

# Mass spectrometric approaches for chemical characterisation of atmospheric aerosols: critical review of the most recent advances

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**Environmental context.** Atmospheric aerosols have profound effects on the environment through several physicochemical processes, such as absorption and scattering of sunlight, heterogeneous gas–particle reactions and adverse effects on the respiratory and cardiovascular systems. Understanding aerosol atmospheric chemistry and its environmental impact requires comprehensive characterisation of the physical and chemical properties of particles. Results from mass spectrometry provide important new insights into the origin of atmospheric aerosols, the evolution of their physicochemical properties, their reactivity and their effect on the environment.

**Abstract.** This manuscript presents an overview of the most recent instrument developments for the field and laboratory applications of mass spectrometry (MS) to investigate the chemistry and physics of atmospheric aerosols. A range of MS instruments, employing different sample introduction methods, ionisation and mass detection techniques are used both for ‘online’ and ‘offline’ characterisation of aerosols. Online MS techniques enable detection of individual particles with simultaneous measurement of particle size distributions and aerodynamic characteristics and are ideally suited for field studies that require high temporal resolution. Offline MS techniques provide a means for detailed molecular-level analysis of aerosol samples, which is essential to gain fundamental knowledge regarding aerosol chemistry, mechanisms of particle formation and atmospheric aging. Combined, complementary MS techniques provide comprehensive information on the chemical composition, size, morphology and phase of aerosols – data of key importance for evaluating hygroscopic and optical properties of particles, their health effects, understanding their origins and atmospheric evolution. Over the last few years, developments and applications of MS techniques in aerosol research have expanded remarkably as evident by skyrocketing publication statistics. The goal of this review is to present the most recent developments in the field of aerosol mass spectrometry for the time period of late 2010 to early 2012, which have not been conveyed in previous reviews.

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## Introduction

Chemistry and microphysics of aerosols (airborne suspensions of fine particles) have been the most active areas in modern environmental science because of their critical role in air-quality issues,<sup>[1,2]</sup> gas–particle atmospheric reactions,<sup>[3–6]</sup> ecosystem–atmosphere interactions,<sup>[7,8]</sup> climate change<sup>[9,10]</sup> and human health.<sup>[11,12]</sup> Aerosols have both natural and anthropogenic sources and are either directly emitted into the atmosphere (primary particles) or formed from gas-phase species following nucleation, heterogeneous gas–particle reactions or condensation processes (secondary particles). Airborne particles continuously evolve in the atmosphere as a result of physical and chemical transformations that are cumulatively referred to as ‘atmospheric aging.’ In turn, these processes change the chemical composition of both particles and gas-phase

atmospheric constituents and have a complex feedback to the Earth’s land and aqueous ecosystems through biogeochemical cycling of carbon, nitrogen, sulfur and other elements.<sup>[7,8]</sup> Aerosols influence radiative forcing of climate by scattering and absorbing incoming solar radiation (direct effect). They also affect climate indirectly by acting as atmospheric ice and cloud condensation nuclei (IN and CCN). Clouds reflect radiation back to space and, therefore, cool the planet. The overall extent, and even sign, of radiative forcing by aerosols is a major uncertainty for predictive understanding of climate change.<sup>[13]</sup> Submicrometre airborne particles may have substantial toxicity and adverse effects on human health upon inhalation. For example, epidemiological studies have shown consistent correlation of cardiovascular diseases with exposure to airborne particulates.<sup>[14]</sup>

The air pollution issues of rapidly expanding megacities are probably the most eloquent examples of aerosols' environmental impact.<sup>[15,16]</sup> Fig. 1 shows photographs of some typical 'haze'-reduced visibility events observed by the authors in



**Fig. 1.** Air pollution by organic particulate matter observed and photographed by the authors in the urban areas of Shanghai (March 2010) – upper panel, and Mexico City (March 2006) – lower panel.

Shanghai and Mexico City (both metropolitan areas exceeding 20 million in population). The economic growth and industrial developments in these areas over the last few decades has led to increased consumption of energy, as well as expansion and intensification of the transportation infrastructure. In turn, these developments have resulted in anthropogenic emissions of unprecedented severity and extent, including emissions of primary and formation of secondary aerosols responsible for the grave pollution events illustrated in the photographs (Fig. 1).

Ambient aerosols are very complex mixtures of particles with diverse variations in their size, and with chemical composition that commonly is multi-component within individual particles (internal mixing) or distinguished between separate particles (external mixing). Characteristic sizes of ambient particles span a range from a few nanometres to tens of micrometres and commonly are described in terms of three characteristic modes: (1) nucleation mode (5–100 nm), corresponding to new particle formation; (2) accumulation mode (100 nm–2  $\mu$ m), produced by subsequent particle growth and coagulation and (3) coarse mode (>2  $\mu$ m), particles produced by direct emissions, such as windblown dust, sea salt spray, plant pollens, etc. A large fraction of both anthropogenic and biogenic aerosols contains organic material with composition that is only partly understood.<sup>[17]</sup> Organic aerosols (OAs) can be classified into primary organic aerosols (POAs), which are emitted directly by the sources, and secondary organic aerosols (SOAs), which are formed in the atmosphere through gas-phase and aqueous chemistry. However, the distinction between POAs and SOAs is blurred by the exchange of materials between particles through various physical and chemical processes. Urban aerosols are of particular complexity and concern due to the range of emission sources, high concentrations of pollutants, numerous photochemical aging mechanisms, and global impact on large groups of human populations and substantial geographic areas. Fig. 2 shows microscopy images of typical ambient particles sampled in recent field studies conducted in Mexico City<sup>[18]</sup> (a and b) and in central California<sup>[19]</sup> (c and d). Fig. 2a shows an external mixture of soot and elongated inorganic Pb- and Zn-containing particles apportioned to industrial waste incineration.<sup>[20]</sup> Fig. 2b and c



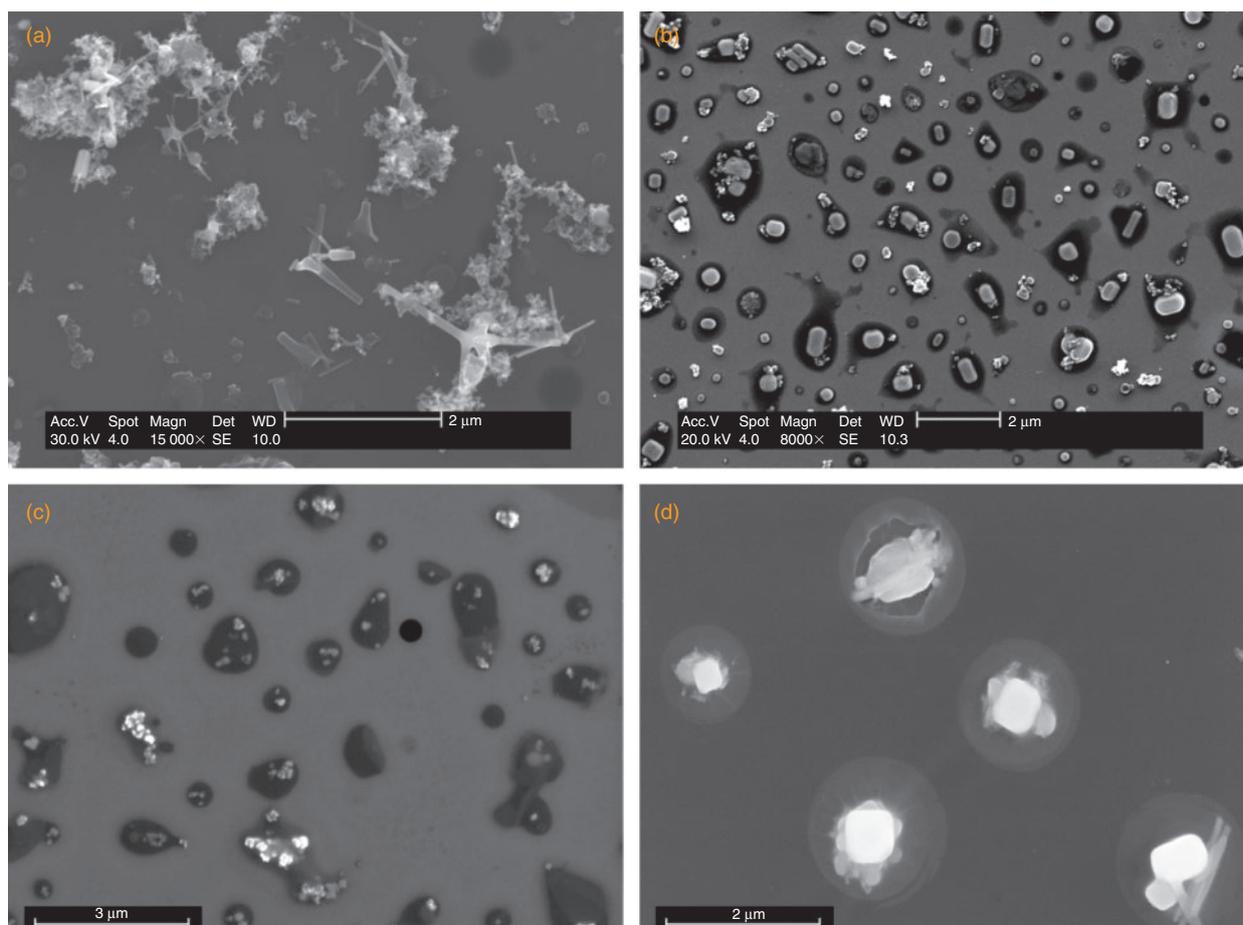
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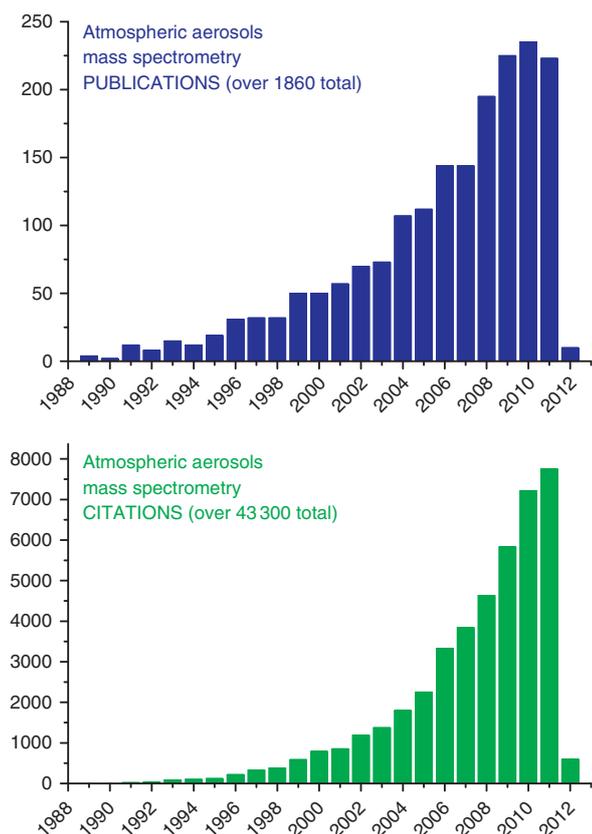
**Fig. 2.** Electron microscopy images illustrating various morphology and the internal heterogeneities (mixing state) of atmospheric particles collected in field studies. (a) Soot aggregates externally mixed with elongated particles containing chloride and nitrate salts of Pb and Zn attributed to waste incineration in Mexico City. (From Moffet et al.,<sup>[20]</sup> ACS, reproduced with permission.) (b) Primary particles of inorganic salts coated with secondary organic material typical for urban environment of Mexico City. (From Moffet et al.,<sup>[21]</sup> EGU, reproduced with permission.) (c) Primary soot (black carbon) particles coated with secondary organic material apportioned to aged urban emissions from Sacramento, CA, urban area. (From Zaveri et al.,<sup>[19]</sup> EGU, reproduced with permission.) (d) Sea salt particles (cubic-shaped cores) coated with photochemically formed secondary organics of anthropogenic origin (circle-shaped outer shell areas).<sup>[22]</sup>

show internally mixed particles containing inorganic cores (mostly black carbon and sulfates of anthropogenic origin) and outer shells of photochemically formed SOA material.<sup>[19,21]</sup>

Fig. 2d shows similar internally mixed morphologies of aged marine particles, where inorganic sea salt crystals (cores) are coated with organics (outer shell areas) of anthropogenic origin.<sup>[22]</sup> Comprehensive analysis of such a diverse mixture of aerosols requires multi-dimensional measurements and applications of complementary analytical methods that provide experimental data, ranging from bulk measurements such as mass loadings of simplified aerosol classes (e.g. black carbon, sulfates, nitrates, organics, etc.) to in-depth properties of individual particles and advanced molecular-level characterisation of complex molecules comprising organic particulate matter.

