Characterising an Extractive Electrospray Ionisation (EESI) source for the online mass spectrometry analysis of organic aerosols

Peter J. Gallimore and Markus Kalberer* (corresponding author: markus.kalberer@atm.ch.cam.ac.uk)

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK

Abstract

Organic compounds comprise a major fraction of tropospheric aerosol and understanding their chemical complexity is a key factor for determining their climate and health effects. We present and characterise here a new online technique for characterising the detailed chemical composition of organic aerosols, namely Extractive Electrospray Ionisation Mass Spectrometry (EESI-MS). Aerosol particles composed of soluble organic compounds were extracted into and ionised by a solvent electrospray, producing molecular ions from the aerosol with minimal fragmentation. We demonstrate here that the technique has a time resolution of seconds and is capable of making stable measurements over several hours. The ion signal in the MS was linearly correlated with the mass of aerosol delivered to the EESI source over the range tested (3-600 μg/m^3) and was independent of particle size and liquid water content, suggesting that the entire particle bulk is extracted for analysis. Tandem MS measurements enabled detection of known analytes in the sub-μg/m^3 range. Proof-of-principle measurements of the ozonolysis of oleic acid aerosol (20 μg/m^3) revealed the formation of a variety of oxidation products in good agreement with previous offline studies. This demonstrates the technique's potential for studying the product-resolved kinetics of aerosol-phase chemistry at a molecular level with high sensitivity and time resolution.

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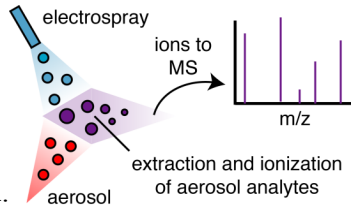

Introduction

Aerosols have an important influence on climate both directly by light scattering and indirectly by influencing cloud formation and cloud processes, through their ability to act as cloud condensation nuclei and ice nuclei.[1] Particulate matter also has significant negative health effects, with exposure to fine-particulate air pollution linked to respiratory and cardiovascular disease[2] and reduced life expectancy.[3]

Organic compounds are often the dominant fraction of tropospheric aerosol.[4] Despite this, our understanding of the sources, formation processes and atmospheric properties of organic aerosol is limited.[5] There is increasing recognition that reactions occurring in the condensed phase are altering the particle composition continuously during its lifetime and are key to explaining observed aerosol yields and composition.[6] A lack of detailed knowledge of their chemical composition is regarded as a limiting factor in understanding their effect on the climate and human health. One of the main challenges for the analysis of organic aerosols is their complex composition; up to several thousand compounds have to be separated.[7] In addition, there are usually only trace amounts of sample available for analysis, often in the nanogram range. Furthermore, atmospheric aerosol composition is often changing very rapidly, favouring fast-response online analytical-chemical techniques. In general, mass spectrometry techniques are well suited to measure highly complex samples at trace concentrations.

Established mass spectrometry techniques for characterising the composition of organic aerosols fall broadly into two categories; “online” measurements where particles are analysed in real time, and “offline” methods where particles are first collected and subsequently processed for analysis. Online particle analysis can be performed using instruments such as the aerosol mass spectrometer (AMS)[8] which employs thermal desorption/electron ionisation, or with laser desorption/ionisation (LDI) techniques such as aerosol time-of-flight MS.[9] These instruments are sensitive to ambient aerosol

concentrations but extensive fragmentation of the organic components is common due to the high energy ionisation conditions. Therefore, identifying specific compounds is a difficult task. Recent instrumental developments are concentrating on "softer" laser ionisation techniques to reduce compound fragmentation, such as near-IR LDI[10] and photo-ionisation AMS.[11] Vogel et al.[12] have recently measured organic acids in boreal forest aerosols using atmospheric pressure chemical ionisation.

