald et al., 2010), hydroxylic and peroxylic groups (Ng et al., 2011; Chhabra et al., 2011). While AMS results seem to be consistent with the detection of poly-carboxylic acids in OA (often referred to as HULIS for Humic Like Substances), the observations needed to confirm the functional group composition proposed for SOA remain currently elusive.

Because functional groups have more chemical specificity than that in m/z fragments or atomic O:C ratios provided by AMS, their relative contributions (termed functionalisation rates, RF) are valuable information to investigate the possible SOA formation and evolution pathways in the atmosphere. While common analytical techniques for functional group analysis include Fourier-Transform InfraRed spectroscopy (FTIR, Liu et al., 2009; Schwartz et al., 2010; Russell et al., 2011) and nuclear magnetic resonance (NMR, Tagliavini et al., 2006; Decesari et al., 2007), we recently proposed a tandem mass spectrometry (MS/MS) approach for the quantitative analysis of carboxylic (RCOOH), carbonyl (RCOR'), and nitro (RNO₂) functional groups, with high sensitivity and good accuracy (Dron et al., 2007, 2008a,b). The application of this approach on OA emitted from different sources has revealed significant differences in their functional group contents (Dron et al., 2010). It was shown that laboratory generated SOA produced through photo-oxidation

of *o*-xylene is dominated by RCOR', whereas RCOOH and RNO₂ are comparatively preponderant in wood smoke and vehicular emissions, respectively. It was hence suggested that these functional group fingerprints offer an interesting potential to discriminate the dominant sources of ambient organic aerosol and its chemical evolution in the atmosphere. More recently, the same approach has been applied to examine the impact of aging on genuine HULIS, clearly showing that such processes increase significantly the oxidation state of the organic matter (Baduel et al., 2011). Here, we present results of functional group analyses in two contrasted urban environments (Marseille in the summer and Grenoble in the winter), with the aim of characterising the functional group fingerprints of OA arising from different sources in real ambient conditions and assessing the impact of photochemistry on these fingerprints.

2. Methods

2.1. PM_{2.5} collection and characterisation

Results presented below were obtained within the two intensive field campaigns of the FORMES project at two contrasted urban environments in France, Marseille in summer (31 June–14 July 2008) and Grenoble in winter (14–29 January 2009). A full description of the sampling sites and the general conditions encountered can be found in El Haddad et al. (2011a,b) and Favez et al. (2010), for Marseille and Grenoble campaigns, respectively.

For both campaigns, particles were continuously collected on a 12 h-basis using high volume samplers (Digitel, DA80) operating at a flow rate of 30 m³ h⁻¹. The collection took place onto 150 mm-diameter quartz fibre filters (Whatman QMA), pre-heated at 500 °C during 3 h (30 samples for Marseille and 30 samples for Grenoble). Samples were then stored at -18 °C in aluminium foil, sealed in polyethylene bags until analysis. Six field blank samples were also prepared following the same procedure.

The collected aerosol was comprehensively characterised, and data are thoroughly presented and discussed in El Haddad et al. (2011a,b) and Favez et al. (2010), for Marseille and Grenoble campaigns, respectively. In particular, data used in this study comprise concentrations of EC and OC, analysed using the thermo-optical transmission method with a Sunset Lab analyzer and following EUSAAR2 temperature program proposed by Cavalli et al. (2010).

The same samples were characterised for the functional group content of the organic carbon, FG [nmol m⁻³]. As fully presented in Appendix A, functional group analysis was performed by atmospheric pressure chemical ionization (APCI)-tandem mass spectrometry. This technique is based on the ability of the carboxylic (RCOOH), carbonyl (RCOR'), and nitro (RNO₂) functional groups to lose a specific neutral fragment or to produce a characteristic ion in the collision cell (Dron et al., 2007, 2008a,b, 2010). It enables the quantitative determination of these functional groups in aerosol extracts, based on the analyses of reference mixtures containing high number of compounds with various chemical structures, bearing the functional groups of interest. Method uncertainties, extraction efficiency, detection limit and sampling artefacts are detailed in Appendix A.

Normalizing the concentration of an individual functional group, FG [nmol m⁻³], by the corresponding OC molar content [μmol m⁻³] gives access to the functionalisation rate (RF = FG/OC), expressed in number of functions per one thousand OC [‰]. The reciprocal ratio OC/FG represents the probability that a carbon bears the functional group of interest (Valorso et al., 2011). Finally, we define the total functionalisation rate, RF_{total}, as the sum of individual RF determined here.

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