Mass spectrometry (MS) techniques have an overall versatility of sensitive detection of a range of chemical species, providing high-throughput qualitative and quantitative data on physicochemical properties of aerosols in laboratory, test facilities, and field studies. Owing to a broad range of MS analytical capabilities, complementary variations in sample introduction approaches, ionisation techniques and mass detectors, a field of 'Mass Spectrometry of Atmospheric Aerosols' has been established and has quickly become the most essential and fastest

growing area of aerosol research. Fig. 3 shows publication and citation statistics indicating dynamics of the MS applications for aerosol characterisation over the last 25 years. Remarkably, nearly half of the records are the most recent studies published within the last 3 years. Among them, there are numerous review manuscripts and book chapters featuring instrument development, analytical methodologies and application advances in the field of MS of atmospheric aerosols, including both offline and online approaches. Offline MS techniques typically are applied to bulk (e.g. filter) samples of aerosols, and their unique advances are in the area of molecular characterisation of organic aerosols.<sup>[23–28]</sup> Online techniques employ rapid sampling of particles followed by evaporation and ionisation of the resulting vapour.<sup>[29–36]</sup> Critical advantages of the online techniques are simultaneous measurements of particle composition, as well as size, high temporal resolution, and ability to distinguish between internally and externally mixed particle components. A comprehensive account of the developments and applications in the entire field recently was presented in a two-part review of Pratt and Prather<sup>[37,38]</sup> written in August 2010. However, since the publication of that review, there have already been more than 250 new manuscripts published in the peer-reviewed literature (Fig. 3).



**Fig. 3.** Publication and citation data reported in response to a search on 'Atmospheric aerosol mass spectromet\*' (where the asterisk is a wildcard) on the *Web of Science* as of January 2012.

This review intends to convey the most recent developments and applications in the field of mass spectrometry of aerosols that took place in a time period between late 2010 and the preparation of this manuscript (January 2012). We note that additional papers have appeared in press since January 2012, which are not included in this review. The manuscript is organised into five sections. Following the introduction, we present the most significant developments in novel MS instrumentation and relevant analytical methodologies. Specific applications and new findings that resulted from field and laboratory studies of aerosols using MS techniques are presented in the next two sections. Summary and future outlooks are provided in the final section.

## Advances in instrumentation and analytical methods

### Online MS methods

Several groups reported the development of compact single particle mass spectrometers (SPMS) and improved sizing and morphology characteristics inherent to SPMS performance. For example, Brands et al.<sup>[39]</sup> and Li et al.<sup>[40]</sup> independently reported the design and performance of lightweight, field-deployable SPMS systems that use bipolar time-of-flight (TOF) mass analysers for simultaneous detection of positive and negative ions produced using laser ablation or laser desorption ionisation. Steele et al.<sup>[41]</sup> described the performance of an SPMS system specially designed for rapid aerosol threat detection. Zelenyuk et al. reported improved approaches for high-throughput measurements of particle number concentrations, size distributions, asphericity and particle density.<sup>[42,43]</sup> The same group also

demonstrated that the combination of an aerosol particle mass analyser with a differential mobility analyser enables separation of aspherical particles of the same size and mass.<sup>[44]</sup>

Soft ionisation aerosol MS techniques that enable the formation of intact ions in SPMS systems also have gained significant attention. Current advances in aerosol MS instrumentation involving tunable vacuum ultraviolet (VUV) light from a synchrotron source, resonant capture of low-energy electrons and chemical ionisation have recently been reviewed.<sup>[35]</sup> More recently, Zimmermann et al.<sup>[45]</sup> described the first field application of resonance-enhanced multiphoton ionisation (REMPI) using a UV laser combined with thermal desorption of the particulate matter. REMPI enables facile and selective multiphoton ionisation of aromatic compounds, resulting in sensitive detection of particle-bound polycyclic aromatic hydrocarbons (PAHs). In that study, PAH signals were used as unique signatures of different combustion sources. Adam et al.<sup>[46]</sup> used this instrument in combination with other techniques for detailed characterisation of heavy-duty vehicle exhaust emissions. In another study, REMPI-TOFMS was coupled to a carbon analyser for the analysis of thermally desorbed organic compounds from collected aerosols in parallel with bulk characterisation of the organic and elemental carbon.<sup>[47]</sup> Single-photon ionisation using synchrotron radiation enables ionisation of a range of compounds in laboratory-generated aerosol samples with minimal fragmentation. Fang et al. used VUV photoionisation in a single-particle aerosol time-of-flight mass spectrometer (ATOFMS) for characterisation of the composition of SOAs produced through photooxidation of toluene in a smog chamber.<sup>[48,49]</sup> Robinson et al.<sup>[50]</sup> reported coupling of a softer ionisation source with an Aerodyne aerosol mass spectrometer (AMS). In that study, a metastable atom bombardment (MAB) ionisation source was incorporated so the system could be readily switched between MAB and traditionally used electron ionisation (EI). In the MAB source, metastable atoms produced using an electrical discharge in N<sub>2</sub>, Ar or Kr are directed at the ionisation volume. Penning ionisation produces significantly less fragmentation than EI with considerably lower ionisation efficiency (<0.1% compared with EI). The authors indicated further optimisation of the MAB source may result in significantly enhanced ion signals.

Development of new techniques related to the AMS-TOF family of instruments focussed on faster data acquisition, improved quantitation<sup>[51–54]</sup> and data visualisation. For example, Meddlebrook et al.<sup>[51]</sup> developed an algorithm for estimating the instrument collection efficiency for field data based on measured aerosol chemical composition and sampling line relative humidity (RH). Ng et al.<sup>[55]</sup> reported the development of a simplified version of the AMS – the aerosol chemical speciation monitor (ACSM) – capable of routine characterisation of mass and chemical composition of submicrometre particles in real time. Kimmel et al.<sup>[56]</sup> developed a new data acquisition system for AMS that enables rapid acquisition of mass spectra with an acquisition rate of 1 kHz. The new data system supports real-time AMS acquisition with millisecond resolution. During the BEARPEX-2007 campaign, Farmer et al.<sup>[57]</sup> used a combination of the standard and a new data acquisition mode to enable eddy covariance flux measurements. Isobaric overlaps present a significant challenge for the interpretation of the AMS-TOF data. Müller et al.<sup>[58]</sup> developed a method for improved spectroscopic analysis of the AMS data that enables separation of isobaric peaks at  $m/z$  43 (e.g. C<sub>2</sub>H<sub>3</sub>O<sup>+</sup> at  $m/z$  43.015 and C<sub>2</sub>H<sub>5</sub>N<sup>+</sup> at  $m/z$  43.043) – 50-ppm mass

accuracy was achieved, which enabled efficient identification of the relative abundance of the isobaric peaks.

Characterisation of the chemical composition of particles smaller than 50 nm is hindered by difficulties in transmission of ultra-small particles through aerodynamic lenses and the limitations of the optical detection methods. To alleviate these problems, Zauscher et al.<sup>[59]</sup> coupled a growth tube to an ultrafine ATOFMS. Small particles (40–60 nm) grow to larger sizes in the growth tube in the presence of water vapour, which enables their detection using the standard optical detection scheme. A comparison between the particle types detected for 175-nm particles characterised using ATOFMS with and without the growth tube indicated that particle growth in the growth tube did not have a measurable effect on the appeared spectra. This result was attributed to the short residence time of the aerosol material in the droplets. It has been demonstrated that this system enables characterisation of the chemical composition of individual particles down to 38 nm in diameter. In the future, it will be used to probe changes in the chemical composition of CCN as a function of meteorological conditions.

The elemental composition of nanoparticles (<50 nm) can be characterised using a nano aerosol mass spectrometer (NAMS), developed by Johnston et al.<sup>[60]</sup> In this system, singly charged particles are stored in an ion trap and analysed using high-power laser ablation that results in a complete disintegration of a particle. Singly and multiply charged atomic ions produced by laser ablation are subsequently analysed using a TOF mass analyser. Accurate elemental composition is obtained from the TOF-MS data using a deconvolution procedure described by Zordan et al.<sup>[61]</sup> Assuming the charge state distribution of a particular element is independent of the particle composition, the ratio between different charge states is calibrated using particles of known composition (e.g. sucrose and ammonium sulfate). Isobaric peaks (e.g.  $O^{4+}$  and  $C^{3+}$ ;  $O^{2+}$  and  $S^{4+}$ ) are subsequently separated based on the expected ratios. It has been demonstrated that this approach enables accurate measurement of elemental ratios of C, N, O and S atoms in aerosol particles of 10–25 nm. Furthermore, carbon mole fraction plots constructed by plotting the elemental composition of individual particles provide a means to explore the effect of the presence of inorganic constituents on the degree of oxidation of organic molecules in field-collected aerosol particles. For example, Klems et al.<sup>[62]</sup> showed correlation between the degree of oxidation of organic compounds and the presence of inorganic species in ambient particles.

Yoder et al.<sup>[63]</sup> developed a new experimental approach for accurate determination of the size distributions of ultrafine particles with sizes ranging from subnanometres to several nanometres. The approach uses sodium doping of aerosol particles followed by UV photoionisation MS. In that study, clusters formed in a supersonic beam were transferred into a reaction chamber filled with Na vapour. The resulting clusters were later ionised using either a 223-nm (5.56 eV) light from a tunable UV laser or a fixed 266-nm (4.66 eV) light from an Nd:YAG laser. Mass analysis of the ionised clusters was performed using a linear TOF mass spectrometer. Because of the low ionisation energy of sodium-containing clusters, sodium doping enables facile photoionisation of ultrafine particles using UV light. A comparison between the cluster size distribution, determined using UV photoionisation of Na-doped clusters, with the relatively soft ionisation of undoped clusters, using a tunable extreme ultraviolet (EUV) laser, demonstrated that EUV results in significant fragmentation of the clusters. The

degree of fragmentation is determined by the binding energy of molecules in the clusters. For example, less fragmentation was observed for the more strongly bound water clusters as compared with clusters of acetic acid or dimethyl ether. Sodium doping is an attractive approach because of the high Na capture efficiency, resulting in efficient conversion of the precursor particles. In addition, Na-doping results in evaporation of only a few molecules from the cluster's surface, which has a negligible effect on the overall composition of nanometre-sized particles. Fig. 4 shows size distributions obtained using this technique for 1.3-, 4.8- and 6-nm ammonia particles. Future studies will focus on improving the instrument's sensitivity and development of an ambient aerosol sampling inlet.

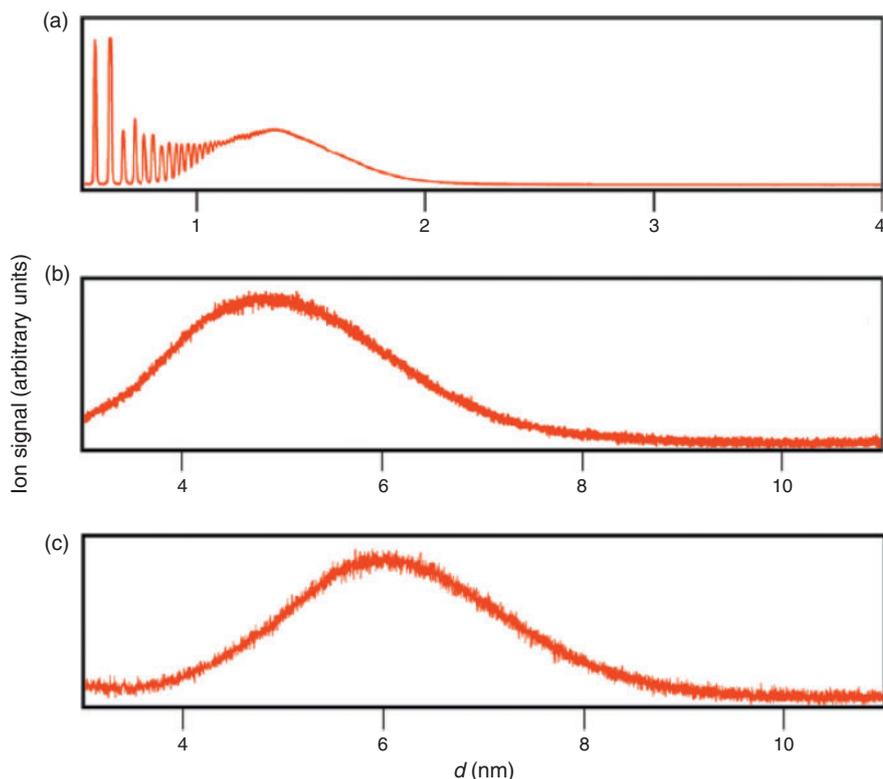
#### Offline MS methods

Several research groups reported on the development of new approaches for more sensitive quantitative offline characterisation of a broader range of organic compounds in aerosol samples collected on filters using gas-chromatography mass spectrometry (GC/MS). For example, González et al.<sup>[64]</sup> developed a new chiral GC/MS method for separation of enantiomers of 2-methyltetrols (2-methylthreitol and 2-methylerythritol), products of isoprene oxidation. The results demonstrated enhanced abundance of one enantiomer in aerosol samples collected from a boreal forest, whereas laboratory generated isoprene SOA contained a racemic mixture of 2-methyltetrols. These results indicate that the 2-methyltetrols in ambient aerosol samples exhibit chirality as observed for 2-methylerythritol present in the leaves of certain plant species.

