
Chapter Eight: Conclusions and Future Work

8.1 Conclusions

The Aerodyne aerosol mass spectrometer is capable of providing quantitative information on the chemical composition of the submicron non-refractory fraction of aerosol particles with a high size and time resolution. The instrument employs an aerodynamic lens, differential pumping, aerodynamic sizing, thermal vaporisation, electron impact ionisation and quadrupole mass spectrometry, where particles are analysed within a few milliseconds of entering the vacuum. This work has demonstrated the applicability of the Aerodyne Aerosol Mass Spectrometer for use in quantifying the abundance of organic material in submicron atmospheric aerosol. It has shown that the organic fraction is ubiquitous, is always significant and often dominates the particle composition.

Laboratory characterisation of the AMS has demonstrated that it produces mass spectra of organic compounds that are qualitatively similar to those reported in the NIST standard library of mass spectra. However, two systematic differences have been observed between the two sets of data. Firstly, more fragmentation of long chain species tends to occur in the AMS data. Secondly, mass fragments arising due to thermal decomposition of highly oxidised organic compounds have been uniquely observed in the AMS spectra. The differences in the intensities of ion fragments produced from long chain species between the AMS and NIST data do not prevent the utilisation of NIST data in the interpretation of AMS ambient data. On the other hand, the formation of the decomposition mass fragment CO_2^+ , uniquely from highly oxidised organic compounds in the AMS and its absence from NIST data, is of much greater importance in interpreting ambient AMS data since it can be used to determine the degree of oxygenation of ambient aerosol particles.

Further characterisation of the AMS has suggested that a vaporiser temperature in the range of 500 – 550 °C would result in the maximum possible detection of ions for a range of inorganic and organic compounds. Also, the AMS has near 100% collection efficiency for spherical organic particles; while particles that have irregular shapes are

collected with a reduced efficiency (less than 50%). Finally, results suggest that, after investigating possible interference from other chemical species, the $\text{NO}^+/\text{NO}_2^+$ (m/z 30 / 46) ratio can be used as an indication of the type of nitrate salt measured in ambient particles or the presence of nitrogenated organic compounds.

Chemical composition and mass size distribution results obtained using the AMS at various locations, representing urban, rural and remote settings around the world, have shown that a significant accumulation mode with a peak around 400 – 500 nm was observed at all locations and was composed of sulphate, organics, ammonium and nitrate. A significant organic mass mode at about 100 – 200 nm was constantly observed at all urban sites and when more freshly polluted air masses affected the other locations. Combustion-related emissions (likely dominated by traffic) have been found to be the main source of the small organic mode at these sites. The chemical composition of organic aerosol at urban locations appeared to be very similar to the composition of lubricating oil and diesel exhaust aerosol, indicating that the organic fraction of urban aerosols is mostly dominated by the recondensed vapor from evaporated engine lubricating oil. Organics in the accumulation mode at the urban locations are composed of compounds of highly oxidised nature.

In contrast to the urban sites, organic aerosols at all the other rural and remote sites appeared to be dominated by highly oxidised compounds with shorter carbon chains. The mass spectral signatures at all of these locations were found to be extremely similar and the most significant contributions to these spectra arise from mass fragments that are characteristic of highly oxidised organic compounds such as carbonyls and dicarboxylic and poly acids. The organic material observed in the accumulation mode appears to be the result of photochemical processing of the aerosols. While organic compounds can have many different initial sources (e.g. vehicle emissions, meat cooking, biomass burning and biogenic VOCs), processing of organic aerosols increases their modal diameter and the resulting compounds have a very similar chemical signature to that of humic-like substances (a group of highly oxidised organic compounds with a macromolecular structure). The highly similar chemical signature of the organic fraction of the accumulation mode at all of the sites discussed in this thesis

suggests that though organic particles may initially be introduced into the atmosphere through a variety of different routes (i.e. primary emission or secondary formation) and in different chemical forms, subsequent homogenous, heterogeneous or multiphase processes in the atmosphere result in further oxidation and polymerisation of the organic compounds, ultimately transforming them to macromolecular material with highly similar chemical signatures.

The formation of macromolecular SOA compounds has been confirmed in a reaction chamber study, in which anthropogenic (1,3,5-TMB) and biogenic (α -pinene) precursors were photochemically processed. The mass spectral signatures of SOA produced from each precursor have broadly similar chemical functionality of a highly oxidised nature. However, their precise molecular compositions appeared to be different. Nitrogenated organic compounds have been observed in the photooxidation products of both precursors. However, different types of nitrogenated compounds may have been formed in each system. The photooxidation of the biogenic precursor explains more of the chemical signature of organic particulate observed at various urban, rural and remote locations compared to the anthropogenic precursor.

