Focus

Advances in Organic Aerosol Characterization: From Complex to Simple

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Air pollution is the "world largest single environmental health risk" (WHO, 2016). According to the World Health Organization, every year ambient air pollution leads to more than 3 million premature deaths, and 84% of the global population is exposed to atmospheric aerosol levels higher than the limits set to protect human health (WHO, 2016). One of the most abundant, and still less characterized components of atmospheric aerosol is organic aerosol (OA). In particular, OA sources, formation mechanisms, atmospheric ageing, and effects on climate and human health are still subject of research.

OA is a mixture of thousands of chemical species, characterized by different physical, chemical, and toxicological properties. Such properties define the effects of OA, and particulate matter, on climate, air quality, and human health (Goldstein and Galbally, 2007). Traditional analytical techniques, based on the identification of single molecular species, describe only a limited fraction of OA mass, generally lower than 30% (Hallquist *et al.*, 2009). During the last decade the use of bulk OA spectrometric analysis introduced simplified descriptions of OA. Such approaches depict OA as formed by a few components with different degrees of oxidation (Aerosol mass spectrometry - AMS) (Zhang *et al.*, 2005), or as the sum of different organic functional groups, (Fourier transform infrared spectrometry - FTIR (Maria *et al.*, 2003), or proton nuclear magnetic resonance spectrometry - H-NMR (Decesari *et al.*, 2007)).

With the acronym AMS we refer here to high-resolution time of flight aerosol mass spectrometer (HR-ToF-AMS), soot photometer aerosol mass spectrometer (SP-AMS), and aerosol chemical speciation monitor (ACSM). The AMSs measure the chemical composition of submicron particles on-line, with a resolution of a few minutes (Jayne *et al.*, 2000; DeCarlo *et al.*, 2006). HR-ToF-AMS and ACSM measure non-refractory OA, which generally accounts for the largest fractions of carbonaceous matter, while SP-AMS allows the quantification of refractory material as well (Onasch *et*

al., 2012). The OA mass measured by AMS correlates well with the organic carbon measured with thermo-optical method, such as online Sunset analyzer (Takegawa *et al.*, 2005; Takegawa *et al.*, 2009). The correlation slope reported in literature varies between 1.6 and 2, in agreement with theoretical values estimated from OA molecular composition (Turpin and Lim, 2001), and with organic mass to organic carbon ratio (OM/OC) measured by AMS and FTIR (Russell, 2003; Aiken *et al.*, 2008). Still, the accuracy of AMS OA measurements depends on the accuracy collection efficiency (CE) determination, which usually varies between 0.5 and 1, and depends on ammonium nitrate mass fraction, aerosol liquid water content (Middlebrook *et al.*, 2012), and organic aerosol composition (Docherty *et al.*, 2013). For such a reason efforts are now focusing on the development of new types of vaporizers, in order to achieved a constant collection efficiency equal to unity (Hu *et al.*, 2017).

Due to the high energy of mass spectrometry fragmentation, the information of original molecular formula is mostly lost. Nevertheless, multivariate statistical analysis of the mass spectra identifies OA components characterized by different oxygen content (Zhang *et al.*, 2005; Canagaratna *et al.*, 2007), which can be linked to primary and secondary OA components. In addition, the analysis of OA fragmentation mass spectra allows the indirect measure of OA elemental composition, and the OM/OC (Aiken *et al.*, 2008; Canagaratna *et al.*, 2015). The elemental analysis algorithms were developed based on the study of a large set of organic standards, representative of OA composition (Aiken *et al.*, 2007; Aiken *et al.*, 2008; Canagaratna *et al.*, 2015). Such algorithm takes into account neutral losses of fragment containing electronegative atoms (i.e., CO_2 and H_2O), and the dependency of thermal decomposition mechanisms on the organic functional group composition. The accuracy of O:C and H:C determinations is 28% and 13%, respectively (Canagaratna *et al.*, 2015).