Schnelle-Kreis et al.<sup>[65]</sup> demonstrated that improved sensitivity of thermal desorption (TD) GC/MS analysis of non-polar organic molecules in field-collected aerosol samples enables chemical characterisation of such compounds with better temporal resolution. When combined with in situ derivatisation,<sup>[66]</sup> TD-GC/MS enables identification of both polar and non-polar constituents of OAs. Furthermore, Kowalewski et al.<sup>[67]</sup> developed a three-step derivatisation for identifying multifunctional oxygenated compounds in SOAs. In this method, carbonyl groups are converted into methyloximes, carboxy groups converted into methyl esters and hydroxy groups converted into trimethylsilyl ethers. The method was demonstrated for several model multifunctional compounds. In another study, Özel et al.<sup>[68]</sup> used GC/MS equipped with a nitrogen chemiluminescence detection system for characterisation of water-soluble organic nitrogen in field-collected aerosol samples. The analysis enabled quantification of nitriles, amides, alkyl nitro compounds, nitrophenols, nitrosamines and nitro-PAHs.

Although GC/MS enables quantitative characterisation of organic nitrogen (ON) compounds in particulate phase, the proton-transfer reaction mass spectrometer (PTRMS) is ideally suited for sensitive detection and quantification of gas-phase ON. Hanson et al.<sup>[69]</sup> developed an ambient pressure PTRMS method for quantification of gaseous amines. In this technique,  $H_3O^+(H_2O)_n$  clusters are generated using a radioactive source in the presence of water vapour. Ionisation of amines occurs in a drift tube, where reagent ions are mixed with the sampled air. The ions are then transferred into a vacuum system and analysed using a quadrupole mass analyser. This technique is capable of detecting amines at parts per thousand by volume levels.

Although GC/MS is a robust technique for quantitative characterisation of organic molecules in aerosol samples, it is limited to fairly small, thermally stable molecules. Liquid



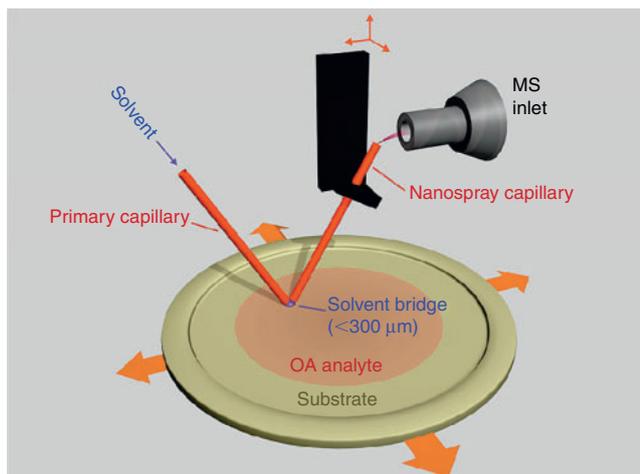
**Fig. 4.** Size distributions ( $d$ , diameter) of ultrafine ammonia aerosol particles obtained using the Na-doping approach followed by UV photoionisation and time-of-flight (TOF) detection of particle masses. (From Yoder et al.,<sup>[63]</sup> ACS, reproduced with permission.)

chromatography mass spectrometry (LC/MS), although less quantitative, enables detection and identification of a broader range of analytes in complex mixtures. Kitanovski et al.<sup>[70]</sup> reported a new approach for LC separation of carboxylic acids, which are commonly present in OA samples. In this study, hydrophilic interaction normal phase LC combined with electrospray ionisation mass spectrometry (ESI/MS) analysis was developed as a tool for separation and identification of aliphatic, alicyclic and aromatic carboxylic acids. Recoveries higher than 90 % and limits of detection (LOD) from 0.03 to 16  $\mu\text{g L}^{-1}$  were reported. Kampf et al.<sup>[71]</sup> developed a method for the quantitative detection of two other common OA constituents, glyoxal and methylglyoxal. The approach involves filter extraction followed by chemical derivatisation, solid-phase extraction and reversed-phase high-performance liquid chromatography (HPLC) coupled with ESI/MS and tandem mass spectrometry (MS/MS) in an ion trap mass spectrometer. Multiple reaction monitoring enabled sensitive detection of both compounds with a LOD of 0.51 and 0.62  $\mu\text{g L}^{-1}$  for glyoxal and methylglyoxal. Samy et al.<sup>[72]</sup> described an advanced LC/MS technique using high-resolution mass analysis in a quadrupole-TOF (Q-TOF) instrument for quantification of amino acids in aerosols collected in a south-eastern United States forest environment. High mass accuracy of a Q-TOF (<2 ppm) is essential for unambiguous identification of amino acids and other organonitrogen compounds in aerosol samples.

Ambient pressure surface ionisation techniques have attracted significant attention because they enable analysis of compounds in laboratory-generated and field-collected OA samples without sample pretreatment. Bruns et al.<sup>[73]</sup> demonstrated the utility of atmospheric solids analysis probe MS

(ASAP-MS) for identification of organic compounds in laboratory-generated SOA and field-collected OA samples. In ASAP-MS, thermal desorption of molecules from the probe using a heated stream of  $\text{N}_2$  is followed by atmospheric pressure chemical ionisation and mass analysis of the resulting ions. OA constituents were identified based on the accurate mass measurement. Another advantage of ambient surface ionisation techniques is the ability to detect molecules that cannot be observed using ESI/MS. For example, it has been demonstrated that desorption electrospray ionisation (DESI) enables detection of chemically labile analytes in OA samples that are not observed in ESI/MS.<sup>[74]</sup> Similarly, chemically labile compounds were detected in laboratory-generated aerosol samples using recently developed nanospray desorption electrospray ionisation (nano-DESI) MS.<sup>[75,76]</sup> This technique relies on localised liquid extraction using a probe composed of two fused silica capillaries (shown in Fig. 5). The analyte molecules are desorbed into an appropriate solvent and transferred to a mass spectrometer inlet where they are ionised through nanospray ionisation. It has been demonstrated that nano-DESI enables sensitive analysis of aerosol samples collected on Teflon or aluminium substrates. Furthermore, it is ideally suited for monitoring chemical changes in aerosol samples subjected to chemical aging.<sup>[75,77,78]</sup>

Secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS) enable sensitive characterisation of inorganic and organic materials on surfaces. Tyler et al.<sup>[79]</sup> demonstrated the utility of laser secondary neutral mass spectrometry (Laser-SNMS) for detection of PAHs in individual aerosol particles. In this technique, molecules sputtered using a primary ion beam are subsequently ionised using a 157-nm



**Fig. 5.** Schematic diagram of a nanospray desorption electrospray ionisation (nano-DESI) mass spectrometer (MS) source configuration for analysis of organic aerosol (OA) samples deposited on flat substrates. (From Roach et al.,<sup>[75]</sup> ACS, reproduced with permission.)

laser, resulting in a several orders of magnitude improvement in the sensitivity. High ionisation yields in single-photon post-ionisation enabled detection of PAHs on 2- $\mu\text{m}$  ambient aerosol particles. This approach can be used for detailed characterisation of organic material on surfaces of individual particles. Brender et al.<sup>[80]</sup> used a combination of temperature-programmed desorption (TPD) and XPS to examine the surface chemistry of organic materials containing different functional groups. Particles of 10–20 nm containing graphitic material decorated with carbonyl, carboxyl and hydroxyl groups were used in that study. TPD-MS was used for quantitative analysis of the released volatile compounds as a function of temperature, whereas XPS provided complementary characterisation of the remaining functional groups on the surface. Although this methodology has not been applied to aerosols, it can be readily extended to studies of chemistry on surfaces of ambient particles collected on substrates.

## Field and test facilities studies

### *Anthropogenic aerosols*

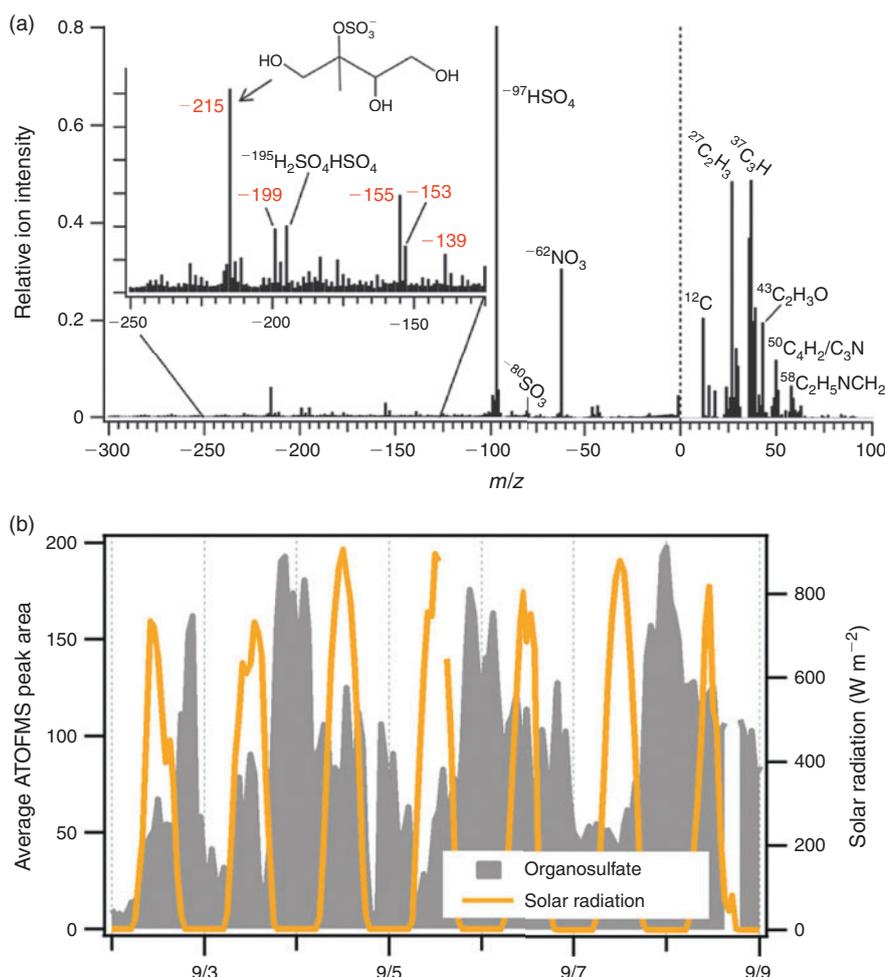
Chemical characterisation of anthropogenic aerosols present in urban and industrial areas is one of the most challenging analytical tasks<sup>[81]</sup> because of a variety of emission sources, complex internal and external mixing of particles that also may change rapidly at any sampling location, and moment of time. Online mass spectrometers provide an important capability to report on aerosol composition, size and their variations with high time resolution. In recent years, these instruments have been increasingly used in all major field studies.

The AMS instruments, with different modifications developed by Aerodyne Research Inc,<sup>[29]</sup> are likely the most widely used commercial online instruments. The AMS sizes particle ensembles sampled over short periods of time (seconds to minutes) and simultaneously records cumulative spectra of non-refractory components detected in each ensemble. The AMS spectra comprise a complex mixture of ions, corresponding to hundreds of individual molecules and their numerous fragments, which complicate spectra interpretation. Methods of multivariate factor analysis have been developed and applied to deconvolute AMS spectra into several orthogonal

component spectra (factors) that indicate different aerosol sources, and can be used to represent their averaged chemical properties, relative contributions of individual factors to the total aerosol, its source apportionment and atmospheric history.<sup>[82]</sup> In recent years, positive matrix factorisation (PMF) analysis has become a common tool for AMS data analysis and provided valuable information about sources of OAs and their atmospheric evolution at many locations affected by anthropogenic emissions.<sup>[83]</sup> Specifically, a hydrocarbon-like OA (HOA) factor was attributed to primary aerosols emissions associated with urban traffic,<sup>[84–90]</sup> residential heating using solid fuel and wood,<sup>[86–88]</sup> fossil fuel combustion and biomass burning<sup>[84]</sup> and food cooking and charbroiling.<sup>[87]</sup> The HOA factor was minor in AMS datasets collected in remote and rural areas.<sup>[91,92]</sup> Photochemically formed SOAs are associated with oxygenated OA (OOA) factors distinguished by consistent variations in AMS spectra. Semi-volatile and low-volatility OOA (SV-OOA and LV-SOA) factors were commonly reported and apportioned to fresh and atmospherically aged anthropogenic SOAs respectively.<sup>[82–92]</sup> Narrowly focussed, source-specific factors, such as cooking OAs,<sup>[87]</sup> biomass burning OAs (BBOAs),<sup>[84,88]</sup> solid fuel OAs<sup>[86]</sup> and amine-containing OAs,<sup>[91]</sup> were also reported in some studies. Furthermore, Sun et al.<sup>[93]</sup> recently conducted analysis of water-soluble organic carbon (WSOC), where the AMS measurements and the PMF data analysis were applied to interrogate aerosolised mist of aqueous extracts from filter samples.