The effect of the organic component of the aerosol on the activation of cloud droplets was investigated during the second Cloud and Aerosol Characterisation Experiment (CLACE2), which took place at the Jungfraujoch mountain top research station in the Swiss Alps. The organic material accounted, on average, for 54% of the total measured aerosol mass during this experiment, and was largely composed of highly oxidised compounds. This demonstrates that even in such a remote site, often in the lower free troposphere, secondary organic aerosols are extremely important, and were much more significant than primary compounds at this location. Near one-to-one correlation between cloud droplet number and aerosol number was observed during clean conditions, while during more polluted conditions the correlation between cloud droplet number and aerosol number appeared to be much lower, but seemed to increase with increasing wind speed, suggesting that high updraft velocities increase particle activation during polluted periods.

Cloud droplets scavenged all of the major aerosol chemical components, including organics. Within the same in-cloud event, the scavenging ratios of the different components were found to be similar in values, implying internal mixing of the different components within the particles. However, variable mass scavenging ratios ranging between 0.3 and ~ 1 were observed for the same chemical species in different cloud events. The differences in the mass size distributions of the activated and interstitial aerosols showed that the scavenged particles are mostly larger than approximately 150 nm, though there is some evidence that nitrate is activated down to 100 nm. During cloud events observed in clean periods, the most efficient mass scavenging was observed when the organic content of the particle was relatively low, and the mass scavenging ratio of organic aerosol increased with aging. On the other hand, the mixing state of aerosol particles appeared to be more important than the organic content in cloud events observed during polluted cases. A high degree of internal mixing between the organic and inorganic components of the aerosols resulted in efficient mass scavenging of the organics, providing that the latter are highly oxidised. However, when the particle number was dominated by small particles (< 200 nm) that were composed almost entirely of organic material then mass and number scavenging were reduced as these particles have a tendency to not grow in a high humidity environment.

8.2 Ongoing and Future Work

A more direct and reliable way of determining the particle collection efficiency (CE) represents one of the most immediate challenges for more accurate AMS quantitative measurements. The dependence on comparisons with external measurements that are made by collocated instruments to derive CE values for different chemical species is not ideal, and a more explicit method is urgently required. Although controlling the humidity of the sample flow into the AMS appears to focus the particle beam, this method is limited to hygroscopic particles, and therefore it is not efficient for focusing small ambient particles (< 150 nm), which are usually dominated by hydrophobic organic compounds. The particle beam probe (briefly mentioned in section 5.2.6) appears to be a promising solution. Work to evaluate this method and to optimize the width of the probe as well as to develop the appropriate inversion tools is ongoing at the

university of Colorado at Boulder [A. Huffman and J. Jimenez, University of Colorado, Boulder, personal communication].

Further laboratory experiments to better explain and quantify the productions of H_2O^+ (m/z 18), CO^+ (m/z 28) and CO_2^+ (m/z 44) during the vaporisation and ionisation of oxidised organic compounds (e.g. dicarboxylic acids) are required. These experiments should be performed in Argon in order to eliminate the contribution of ambient gases to these mass fragments. The ratios of these fragments can then be determined and employed in the fragmentation tables used to calculate the mass concentrations of various species from ambient data. To date, a relative ionisation efficiency (RIE_s) of 1.4 has been used to relate the IE of organics to that of nitrate. More laboratory experiments need to be conducted to determine the RIE_s for organic compounds with a wide range of functional groups, spanning from alkanes to humic-like substances.

The identification of macromolecular compounds as major part of secondary organic aerosols formed from the photooxidation of anthropogenic as well as biogenic precursors in reaction chambers and measurements of compounds with similar characteristics in ambient samples represent a significant advance in the area of organic aerosol analysis. More reaction chamber experiments should be performed using a wide range of VOCs that are known to be emitted from different sources in the atmosphere. The SOA formed should be studied in detail using a range of instrumentation to determine their chemical, physical, optical, hygroscopic and CCN properties. Results from such experiments should be extremely useful input for models predicting the behaviour of organic aerosols in the atmosphere. Furthermore, the AMS may be used to measure the chemical signatures of aerosols generated from these experiments as well as from other controlled sources such as combustion engines and wood burning facilities with the aim of compiling a database of mass spectral fingerprints that can be used in interpreting the chemical composition of atmospheric aerosols.

Finally, work has been ongoing at Aerodyne Research Inc., to replace the quadrupole mass spectrometer part of the AMS with a new type of time of flight mass spectrometry, which employs orthogonal extraction (Tofwerk model C-TOF, Thun, Switzerland)

[Chen *et al.*, 1999]. This technique produces mass spectra with much higher resolution compared to the current techniques. The increased resolution reduces the length of the time of flight region needed. This means that, in addition to reducing the bulk of the instrument, the time required to generate a full mass spectrum can be of the order of microseconds, which is short enough to be compatible with the particles sizing method employed in the current AMS. This new development of the AMS (known as the ToF-AMS) has the potential to produce complete mass spectra and aerodynamic sizes for individual particles, as well as providing data on sizes particles associated with hundreds of m/z channels. The new ToF-AMS should be capable of providing direct and quantitative information on the mixing states of aerosol particles, allowing for studies on the source apportionment to be performed. A number of ToF-AMS instruments are already available and are being developed and used by ARI, the University of Colorado, Boulder, USA and the Max Planck Institute for Chemistry at Mainz, Germany.