FT-IR analysis of bulk OA is performed by collecting infrared absorption spectra of particulate matter, or spectra of OA fractions isolated by organic solvent extraction. When particulate matter samples are analyzed directly, the totality of OA can be characterized. OA is described by FT-IR analysis as the sum of organic functional groups, i.e.,

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alkyl (C-H) bonds, carbonyl (C=O), carboxyl (C(OH)=O), amine (NH), hydroxyl (C-OH) groups, organic sulfate, and organic nitrate (Russell *et al.*, 2011; Ruggeri and Takahama, 2016). Time resolution is limited by the detection limit and ambient OA concentrations. It can range from less than 1 hour up to 24 hours (Gilardoni *et al.*, 2009). The calculation of OA mass based on FTIR assumes that all functional groups that compose OA are above the limit of quantification, and the mass fraction of functional groups transparent to IR radiation (i.e., tertiary carbon) is negligible. The comparison of FTIR and off-line thermal/optical organic carbon shows a Pearson correlation coefficient higher than 0.93 and errors smaller than 10% (Maria *et al.*, 2003; Weakley *et al.*, 2016). The OA concentration and OM/OC ratio measured by FTIR agree within 20% and 10% with AMS results, respectively (Russell *et al.*, 2009; Gilardoni *et al.*, 2014). The main limitations of FTIR are the potential evaporative losses of volatile OA during filter sampling, which could also explain the larger discrepancy with on-line OA (AMS) compared to off-line OA (thermal/optical).

H-NMR was developed for off-line analysis of water-soluble OA fraction. H-NMR is able to identify the following functional groups: aryl and alkyl C-H bonds, C=O from ketones, aldehydes, and carboxylic acids, C-O from ethers and alcohols, and O-C-O moieties (Decesari *et al.*, 2007). The time resolution ranges usually from a few hours up to 24 hours (Finessi *et al.*, 2012; Paglione *et al.*, 2014).

The ability of these bulk OA analysis to characterize a larger fraction of OA mass, compared to traditional techniques, promoted the investigation of OA sources, especially through receptor modeling. The analysis of AMS OA fragmentation spectra led to the identification of oxygenated organic aerosol (OOA), a proxy of secondary OA (SOA), which dominates over hydrocarbon like OA (a proxy of primary OA) in urban, rural, and remotes areas (Zhang *et al.*, 2007; Crippa *et al.*, 2014). AMS and FT-IR analysis of aerosol collected in different continents identified the following main OA sources: fuel combustion, biogenic, biomass burning, cooking, and marine OA (Hawkins and Russell, 2010; Russell *et al.*, 2011; Mohr *et al.*, 2012; Corrigan *et al.*, 2013; Crippa *et al.*, 2013). The comparison between H-NMR reference and ambient spectra allowed the identification fresh and aged wood burning aerosol (Paglione *et al.*, 2014), primary and secondary marine OA (Decesari *et al.*, 2011), and biogenic SOA (Finessi *et al.*, 2012).

The information about the chemical structure of bulk OA was used to gain insights into SOA formation mechanisms. For example, FTIR and AMS studies identified the contribution of gas-phase ammonia in the formation of secondary organic nitrate (O'Brien *et al.*, 2013), gave insights into oligomerization chemical mechanisms involved in the formation of biogenic SOA (Russell *et al.*, 2011), and identified phenols as precursors of aqueous SOA (Sun *et al.*, 2010). The analysis of aqueous SOA with FT-IR and H-NMR indicated that different chemical mechanisms occur during processing in cloud and in wet aerosol particles (George *et al.*, 2015; Gilardoni *et al.*, 2016).

The ability to describe the complexity of the bulk OA with a limited set of variables helped the parameterization of OA atmospheric evolution, and climate properties (Jimenez *et al.*, 2009). The elemental ratios (i.e., O/C ratio and H/C ratio) from AMS studies were used to infer the OA compositional change with ageing (Ng *et al.*, 2010, 2011). Kroll *et al.* (2011) showed that the carbon oxidation state (derived from OA elemental composition) varies with the OA carbon number, and such variables together describe the chemical mechanisms behind OA atmospheric evolution. O/C ratio and oxidized organic functional groups were used to parameterize OA hygroscopicity and optical properties (Duplissy *et al.*, 2011; Lambe *et al.*, 2011; Kim *et al.*, 2014).

During the last decade, bulk OA spectrometry improved the ability of the scientific community to describe and predict spatial distribution, temporal evolution, and climate impact of OA. Still open questions remain, especially on the health outcome of OA. Deployment of FTIR and NMR is so far limited by the low measurement time resolution, and the OA sampling artifacts. Conversely, the high time resolved AMS measurements do not describe the OA chemical composition, which could be used to understand and eventually model aerosol toxicity. Further studies should be encouraged to deploy an integrated approach, to take advantage of the completeness, the link to chemical composition, and the simplicity of the different bulk OA spectrometric techniques.

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