In addition, AMS instruments were used in several experimental projects conducted at test facilities,<sup>[94–98]</sup> where mixtures of particles and gases from exhaust plumes of commercial engines were sampled into a smog chamber and exposed to a simulated photochemical oxidation environment. Continuous, real-time AMS measurements then were used to monitor the concentration of OAs in the smog chamber and evolution of its chemical properties. Consistently, all of these studies showed an overall increase in the OA mass and its oxidation extent (O/C ratio) after aging. These results underscore the dynamic evolution of anthropogenic OAs that has not been accounted for in modelling efforts.

In field studies, SPMS instruments provide a valuable opportunity to probe the chemical composition of individual particles with high-throughput data acquisition, and then correlate properties of specific particles with other measurements and meteorology data, providing a unique approach to study chemical changes in individual ambient particles as they evolve in the atmosphere. Fig. 6 highlights recent results reported by Hatch et al. on the detection<sup>[99]</sup> and temporal variability<sup>[100]</sup> of organosulfate species in individual particles from an urban area in Atlanta. Although the presence and significance of organosulfates has been previously reported in several works using bulk analysis of aerosol samples, the work of Hatch et al.<sup>[99,100]</sup> was the first study where single-particle measurements were used to investigate specific formation mechanisms occurring at ambient conditions. In particular, a group of peaks with the most prominent peak at  $m/z = -215$  was ascribed to organosulfates derived from isoprene epoxydiol, found to be ubiquitous in ambient aerosol during two separate field studies in the Atlanta area. Real-time ATOFMS measurements revealed that their highest concentrations were reproducibly observed at night when the RH was measured at 80–90%. These observations suggested that efficient heterogeneous chemistry of organosulfate precursors and their subsequent aqueous-phase chemistry play an important role in enhancing SOA formation



**Fig. 6.** (a) Averaged negative and positive aerosol time-of-flight mass spectrometry (ATOFMS) spectra of organic particles measured in urban area of Atlanta, USA. The peak at  $m/z = -215$  corresponds to isoprene-epoxydiol-derived organosulfate shown as the insert molecule. (From Hatch et al.,<sup>[99]</sup> ACS, reproduced with permission.) (b) Comparison of temporal variations of the  $m/z = -215$  peak and solar radiation indicates night-time formation of organosulfates through suggested aqueous-phase chemistry in deliquesced particles. (From Hatch et al.,<sup>[100]</sup> ACS, reproduced with permission.)

in the areas with mixed biogenic and anthropogenic emissions. Similarly, the significance of gas-particle uptake and aqueous-phase chemistry in deliquesced particles and fog droplets was reported in a separate SPMS study that focussed on the ambient processing of trimethylamine conducted at urban and rural areas of Southern Ontario, Canada.<sup>[101]</sup>

Particle type classification, source apportionment and temporal trends of individual classes were elucidated based on statistical sorting of combined SPMS and meteorological datasets collected in two unrelated field studies conducted in Shanghai<sup>[102]</sup> and Southern Ontario.<sup>[103]</sup> In Shanghai, ambient measurements by ATOFMS indicated a persistent contribution of biomass-burning particles from multiple regional sources, and several particle classes were apportioned to local emission sources using a neural network algorithm.<sup>[102]</sup> PMF analysis of the ATOFMS dataset from the Southern Ontario study identified several factors associated with regional and long-range transport of biomass-burning aerosols, aged carbonaceous particles, and pyrotechnical particles from fireworks, as well as several factors ascribed to local emission sources.<sup>[103]</sup> Other recent studies demonstrated complementary use of datasets from co-deployed SPMS and ion chromatography techniques<sup>[104]</sup> and SPMS and

AMS instruments<sup>[105]</sup> that allowed a quantitative analysis of the neutralisation process of ambient sulfate aerosol.

Offline MS techniques with either GC or LC separation stages were used to characterise and quantify selected organic constituents in bulk samples of anthropogenic aerosols and provided important insights on molecular speciation of particulate matter characteristic for specific areas of field studies.<sup>[106–110]</sup> Yu et al.<sup>[108]</sup> examined non-polar organic compounds in ambient aerosol collected in Hong Kong using TD-GC/MS. For the area of study, hopanes and alkanes were apportioned to local emissions from gasoline vehicles, whereas PAHs were ascribed to regional emissions from rice straw burning and coal combustion. The analysis of PAH was also a focus of the field study in Spain, conducted in both urban and rural areas, where the PAH content of aerosol was attributed to vehicle emissions and crude oil combustion.<sup>[107]</sup>

Accelerator MS is commonly used in environmental studies to distinguish between fossil and non-fossil carbon based on quantitative measurements of  $^{14}\text{C}$  radiocarbon.<sup>[111]</sup> Because of a radioactive decay on an  $\sim 5700$ -year time scale, fossil carbon is devoid of  $^{14}\text{C}$ . Therefore, the isotopic ratio of  $^{14}\text{C}/^{12}\text{C}$  is used to apportion carbonaceous aerosols to either anthropogenic

emissions from fossil fuel combustion or modern carbon sources that can be relevant to both natural (e.g. biogenic SOAs) and man-made (e.g. biomass combustion, cooking) emissions. Recent field studies used radiocarbon measurements to ascribe emission sources contributing to black and organic carbon,<sup>[112–114]</sup> SOA<sup>[115]</sup> and WSOC<sup>[116]</sup> at specific geographic locations in Europe, the United Kingdom and North America.

Combined datasets from online and offline MS analysis of aerosols, cross-correlated with meteorology records and emission inventories, were also used to apportion origins and composition of regional plumes of anthropogenic aerosols transported over long ranges.<sup>[117–120]</sup>

#### *Biomass burning organic aerosols (BBOAs)*

Physico-chemical properties of BBOAs and its atmospheric transformations were investigated in recent field<sup>[116,121–123]</sup> and test facility<sup>[124–128]</sup> studies. Hennigan et al.<sup>[127]</sup> reported results on the physicochemical transformation of BBOA particles from photooxidation experiments conducted in a smog chamber. In their work, smoke emissions (both particles and gases) from separate controlled burns of 12 different types of wood were introduced into the smog chamber, and the aging transformations were monitored by AMS and PTRMS instruments for particles and gases respectively. The results showed, under atmospherically relevant conditions, that BBOA particles undergo extensive chemical processing that results in a substantial increase of OA mass in aged smoke plumes. The increase in the aerosol mass averaged over all experiments was a factor of 1.7 with variations between individual experiments in a range of 1.1–2.8. Heringa et al.<sup>[129]</sup> independently reported similar results, where an increase in the OA mass by a factor as high as 4 was also observed. In both studies, changes in chemical composition were inferred from the AMS datasets that showed increasing oxygenation and lower volatility of the aged particles. An increase in the OA mass in regional biomass burning plumes was also supported by AMS field measurements taken aboard the NASA DC-8 research aircraft following plume advection.<sup>[122]</sup> These highly dynamic transformations of BBOAs challenge traditional assumptions of chemical transport models and emission inventories, where BBOA is usually assumed to be non-reactive.

Bateman et al.<sup>[130]</sup> demonstrated the utility of a particle-into-liquid-sampler (PILS) for high-resolution mass spectrometry (HR-MS) analysis of water-soluble organics in chamber-generated and BBOAs. Chang-Graham et al.<sup>[124]</sup> used the PILS technique to sample the WSOC fraction of BBOAs followed by ESI/HR-MS that enabled accurate mass measurements and assignments of elemental formulae in a mass range of 70–1000 Da. In that work, BBOA samples from test facility burns of biomass fuels collected at the USA sites managed by prescribed fires were analysed. A substantial presence of N-, S- and P-containing organics, as well as organometallic species containing alkaline earth metals (Ca, Ba and Mg) and transition metals (Mn, Fe, Ni, Cu and Zn) were detected in the WSOC extracts. The results suggest the potential importance of BBOAs in the dispersion and persistence of airborne metals – a potential environmental issue that requires future focussed studies.

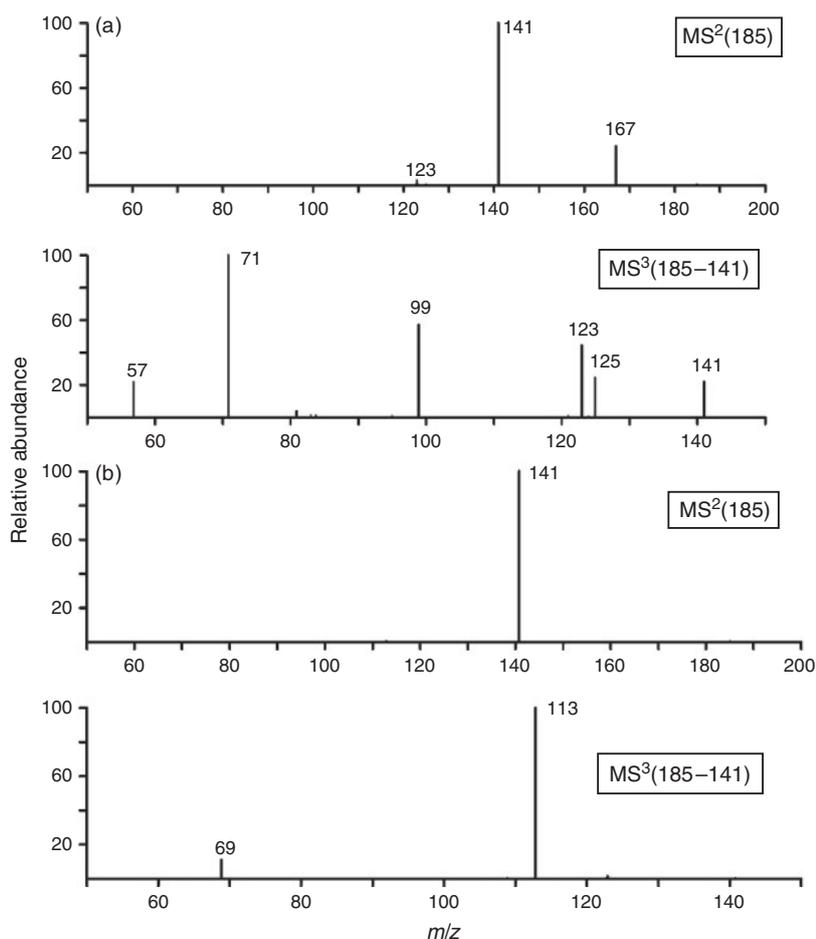
The emission factors and occurrence of selected compounds in BBOA emissions typical for residential wood burning, agricultural field burning and wildfires in Portugal were studied using GC/MS and additional bulk sample techniques in a set of interrelated studies.<sup>[121,125,126]</sup> Several unique chemical markers

characteristic for the BBOA samples were identified and apportioned to specific sources of biomass fuel. A separate study by Iinuma et al.<sup>[131]</sup> reported on the detection of methyl-nitrocatechols using LC/(–)ESI-MS analysis. The authors suggested these molecules may serve as potential tracers of SOA-related wood combustion. These tracers are formed by oxidation of m-cresol emitted during wood combustion. In ambient samples collected at a rural site in Germany affected by wood combustion, these tracers were found in particulate matter less than 10 µm in size (PM<sub>10</sub>) in significant concentrations (on average, 29 ng m<sup>-3</sup>), and they were well correlated with levoglucosan, a primary BBOA tracer.

#### *Biogenic organic aerosols*

Chemical speciation, physical properties, sources and fluxes of biogenic organic aerosols were reported in several recent field studies conducted in rural,<sup>[132]</sup> forest<sup>[133–138]</sup> and marine<sup>[133–142]</sup> environments. Rural site measurements by co-deployed AMS and PTRMS instruments were employed to evaluate the role of different volatile organic compounds (VOCs) for SOA formation in Southern Ontario, Canada. Systematic comparison of the diurnal profiles of SOA mass concentrations and mixing ratios of individual VOCs led to the conclusion that biogenic precursors dominate SOA production in the area of study.<sup>[132]</sup> In another study at the same geographical region, AMS measurements were taken at a tower above a mixed forest as a part of a field experiment to quantify aerosol fluxes with limited chemical speciation. The results indicated interesting diurnal dynamics between the air masses above and below the canopy, whereby SOA formed within the canopy is accumulated during the night-time then is driven upward during the day through mixing with air above the canopy.<sup>[133]</sup> Leaitch et al.<sup>[135]</sup> compiled data of long-term, multi-seasonal measurements from AMS, ACSM and other aerosol instruments deployed at forest sites in Canada with the goal to assess the temperature dependence of SOA production in forests. The results indicated an exponential dependence of SOA mass concentrations with temperature increases in a range of 7 to 34 °C. Two other studies employed AMS measurements in tropical rainforests in Amazonia<sup>[137]</sup> and Borneo,<sup>[136]</sup> where PMF analysis of the obtained datasets produced site-specific SOA factors identified by trace compounds unique to the areas of study.

HPLC/ESI/MS measurements were employed for chemical characterisation of SOA samples collected at European forest sites.<sup>[134,138,143,144]</sup> Yasmineen et al.<sup>[138]</sup> reported an extended dataset on molecular and structural characterisation for a range of isobaric terpene-derived acids, distinguished based on MS/MS fragmentation patterns. Fig. 7 illustrates representative, structure-specific MS/MS spectra of two isobaric *cis*-pinic and *cis*-caric acids ( $[M - H]^-$ ,  $m/z = 185$  Da) – distinct tracers of  $\alpha$ -pinene SOA and  $\Delta^3$ -carene SOA. The study provided the reference data necessary for molecular-level speciation of biogenic SOA that also will be useful for more detailed descriptions of SOA sources and aging. Kristensen and Glasius<sup>[134]</sup> performed molecular speciation and quantitative analysis of a range of individual molecules in forest SOA samples, particularly those including organosulfates and nitrooxy organosulfates. Gómez-González et al.<sup>[143]</sup> conducted a comprehensive analysis of SOA field samples collected at a Belgian forest site influenced by urban emissions and measured the particulate matter less than 2.5 µm in size (PM<sub>2.5</sub>) concentrations of a range of biogenic tracers relevant to the oxidation of isoprene,  $\alpha$ -pinene,  $\beta$ -pinene,  $\Delta^3$ -carene and D-limonene, including



**Fig. 7.** Representative tandem mass spectrometry (MS/MS) fragmentation spectra of isobaric ( $[M - H]^-$ ,  $m/z = 185$  Da) *cis*-pinic (a) and *cis*-caric (b) acids characteristic of secondary organic aerosols (SOAs) formed from photooxidation of  $\alpha$ -pinene SOA and  $\Delta^3$ -carene SOA. (From Yasmeen et al.,<sup>[138]</sup> Wiley, reproduced with permission.)

organosulfates and nitrooxy organosulfates. They also examined temperature-dependent trends in their concentrations. The study revealed the highest concentrations for 3-methyl-1,2,3-butanetricarboxylic acid and the lowest ones for *cis*-pinonic acid at high ambient temperatures  $>22$  °C, indicative of an aged biogenic aerosol.

AMS<sup>[142]</sup> and ATOFMS<sup>[141]</sup> field measurements of marine OAs revealed unique fingerprints of submicrometre primary organic particles generated by sea spray and bubble-bursting in the areas of phytoplankton bloom. Mass concentrations of these particles suggested that the ocean might be a substantial source of OA.<sup>[142]</sup> Conversely, extensive filter sampling and GC/MS analysis of tracer compounds in marine aerosol during an around-the-world cruise study suggested that long-range transport of continental aerosol is the most important factor determining chemical composition of OAs in marine areas.<sup>[140]</sup> Given the large areas covered by the oceans and variability in OA sources, the overall effect of marine OA emissions remains uncertain and more field and laboratory studies are needed to address this issue.<sup>[139]</sup>

#### New particle formation (NPF)

Understanding the physico-chemical processes of NPF is one of the most challenging topics in the physical and analytical chemistry of aerosols. NPF may be viewed as a two-step process that includes nucleation of neutral or ion clusters within the size

of a few nanometres or less ( $< \sim 3$  nm) and growth of nucleated clusters into stable particles of ultrafine sizes ( $< 100$  nm). The difficulties in investigating NPF processes are inherent to the small amount of available material in the particles. Furthermore, approaches for sample collection, introduction, and ionisation are quite different for clusters and ultrafine particles. Therefore, two separate MS methodologies are usually employed to study NPF events: (1) MS methods for cluster detection and analysis that can be regarded as gas-phase MS approaches pushed to the limits of larger molecules and clusters and (2) MS methods of aerosol detection and analysis pushed to the limits of small, ultrafine particles.

Chemical composition and dynamics of atmospheric clusters relevant to NPF events have been discussed in several recent field studies conducted at forest,<sup>[145]</sup> boreal<sup>[146]</sup> and other rural<sup>[147]</sup> sites. Kanawabe et al.<sup>[145]</sup> performed a month-long field study at a remote site in a Michigan forest and concluded that NPF can be efficiently suppressed by elevated emissions of isoprene. Kiendler-Scharr et al.<sup>[148]</sup> also reported the same effect in an earlier laboratory study. However, the mechanistic understanding of this suppression effect remains unclear. A recently developed atmospheric pressure interface-TOF (APi-TOF) MS instrument, capable of detecting ambient ions,<sup>[149]</sup> was deployed for a field study at a boreal forest site in Finland.<sup>[146]</sup> Elevated concentrations of ambient sulfuric acid clusters and number concentrations of neutral nanoparticles (1.3–5 nm) were well

correlated, indicating an ion-induced nucleation mechanism. Zhao et al.<sup>[147]</sup> reported field measurements using a novel chemical ionisation mass spectrometer (CIMS) developed for sensitive detection of ambient neutral clusters during NPF events. The results indicated that clustering of sulfuric acid and amines was a dominant nucleation process for the area of study. The broader relevance of amines to NPF events at other geographic locations also was suggested by independent measurements of ultrafine particles grown to sizes of 25–100 nm. In particular, the presence of amines detected by ATOFMS measurements was reported by Creamen et al.<sup>[150]</sup> for the field study in the Sierra Nevada Mountains, California, and Laitinen et al.<sup>[151]</sup> reported detection of amines using modified AMS with laser-assisted desorption and ionisation of bulk particle samples. Significant amounts of ammonium nitrate and organic material, including amines, also were detected with the NAMS instrument in freshly nucleated particles (<20 nm).<sup>[152]</sup>

#### *Climate-related properties or aerosols*

MS and complementary measurements correlating aerosol composition and its climate-related properties, such as hygroscopicity, CCN and IN activity, absorption and scattering of light, were commonly reported in recent field studies. CCN activity is quantified as the fraction of particles of a given size that activate at a particular supersaturation. Often, it is parameterised using semi-empirical hygroscopicity parameter  $\kappa$  introduced by Petters et al.<sup>[153]</sup> (smaller  $\kappa$  implies less hygroscopic material that needs higher supersaturation for CCN activation). Measurements from collocated AMS and CCN counters at different geographic locations<sup>[151,154–161]</sup> were used to provide field data for simplified parameterisation of aerosol effective  $\kappa$  as a function of AMS-reported organic and inorganic mass fractions ( $f_{\text{org}}$ ,  $f_{\text{inorg}}$ ) that would be practical for climate modelling efforts. Overall,  $\kappa$  values were reasonably estimated from AMS data using a mixing rule of  $\kappa = \kappa_{\text{org}} \cdot f_{\text{org}} + \kappa_{\text{inorg}} \cdot f_{\text{inorg}}$ , where  $\kappa_{\text{org}} = \sim 0.1$  and  $\kappa_{\text{inorg}} = \sim 0.7$  for most of the studies. In some instances, improved parameterisation was also achieved by incorporating additional subfractions of organics in to the mixing rule, such as highly hygroscopic WSOC<sup>[154]</sup> and largely insoluble LV-SOA.<sup>[160]</sup> The possible positive correlation of  $\kappa_{\text{org}}$  with O/C ratio measured by AMS was also suggested.<sup>[162]</sup>

Slowik et al.<sup>[163]</sup> and Zelenyuk et al.<sup>[164]</sup> respectively used AMS and SPMS instruments with the inlets connected to counterflow virtual impactors that segregate dry residuals of cloud and fog droplets from inactivated background aerosol. In their studies, cloud droplet residuals were probed directly by online MS techniques, yielding explicit data on the chemical composition of CCN active particles present in ambient air.

Closure studies on optical properties and the inferred mixing state of black carbon were reported in independent studies based on combined datasets from an AMS and a single-particle soot photometer<sup>[165]</sup>, AMS and a laser-induced incandescence instrument<sup>[166]</sup> and AMS and a set of instruments containing a nephelometer, an aethalometer and a passive cavity aerosol spectrometer.<sup>[167]</sup>

### **Laboratory studies**

#### *Clusters and NPF*

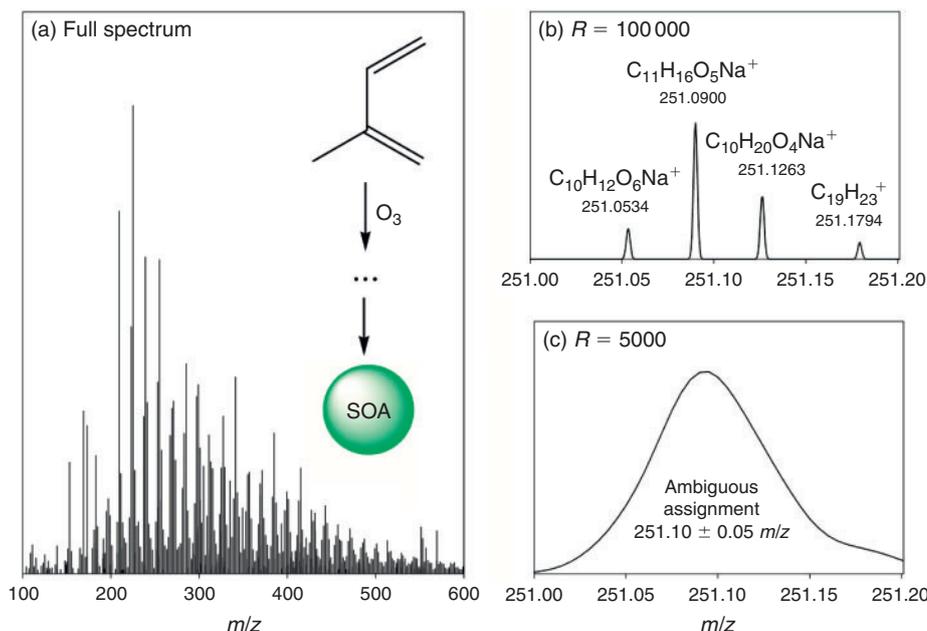
MS is the method of choice for laboratory investigations of the initial steps in NPF. In the case of ion-induced nucleation, the

charged clusters can be detected directly. Neutral precursors to the nucleation and nucleating clusters can be ionised by appropriate CIMS methods. For example, recent investigation of binary nucleation in  $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$ <sup>[168]</sup> and ternary nucleation in  $\text{H}_2\text{SO}_4\text{--H}_2\text{O--NH}_3$ <sup>[169]</sup> mixtures took advantage of CIMS to quantify the concentration of  $\text{H}_2\text{SO}_4$  and  $\text{NH}_3$ . One of the most comprehensive investigations of neutral and ion-induced particle nucleation rates in  $\text{H}_2\text{SO}_4\text{--H}_2\text{O--NH}_3$  (or urea) ternary mixtures was published recently by the CLOUD (cosmics leaving outdoor droplets) team at CERN.<sup>[170]</sup> They used an APi-TOF instrument to observe negatively charged clusters of the type  $[(\text{NH}_3)_m(\text{H}_2\text{SO}_4)_n(\text{HSO}_4)]^-$  with  $n$  and  $m$  up to 16. They concluded that the rate of binary  $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$  nucleation, a subject of long-standing controversy, is too slow for this process to occur in the boundary layer. Although  $\text{NH}_3$  enhances the nucleation rate, the enhancement is not sufficient to explain the high nucleation rates observed in field experiments.<sup>[170]</sup> Amines have long been the primary suspects behind this discrepancy. Bzdek et al.<sup>[171]</sup> took advantage of the high resolving power of Fourier transform ion cyclotron resonance MS (FTICR-MS) to investigate addition and displacement reactions of amines with negatively charged sulfuric acid clusters. Dimethylamine was shown to displace ammonia from  $[(\text{NH}_4\text{HSO}_4)_x(\text{H}_2\text{SO}_4)_3(\text{HSO}_4)]^-$  at collision limited rates, but its addition to small  $[(\text{HSO}_4)(\text{H}_2\text{SO}_4)_x]^-$  clusters was slow. The same group also showed that dimethylamine efficiently displaces ammonia from the salts of methanesulfonic acid, believed to be important in nucleation of marine aerosols.<sup>[172]</sup> The important role of amines in nucleation was confirmed in a study by Erupe et al.<sup>[173]</sup> who found that trimethylamine enhances nucleation rates much more efficiently than ammonia, especially under dry conditions. Efficient displacement of ammonium by ammonium ions was also observed in amine and bulk ammonium sulfate and bisulfate reactions.<sup>[174]</sup>

Following the initial nucleation, particles grow by capturing low-volatility compounds from the air. Recent advances in MS have made it possible to analyse the chemical composition of growing particles in the 1–20-nm size range. Using nanoparticle tandem mobility methods, Wang et al.<sup>[175]</sup> showed that homogeneously nucleated  $\text{H}_2\text{SO}_4$  nanoparticles efficiently take up other organic compounds in addition to amines, such as methylglyoxal, heptanol, decanol and even volatile molecules such as ethanol. We expect several exciting new developments in this area in the near future.

#### *Phase state of organic particles and gas–particle partitioning*

Advanced MS methods are increasingly applied to measurement of vapour pressures of low-volatility organics that can partition into growing particles. For example, Booth et al.<sup>[176]</sup> used Knudsen effusion MS to quantify vapour pressures of cyclic dicarboxylic acids, as well as *cis*-pinonic acid and levoglucosan. Isaacman et al.<sup>[177]</sup> described a novel method for investigating the volatility distribution of SOA organics. They used two-dimensional thermal desorption aerosol gas chromatography (2D-TAG) coupled to an AMS to investigate the temporal evolution in the volatility of nearly 200 oxidation products produced during oxidation of the sesquiterpene, longifolene. In a related study, Salo et al.<sup>[178]</sup> examined the volatility of  $\alpha$ -pinene and  $\text{O}_3$  SOA and D-limonene and  $\text{O}_3$  SOA, which were subsequently aged with OH, using a tandem particle mobility approach. They observed a decrease in particle volatility during



**Fig. 8.** Sample positive electrospray ionisation high-resolution mass spectrometry ((+)ESI/HR-MS) spectrum of secondary organic aerosols (SOAs) produced by ozonolysis of isoprene. (b) and (c) illustrate the improvement in peak assignments afforded by the high resolving power of the Orbitrap instrument ( $R = 100\,000$ ) in comparison to a standard time-of-flight (TOF) instrument ( $R = 5000$ ). (From Nizkorodov et al.,<sup>[26]</sup> Royal Society of Chemistry, reproduced with permission.)

OH aging and attributed most of this decrease to gas-phase OH oxidation of organics in equilibrium with particles and small contributions from the particle-phase chemistry. Cappa and Wilson used synchrotron VUV photoionisation aerosol MS to compare the thermal evaporation of aerosols composed of lubricating oil and products of the  $\alpha$ -pinene and  $O_3$  reaction.<sup>[179]</sup> They found that lubricating oil particles evaporated as predicted by gas-particle partitioning theory, whereas  $\alpha$ -pinene SOA did not, suggesting they were in a glassy state. Using SPMS, Vaden et al.<sup>[180,181]</sup> also observed exceptionally slow evaporation of  $\alpha$ -pinene SOA ( $\sim 24$  h instead of the expected minutes at room temperature) and ambient OA particles. These observations support the emerging picture of a highly viscous glassy organic phase in certain types of OA.<sup>[182]</sup>

#### Molecular-level characterisation of SOA

Several new papers deconstructing chamber-generated SOA at a molecular level with help from various MS-based methods have appeared within the time period covered by this review. Because of its large contributions to the global OA budget, SOA prepared by oxidation of isoprene has received considerable attention. Nguyen et al.<sup>[183]</sup> examined the composition of isoprene and  $O_3$  SOA using HR-MS methods and found several highly oxidised oligomeric compounds containing peroxy and carbonyl groups. Fig. 8 reproduces the mass spectrum obtained in that work and also illustrates the utility of HR-MS in the assignment of individual aerosol compounds. A study of high- $NO_x$  SOA from isoprene by the same group<sup>[184]</sup> revealed similarly extensive oligomerisation, as well as the presence of  $-ONO_2$  groups in one-third of the products. Nguyen et al.<sup>[78]</sup> and Zhang et al.<sup>[185]</sup> independently investigated the effect of RH on the chemical composition of high- $NO_x$  isoprene SOA. Dry conditions significantly enhanced the fraction of oligomeric compounds in SOA formed by condensation reactions.<sup>[78]</sup> For example, the

amount of 2-methylglyceric acid and the average chain length of its oligomers were reduced under humid conditions.<sup>[78,185]</sup> Organonitrates were suppressed by high RH,<sup>[78]</sup> whereas organosulfates were enhanced.<sup>[185]</sup> Galloway et al.<sup>[186]</sup> quantified yields of several low-yield ( $< 5\%$ ) first-generation products of isoprene photooxidation (glyoxal, methylglyoxal, glycolaldehyde, hydroxyacetone, etc.) using a combination of spectroscopic, CIMS, and chromatographic methods, and investigated the effect of inclusion of these products in the master chemical mechanism (MCM). A reexamination of the MCM and other kinetic mechanisms of isoprene- $NO_x$  photooxidation<sup>[187]</sup> resulted in improved predictions of chamber ozone and identified the low- $NO_x$  oxidation regime as an area where further experiments are urgently needed.

Monoterpenes and sesquiterpenes have lower emissions compared with isoprene, but they contribute significantly to global SOAs because their oxidation produces low-volatility products in higher yields. Hall and Johnston<sup>[188]</sup> were able to estimate that oligomers account for more than 50% by mass in  $\alpha$ -pinene SOA using ESI/FTICR-MS and the method of standard addition. By experimenting with OH scavengers in chamber ozonolysis of  $\alpha$ -pinene, Putman et al.<sup>[189]</sup> concluded that OH does not significantly alter the distribution of particle-phase products as observed by ESI/FTICR-MS. Chan et al.<sup>[190]</sup> took advantage of ultra performance liquid chromatography (UPLC) coupled to ESI/TOF-MS to investigate the effect of aerosol acidity on the chemical composition of SOAs from photooxidation of the sesquiterpene,  $\beta$ -caryophyllene. They were able to identify several products, including multifunctional carbonyls and carboxylic acids, as well as products of particle-phase acid-catalysed reactions, such as organosulfates. Li et al.<sup>[191]</sup> also used UPLC/ESI/TOF-MS to investigate SOA from ozonolysis of  $\beta$ -caryophyllene. They positively identified 15 new particle-phase products, including highly substituted compounds, and

concluded that second-generation products make a significant contribution to the aerosol mass. Hamilton et al.<sup>[192]</sup> used SOA from  $\beta$ -caryophyllene as a seed for the condensation of oxidised monoterpenes, such as D-limonene. The fraction of cross-products between D-limonene and  $\beta$ -caryophyllene identified by HR-MS was minimal, suggesting that  $\beta$ -caryophyllene SOA is a suitable seed material for chamber studies. Yasmeen et al.<sup>[193]</sup> elucidated the chemical structure of the  $m/z$  358  $\alpha$ -pinene SOA product, which is also observed in ambient aerosol from a boreal forest site as a diester formed between *cis*-pinic and diaterpenylic acid, a hydrolysis product of terpenylic acid. Of note, this molecule received considerable attention from several groups in previous studies, but its structure remained unresolved until the Yasmeen et al. study. The  $m/z$  358 compound could be structurally identified mainly because of the prior structure characterisation<sup>[194]</sup> of the precursor of one the composing monomers, terpenylic acid, a first-generation lactone-containing product in  $\alpha$ -pinene SOA.

Aromatic precursors contribute significantly to SOA production, especially in urban areas. Nakao et al.<sup>[195]</sup> investigated photooxidation of a series of phenolic compounds using a novel online PILS coupled with a TOF-MS instrument and identified multiple products consistent with OH addition to the aromatic ring. The same group investigated photooxidation of diesel exhaust in a smog chamber.<sup>[96]</sup> Ofner et al.<sup>[196]</sup> described a comprehensive study of SOA production from catechol and guaiacol, which relied on FTICR-MS, temperature-programmed-pyrolysis MS, Fourier transform infrared (FTIR) spectroscopy, and ultraviolet and visible (UV-vis) spectroscopy. They concluded that SOA produced from these precursors may serve as a good proxy for humic-like substances (HULIS). Gratien et al.<sup>[197]</sup> reported a rather unexpected formation of an aromatic product, *p*-cymene, in the oxidation of  $\alpha$ -pinene by OH, O<sub>3</sub> and NO<sub>3</sub>. Such conversion of non-aromatic precursors into aromatic ones may potentially complicate source apportionment, which relies on specific tracers.

A recent review of Ziemann<sup>[198]</sup> summarises the present state of the knowledge on contributions of long-chain saturated hydrocarbons to SOA formation from vehicular emissions in urban areas. Despite their relative simplicity (compared with terpenoid and aromatic VOCs), the chemical composition of SOAs from long-chain saturated hydrocarbons is quite complex. Kessler et al.<sup>[199]</sup> conducted chamber experiments with the reaction initiated by direct photolytic production or alkylperoxy radicals from alkyl iodides in air (as opposed to the more conventional OH or O<sub>3</sub> oxidation of VOC). Although the AMS mass spectra of the resulting SOAs were still complex, this approach holds promise for mechanistic investigations of the initial stages of SOA formation. Chacon-Madrid and Donahue<sup>[200]</sup> examined the role of fragmentation versus functionalisation by cleverly selecting either straight-chain saturated hydrocarbons or corresponding aldehydes and ketones as aerosol precursors. They found the aerosol yield depended sensitively on the location of the carbonyl group within the precursor.

Isotope-resolved studies help constrain the mechanisms of atmospheric reactions and increase the accuracy of global VOC emission estimates. Using thermal desorption gas chromatography isotope ratio mass spectrometry (TD/GC/IRMS), Gensch et al.<sup>[201]</sup> studied the temperature dependence of the <sup>12</sup>C → <sup>13</sup>C kinetic isotope effect in the ozonolysis of  $\beta$ -pinene. They showed that neglecting the temperature dependence of the kinetic isotope effect led to a significant underestimation of

the average  $\beta$ -pinene age in the atmosphere. Moukhtar et al.<sup>[202]</sup> developed a GC/IRMS-based method to determine the stable carbon isotope ratio of methylnitrophenols in atmospheric particulate matter.

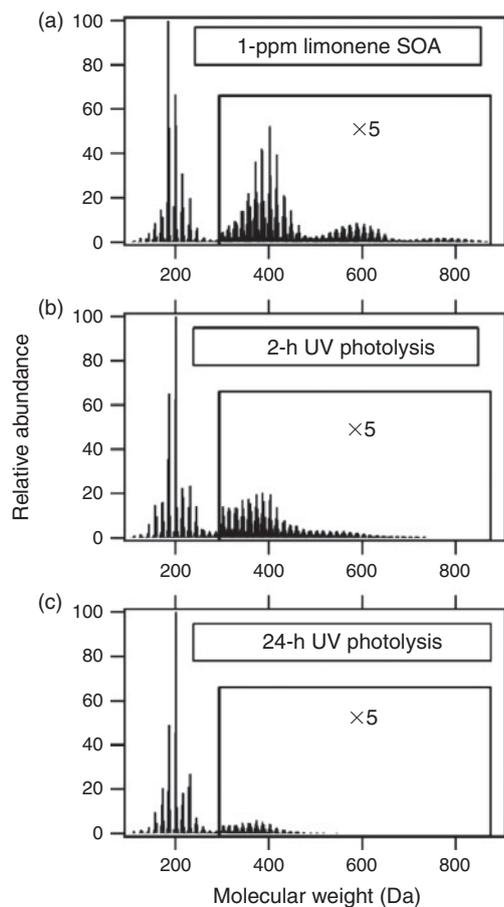
#### *Organosulfate and organonitrate compounds*

It is well established that organic compounds containing nitrogen, sulfur and other hetero elements can be incorporated into OAs by several mechanisms. For example, esters of nitric acids (organonitrates) are produced in high yields in reactions between peroxy radicals (RO<sub>2</sub>) and NO. Auld and Hastie<sup>[203]</sup> examined formation of keto- and hydroxy-nitrates in high-NO<sub>x</sub> oxidation of  $\beta$ -pinene using atmospheric pressure ionisation MS. Fry et al.<sup>[204]</sup> found that oxidation of limonene by NO<sub>3</sub> produces particle-phase nitrates in high yields (~30%). A HR-MS study by Nguyen et al.<sup>[77]</sup> found that organosulfates form efficiently during evaporation of an aqueous solution of OA acidified with sulfuric acid. Although organosulfates and organonitrates are thermodynamically unstable with respect to hydrolysis, bulk kinetic measurements found that only tertiary organonitrates hydrolyse quickly.<sup>[205–207]</sup> This is consistent with the high frequency of organosulfate and organonitrate observations in field studies of OAs (refer to the examples in the field section of this review).

#### *Aqueous-phase chemistry of OAs*

A recent review by Ervens et al.<sup>[208]</sup> presented convincing evidence from field, laboratory and modelling work indicating that a significant fraction of OAs can be produced through aqueous photochemistry and dark chemistry occurring in cloud droplets, fog droplets and aerosol water. MS methods have been invaluable in elucidating the mechanistic details of atmospheric aqueous chemistry. Lee et al.<sup>[209,210]</sup> described a novel approach for studying aqueous OH chemistry, wherein the solution is atomised directly from a photochemical reactor and the resulting aerosol is analysed using AMS. They observed the formation of highly oxidised, oligomeric products in the OH oxidation of glyoxal solutions,<sup>[210]</sup> as well as aqueous extracts of ambient aerosol and cloud water.<sup>[209]</sup> In addition to the aqueous OH oxidation, direct photolysis of dissolved organics is an important mechanism of cloud-processing as demonstrated recently in a HR-MS study by Bateman et al.<sup>[211]</sup> Fig. 9 shows the evolution of the HR mass spectrum of an aqueous aerosol extract of D-limonene SOA resulting from 2 and 24 h of irradiation by 300–400-nm light. The changes in the mass spectrum are driven primarily by the direct photolysis of carbonyls and peroxides. The OH-driven chemistry becomes even more complex in ice. For example, Gao et al.<sup>[212]</sup> found that an aqueous reaction of OH with dicarboxylic acids slowed down upon freezing, largely as a result of freezing-induced phase separation of the organic and aqueous phase.

Although the OH-driven oxidation is believed to dominate the atmospheric aqueous chemistry,<sup>[213]</sup> dark reactions of carbonyls, such as glyoxal with nitrogen-containing compounds, may contribute to SOA formation at night.<sup>[214]</sup> For example, De Haan et al.<sup>[215]</sup> observed light-absorbing, nitrogen-containing oligomers upon simulated evaporation of cloud droplets containing glyoxal and methylglyoxal using a combination of AMS and ESI/MS methods. Formation of light-absorbing compounds was also observed upon evaporation of aqueous mixtures of ammonium sulfate and SOA.<sup>[77]</sup> Galloway et al.<sup>[216]</sup> investigated uptake of glyoxal onto deliquesced



**Fig. 9.** Electrospray ionisation high-resolution mass spectrometry (ESI/HR-MS) spectra of irradiated aqueous extracts of secondary organic aerosols (SOAs) produced by ozonolysis of D-limonene. Direct photolysis of carbonyls and peroxides results in significant changes in the molecular composition of the dissolved SOA. (From Nizkorodov et al.,<sup>[211]</sup> Royal Society of Chemistry, reproduced with permission.)

ammonium sulfate aerosol under both dark and irradiated conditions. Surprisingly, the glyoxal uptake did not depend on the presence of radiation, suggesting that the dark chemistry may, in fact, dominate in this case. Trainic et al.<sup>[217]</sup> examined the dark glyoxal and ammonium sulfate aerosol reaction at different RH levels using AMS and cavity ring-down spectroscopy methods. The growth of glyoxal oligomers depended on RH in a complicated way and was the most efficient at  $\sim 40\%$  RH, below the deliquescence point of AS. In contrast, the fraction of nitrogen-containing absorbing species increased with RH. These examples clearly demonstrate the high degree of sensitivity of aqueous reactions to the amount of available water in particles.

#### *Simplified approaches for SOA characterisation*

The high level of molecular complexity of OAs has prompted attempts to correlate various physical and chemical properties of OAs to parameters that are straightforward to measure with a mass spectrometer. These parameters include average elemental ratios O/C and H/C, which can be measured with an AMS,<sup>[218]</sup> and a more chemically intuitive metric ‘average carbon oxidation state’ ( $OS_C$ ) introduced by Kroll et al.<sup>[219]</sup> Ng et al.<sup>[52]</sup> introduced a ‘triangle plot’, which graphs normalised the  $m/z$  44 signal ( $f_{44}$ , mostly from  $CO_2^+$ ) against the  $m/z$  43 signal ( $f_{43}$ , mostly from  $C_2H_3O^+$ ), as a way visualising the evolution of

AMS data. Most existing field data on OAs appear to occupy a limited triangle-shaped area in the  $f_{44}$ – $f_{43}$  space with the most oxidised (aged) SOAs converging to the top corner of the triangle. Chhabra et al.<sup>[220]</sup> studied how different types of chamber-generated SOAs evolve in the  $f_{44}$ – $f_{43}$  space. They found that SOAs, formed from already oxidised precursors, can achieve a higher placement on the ‘triangle plot’ (i.e. closer to the field observations) not easily accessible to non-oxidised precursors. Chen et al.<sup>[221]</sup> examined the SOA yields and O/C and H/C ratios measured with AMS in the photooxidation of isoprene, ozonolysis of  $\alpha$ -pinene and ozonolysis of  $\beta$ -caryophyllene. They found that an MCM-based model did a reasonable job in predicting the SOA yield, but it produced significant deviations from the average particle composition, implying missing pathways in the mechanism.

#### *Gas–solid heterogeneous kinetics, interfacial chemistry and aerosol aging*

Chemistry at the air–particle interface continues to enjoy increased attention because several unique and important chemical and physical processes are believed to occur right at or close to the interface. Laboratory studies of gas–surface reactive uptake can be conducted using either bulk samples or aerosolised materials. MS methods are instrumental in providing information on the composition of the surface, particles and gas-phase compounds interacting with the surface and particles. Net et al.<sup>[222]</sup> showed that the heterogeneous reaction of ozone with surfaces coated by phenolic compounds accelerated under irradiated conditions implied the existence of photosensitised reactions on the surface. Nájera et al.<sup>[223]</sup> identified several reaction products by atmospheric pressure CIMS in reactions of ozone with anthracene-coated surfaces and ammonium sulfate particles. Oldrgide and Abbatt<sup>[224]</sup> investigated the interaction of ozone with frozen and liquid solutions of NaCl/NaBr with the ozone and released halogens detected by negative-ion CIMS and found evidence for the surface and bulk reactions occurring in parallel. Gallimore et al.<sup>[225]</sup> found a surprisingly strong effect of RH on reactive uptake of ozone by maleic acid aerosol with considerably more reaction products observed above 50% RH. The preceding examples amply illustrate the complexity of ozone reactions with surfaces with phase state, radiation and humidity all affecting reaction rates and mechanisms.

Due to its important role in controlling  $NO_x$  levels in the atmosphere and aerosol aging chemistry, reactive uptake of nitrogen oxides by various surfaces has been studied by multiple groups. Using ESI/MS, Kinugawa et al.<sup>[226]</sup> investigated disproportionation of  $NO_2$ , leading to HONO and  $NO_3^-$  on aqueous surfaces containing cationic, anionic, and neutral surfactants. They observed significant enhancement in the uptake of  $NO_2$  in the presence of cationic surfactants, an important finding in view of the widespread occurrence of surface-active organics in the environment. Knopf et al.<sup>[227]</sup> carried out an extensive study on the uptake of  $O_3$ ,  $NO_2$ ,  $NO_3$  and  $N_2O_5$  by mixtures of levoglucosan, abietic acid and nitroguaiacol (surrogates for BBOA particles) over a range of RH values in a wall-coated flow reactor. They observed deactivation of the surface with respect to the  $NO_3$  uptake in all cases – except for the pure nitroguaiacol surface. The estimated lifetimes of these organic compounds under typical atmospheric conditions imply significant processing of BBOAs on a time scale of minutes to hours. Using an aerosol-CIMS approach, Zhao et al.<sup>[228]</sup> examined the particle-phase products formed in

reactive uptake of  $\text{NO}_3$  by unsaturated fatty acid aerosols and found that the reaction mechanism depends on the presence of  $\text{O}_2$  (reactive uptake of chlorine atoms by squalane aerosol<sup>[229]</sup> also exhibited a strong dependence on the presence of  $\text{O}_2$ ). Measurements of the  $\text{NO}_3$  uptake by mixed solid organics and liquid unsaturated fatty acids by Xiao and Bertram<sup>[230]</sup> confirmed that lifetimes of unsaturated organics should be short in liquid particles and increase when the unsaturated organics are embedded in a solid matrix. The kinetics of reactions of  $\text{NO}_3$  with aerosolised insecticide (Phosmet)<sup>[231]</sup> and pesticide (Carbaryl)<sup>[232]</sup> was investigated using a VUV ATOFMS method. The results imply surprisingly short lifetimes of these compounds (0.3–1.3 h) with respect to oxidation by atmospheric  $\text{NO}_3$ . The same group also investigated reaction of  $\text{NO}_3$  with various nitro-, oxy- and hydroxy-PAHs coated onto azelaic acid particles<sup>[233]</sup> and observed extensive nitration of the aromatics with both VUV ATOFMS and GC/MS.

The uptake of organics by atmospherically relevant solutions has also been investigated in the review period. Liu et al. examined uptake of 2-methyl-3-buten-2-ol<sup>[234]</sup> and methacrolein<sup>[235]</sup> into fairly concentrated aqueous solutions of  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$  in a rotating wall flow reactor coupled to a single-photon-ionisation TOFMS instrument. Acetone, acetaldehyde and isoprene were observed as products. Reactive uptake of nonanal by acidic aerosols (sulfuric acid by itself or mixed with levoglucosan or oleic acid) was measured with the help of an electrodynamic balance. The conclusion was that the acid-catalysed uptake of carbonyls is highly dependent on the presence of organics in particles.<sup>[236]</sup>

#### CCN and IN propensities of aerosols

The ability of aerosol particles to serve as CCN and IN is the primary mechanism behind their indirect effect on climate. Laboratory CCN studies have benefitted greatly from parallel characterisation of particles by various MS-based methods. For example, the expectation that more oxidised organic material should be more hygroscopic has prompted several attempts to correlate  $\kappa$  with the average level of oxidation in the particle material, expressed as either  $f_{44}$  (normalised  $\text{CO}_2^+$  signal) or average O/C, measured by AMS. Engelhart et al.<sup>[237]</sup> reported  $\kappa = 0.12$  for isoprene photooxidation SOA and found that CCN activation kinetics was similar to that for pure ammonium sulfate aerosol. CCN measurements by Frosch et al.<sup>[238]</sup> for  $\alpha$ -pinene photooxidation SOA found that  $\kappa$  increased insignificantly with the oxidation state in the O/C range of 0.3–0.6. Kuwata et al.<sup>[239]</sup> conducted a related study for  $\alpha$ -pinene ozonolysis SOA. The measured  $\kappa$  did not depend on the particle mass loading in the chamber or the average O/C ratio in the 0.38–0.50 range. However, particles subjected to thermodesorber treatment before the CCN measurements did have mass-loading-dependent hygroscopicity, and their CCN activity decreased. This effect was attributed to the higher fraction of less hygroscopic oligomeric compounds in particles exposed to elevated temperature. Using a potential aerosol mass flow reactor, Lambe et al.<sup>[240]</sup> were able to achieve a significantly wider range of O/C ratios (0.05–1.42) for chamber-generated SOAs and oxidised POAs. Before the CCN measurements, the particles were exposed in the potential aerosol mass flow reactor to OH or  $\text{O}_3$  for an equivalent of 1–20 days in ambient air. The hygroscopicity of the aged particles ranged from  $\kappa = 8.4 \times 10^{-4}$  to 0.28 and was reasonably correlated with the average O/C (shown in Fig. 10). Another paper by the same group<sup>[241]</sup>

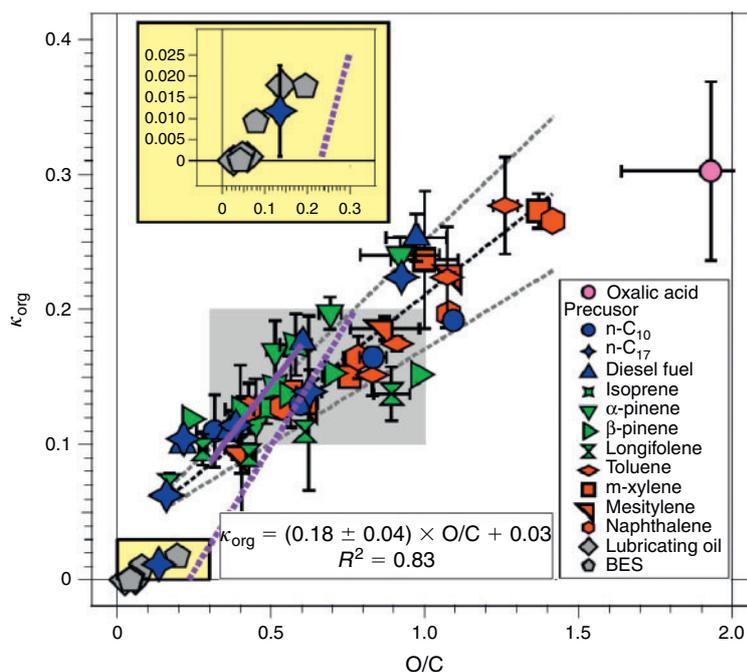
investigated the complicated (and still unanswered) question regarding to what extent the accelerated oxidation in various types of aging reactors approximate the slower oxidation in ambient air. Meanwhile, Kang et al.<sup>[242]</sup> examined the effect of OH exposure in a potential aerosol mass flow reactor on the measured degree of oxidation. To complete the story, we should note that the oxidation of organics in particles does not always increase their CCN activities. For example, ozone oxidation of particles containing oleic acid and sodium oleate internally mixed with sodium chloride or ammonium sulfate has little effect on their critical diameters.<sup>[243]</sup>

In contrast to the moderate level of understanding of the CCN activity of organic particles, which can be parameterised using  $\kappa$  and correlated with the average O/C, there are no simple correlations between IN activity and particle composition. However, IN studies also benefit greatly from MS-based particle characterisation. Friedman et al.<sup>[244]</sup> investigated whether carboxylic acid coatings (adipic acid, malic acid, oleic acid and oleic acid exposed to ozone) can improve the IN ability of soot particles. The composition and morphology of particles were characterised by a SPMS method. Although the coatings aided in water uptake, they did not induce heterogeneous IN by the core soot particles. Reitz et al.<sup>[245]</sup> studied the effect of exposure of mineral dust particles to sulfuric acid, humidity and ammonia vapours on their IN activities. The change in particle composition was characterised by ATOFMS and AMS. Generally, surface modification by chemical exposure was found to decrease the IN activity of dust particles.

Once the cloud droplets are activated, they can scavenge additional aerosol particles. Ladino et al.<sup>[246]</sup> measured scavenging efficiencies by crossing a laminar flow of lithium metaborate particles (0.05–0.3  $\mu\text{m}$ ) and free-falling droplets (12–20  $\mu\text{m}$ ) with the droplets collected and analysed by an inductively coupled plasma MS instrument. They were able to observe the so-called ‘Greenfield gap’, the particle size resistant to scavenging, at  $\sim 0.24 \mu\text{m}$ .

#### Optical and hygroscopic properties of aerosols

In addition to the indirect effect of aerosols on climate through cloud and ice nucleation, aerosols can also affect the climate directly by scattering and absorbing solar radiation. As particle absorption ( $\sigma_a$ ), scattering ( $\sigma_s$ ) and extinction ( $\sigma_{\text{ext}} = \sigma_a + \sigma_s$ ) coefficients depend sensitively on the presence of adsorbed water, laboratory studies of the optical properties of aerosols are often conducted in parallel with particle hygroscopic growth measurements at sub-saturated RH (<100%). MS methods provide invaluable information for interpreting the optical and hygroscopic properties of OAs and relating them to chemical composition. Cappa et al.<sup>[247]</sup> measured  $\sigma_{\text{ext}}$  (500 nm) for particles of squalane and azelaic acid as they were oxidised by OH. In both cases, there was an increase in  $\sigma_{\text{ext}}$  with oxidation correlated with the average O/C ratio. At the same time, there was a significant increase in hygroscopicity for the oxidised azelaic acid particles but not for the squalane ones. Redmond and Thomson<sup>[248]</sup> proposed a promising approach for correlating  $\sigma_{\text{ext}}$  with the molecular structure by means of structure–polarisability relationships. Correlations of this type should be especially useful for aerosols characterised by HR-MS methods. Duplissy et al.<sup>[249]</sup> were able to correlate hygroscopicity of chamber-generated SOAs with the average degree of oxidation and proposed a correlation between the effective hygroscopicity parameter and  $f_{44}$  (previously defined):  $\kappa_{\text{organic}} = 2.2 \cdot f_{44} - 0.13$ .



**Fig. 10.** Experimentally determined relationship of hygroscopicity parameter ( $\kappa$ ) and O/C ratio in organic aerosol (OA) as measured by an aerosol mass spectrometer (AMS) instrument. (From Lambe et al.,<sup>[240]</sup> EGU, reproduced with permission.)

Tritscher et al.<sup>[250]</sup> examined how hygroscopicity and volatility of  $\alpha$ -pinene SOA evolve with initial formation, ripening and OH-induced chemical aging. In their measurements,  $\kappa_{\text{organic}}$  initially increased with OH-aging then reached a plateau, whereas the particle volatility continued to drop. Lu et al.<sup>[251]</sup> quantified  $\sigma_{\text{ext}}$  using cavity ring-down spectroscopy, and  $\sigma_a$ , using photoacoustic spectroscopy for benzo[a]pyrene-coated particles during their reaction with  $\text{NO}_2$  and  $\text{NO}_3$ . When some benzo[a]pyrene in particles was nitrated, evident by the parallel AMS measurements, both the scattering and absorption coefficients increased.

Internally mixed organic–inorganic particles offer an additional layer of complexity in interpreting their hygroscopic and optical properties. Work by Trainic et al.,<sup>[217]</sup> which has already been mentioned in conjunction with the aqueous chemistry of SOAs, characterised optical properties of ammonium sulfate aerosols interacting with glyoxal vapour at different RH. Zhong and Jang<sup>[252]</sup> developed a promising method for measurements of  $\sigma_a$  using filter samples of aerosols in an integrated sphere and applied it to internally mixed ammonium sulfate and SOA particles. A study by Smith et al.<sup>[253]</sup> examined deliquescence and efflorescence phase transitions in ammonium sulfate coated with  $\alpha$ -pinene SOA organic material. The surprising result of this study was that the organic coating had an insignificant effect on the phase transition in the ammonium sulfate core. Even in the deliquesced state, the phase separation between the organic and inorganic fractions appeared to persist. This represents a significant change in how the phase states of internally mixed particles are viewed. Several interesting new developments can be expected in this research area. To make matters even more interesting, Nguyen et al. observed chemical reactions between ammonium ions and SOA carbonyls occurring during evaporation of ammonium sulphate–SOA solutions<sup>[184]</sup> leading, among other things, to light-absorbing,

nitrogen-containing compounds. Once again, these examples emphasise the role of RH in controlling not only the phase state but the chemistry of internally mixed aerosols.

### Summary and outlook to the Special Issue

Developments and applications of novel MS methodologies discussed herein are at the forefront of aerosol chemistry and physics research. Over a span of a few years, we have witnessed tremendous expansion and growth in this research area, and this trend likely will continue. Several scientific challenges related to complex, multi-phase chemistry and physics of aerosols that are yet to be resolved would benefit from experimental capabilities of complementary MS techniques. The synopsis that we present is not intended to convey an inclusive list of all possible topics. Rather, it embraces selected areas where the authors of this special issue are currently working in parallel with other groups.

- Elucidation of the effect of OA chemistry and changes in its molecular composition on the increased viscosity and formation of glassy SOA particles is particularly important for understanding how these changes affect the atmospheric lifetime of particles, their heterogeneous reactions, optical and hygroscopic properties. Coupled experimental and modelling studies in this area are needed to develop a parameterisation framework to include these effects in aerosol and cloud models. Although this research topic is not explicitly presented in the collection of manuscripts for this special issue, advances in this area have been discussed in great detail in a recent perspective manuscript by Koop et al.<sup>[182]</sup> and references therein.
- Identification of ‘brown carbon’ chromophores in OAs, as well as a molecular-level understanding of their composition, light-absorption properties, atmospheric sources, possible

formation and aging mechanisms, is also important. The work of Claeys et al.<sup>[254]</sup> illustrates efforts in this area and reports on the chemical speciation of HULIS in field-collected aerosol samples ascribing chromophoric substances to nitrocatechols based on LC/UVVIS/MS measurements.

- Identification of molecular markers unique to POA and SOA from different biogenic and anthropogenic sources is needed to improve aerosol emission inventories, including source-specific attribution of OA in the atmospheric environment. Detection and molecular-level speciation of OA markers are commonly used in focussed laboratory studies designed to investigate different aspects of aerosol chemistry inferred from field observations. In this issue, Zhang et al.<sup>[255]</sup> use GC/MS and UPLC/ESI/MS techniques to analyse samples of laboratory-generated and ambient aerosols and systematically evaluate the role of environmental conditions, such as RH, aerosol, acidity and NO<sub>x</sub> level, on yields and composition of SOA derived from the photochemical oxidation of isoprene. A separate study by Yasmeen et al.<sup>[256]</sup> focussed on the structural characterisation of molecular markers and the reaction mechanism of  $\alpha$ -pinene SOA aging. Stone et al.<sup>[257]</sup> evaluates biogenic contributions to SOAs at a specific geographic location (Kathmandu Valley, Nepal) based on the GC/MS analysis of field samples and quantitative analysis of targeted molecular markers.
- Molecular-level understanding of the interactions of anthropogenic and biogenic/geogenic emissions and their effects on the physicochemical properties of aerosols is a topic of intensive ongoing research in many groups and has a direct effect on air quality management and emission regulation in urban areas. In this issue, the Huang et al.<sup>[258]</sup> field study presents ATOFMS measurements from an urban area of Shanghai, discusses the formation mechanism of amine-containing OAs and describes plausible environmental factors enhancing their formation and growth. Kroll et al.<sup>[259]</sup> presents key chemical characteristics and oxidation trends of anthropogenic diesel exhaust particles generated in a test laboratory study and investigated using an AMS instrument coupled to the synchrotron-based VUV ionisation source.
- The investigation of the aqueous-phase chemistry of organics relevant to processes in cloud and fog droplets and deliquesced aerosols has been the subject of many studies.<sup>[208]</sup> Although condensed water is an abundant medium in atmospheric processes, the importance of the aqueous processes in the formation and aging of SOAs was not considered until recently. To explore the molecular composition of organics in cloud and fog water, more studies are needed, which, in turn, would facilitate laboratory studies with selected model systems. Ge et al.<sup>[260]</sup> report results of AMS measurements during fog episodes in the Central Valley, California, and indicates significant oxidation of organics through aqueous-phase atmospheric chemistry.
- One of the most challenging tasks in aerosol chemistry research is experimental studies of NPF events that require development and application of MS techniques capable of detection and chemical characterisation of the smallest, nucleation mode particles and sensitive measurements of their gas-phase precursors. This research area is illustrated by the work of Yu and Lee,<sup>[108]</sup> which presents a novel CIMS instrument uniquely configured for sensitive detection of gaseous amines and its first field application.
- Methods of HR-MS (>50 000 m/ $\Delta$ m) coupled to soft ionisation methods, such as ESI and its variations, arguably are

among the most powerful techniques to probe the molecular-level composition of individual molecules in complex OA mixtures.<sup>[26]</sup> The ESI/HR-MS analysis can detect thousands of individual molecules at once and provide their elemental composition, and additional structural information can be obtained from fragmentation experiments using MS/MS. Applications of these techniques to unravel the chemical complexity of aerosols have increased remarkably over the last few years for analysis of both laboratory and field-collected aerosols – with many more novel developments and applications in this area expected in the near future. In this issue, Mazzoleni et al.<sup>[261]</sup> used HR-MS analysis to characterise individual constituents of the WSOC fraction of ambient aerosol, whereas Rincon et al.<sup>[262]</sup> used HR-MS to investigate seasonal variations in the composition of ambient OAs collected at an urban site.

### Abbreviations used

2D-TAG, two-dimensional thermal desorption aerosol gas chromatography  
 ACSM, aerosol chemical speciation monitor  
 AMS, aerosol mass spectrometer  
 APi-TOF, atmospheric pressure interface time-of-flight (mass spectrometer)  
 ASAP, atmospheric solids analysis probe  
 ATOFMS, aerosol time-of-flight mass spectrometer  
 BBOA, biomass burning organic aerosol  
 CIMS, chemical ionisation mass spectrometry  
 CCN, cloud condensation nucleus  
 DESI, desorption electrospray ionisation  
 EI, electron ionisation  
 ESI, electrospray ionisation  
 EUV, extreme ultraviolet  
 FTIR, Fourier transform infrared (spectroscopy)  
 FTICR, Fourier transform ion cyclotron resonance  
 GC/MS, gas chromatography mass spectrometry  
 HPLC, high-performance liquid chromatography  
 HR-MS, high-resolution mass spectrometry  
 HOA, hydrocarbon-like organic aerosol (as observed by AMS)  
 HULIS, humic-like substances  
 IN, ice nucleus  
 IRMS, isotope ratio mass spectrometry  
 LC/MS, liquid chromatography mass spectrometry  
 LOD, limit of detection  
 LV-OOA, low-volatility oxygenated organic aerosol (as observed by AMS)  
 MAB, metastable atom bombardment  
 MCM, master chemical mechanism  
 MS, mass spectrometry  
 NAMS, nano aerosol mass spectrometer  
 NPF, new particle formation  
 OA, organic aerosol  
 OOA, oxygenated organic aerosol (as observed by AMS)  
 PAH, polycyclic aromatic hydrocarbon  
 PILS, particle-into-liquid sampler  
 PMF, positive matrix factorisation  
 POA, primary organic aerosol  
 PTRMS, proton-transfer reaction mass spectrometer  
 REMPI, resonance enhanced multi-photon ionisation  
 Q-TOF, (hybrid) quadrupole time-of-flight  
 SIMS, secondary ion mass spectrometry  
 SNMS, secondary neutral mass spectrometry

SPMS, single particle mass spectrometer  
 SOA, secondary organic aerosol  
 SV-OOA, semi-volatile oxygenated organic aerosol (as observed by AMS)  
 TD, thermal desorption  
 TOF, time-of-flight  
 UPLC, ultra performance liquid chromatography  
 UV-vis, ultraviolet and visible (spectroscopy)  
 VOC, volatile organic compound  
 VUV, vacuum ultraviolet  
 WSOC, water-soluble organic carbon  
 XPS, X-ray photoelectron spectroscopy

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