A variety of offline analytical techniques have been used to characterise aerosol samples collected onto filters or impactors.[13] The disadvantage of offline techniques is that after an extended sample collection period (typically hours) where the aerosol chemical composition may change due to evaporation or reaction of components, extracting material from the substrate can be time-consuming and introduce further artefacts into the resulting measurements.[14] The low time-resolution also often limits the use of offline techniques for atmospheric studies where many processes have time scales of seconds to minutes.

A number of new offline techniques overcome the need for an extraction step by directly sampling collected aerosol from the substrate surface. Desorption electrospray ionisation[15] has proved useful in analysing both field and laboratory samples and is especially suitable for characterising labile compounds and particles subjected to chemical aging. Bruns et al.[16] have exploited the atmospheric solids analysis probe technique to analyse organic compounds in secondary organic aerosol (SOA). Liquid extraction surface analysis has recently been used to analyse time-resolved aerosol samples collected onto a rotating drum impactor.[17] An alternative approach is to dissolve the water-soluble particle components directly using a particle-into-liquid sampler (PILS). PILS can be used to collect fractions for subsequent analysis or directly coupled with techniques such as ion chromatography[18] or mass spectrometry[19] for online analysis.

Extractive electrospray ionisation (EESI) is a new and promising technique for the online analysis of organic compounds, first introduced by Cooks et al.[20] In this method, a spray of charged droplets is formed by infusing a solvent mixture into a conventional ESI source. A sample flow containing analytes in the gas or particle phase is analysed by directing it into the ESI spray without prior collection on a substrate, eliminating potential offline sampling artefacts. Collision of aerosol particles with the solvent droplets extracts the soluble components from the aerosol. As solvent from the charged droplets evaporates, analyte ions are ejected into the gas phase via a Coulomb explosion mechanism[21] and enter the mass spectrometer for analysis.

EESI has been used to measure the composition of a diverse range of substances, including aerosolised drugs,[22] human breath[23] and olive oil.[24] It has also shown promise as a technique to follow the kinetics of organic chemical reactions occurring in the bulk solvent phase.[25] Doezema et al.[26] recently used EESI to detect SOA products from the ozonolysis of α-pinene in both the gas and particle phase. A related technique, Ambient ESI, was recently used for molecular characterisation of gas and particle phase organic compounds and detected oligomers in SOA formed from α-pinene ozonolysis.[27]

We report here the development of an EESI source for the real-time analysis of organic compounds in aerosol particles. The source was adapted from a commercially-available ESI source and optimised with aerosols composed of tartaric acid or oleic acid. Tartaric acid aerosol is highly functionalised and is used as a proxy for oxygenated organic compounds formed as a result of aging in the atmosphere. At low relative humidity (RH), tartaric acid could form glassy particles which are increasingly being recognised as important in the atmosphere.[28] Oleic acid is an unsaturated fatty acid and its reaction with ozone is well-characterised model system for organic aerosol aging.[29] Results from online EESI measurements of pure and oxidised particles are compared with previous offline studies.

Experimental

Ionisation source design and mass spectrometer description

A new EESI source for online aerosol characterisation was built by adapting a commercially-available Electrospray Ionisation (ESI) source from an ion-trap mass spectrometer (Thermo Scientific Ion Max S Atmospheric Pressure Ionisation source). A custom-built aerosol injector and housing were designed for the front of the source and are illustrated in Figure 1(a).

The primary electrospray was produced by infusing solvent through a commercial electrospray probe (Thermo Scientific HESI-II). Aerosol was directed into the electrospray plume using a flexible 3 mm inner diameter PTFE tube connected to a custom aerosol nozzle (2 mm inner diameter). The housing enables the user to control the two-dimensional position and angle of the injector nozzle while the EESI source is sealed and in operation, to optimise the source for a particular application (see Figure 1(a)).

The nozzle is connected via a rod to a movable plate on the outside of the housing which allows its vertical position to be set over a 20 mm range (y-displacement in Figure 1(a)). The whole plate is moved horizontally via an adjuster ring and screw thread over a 16 mm range (x-displacement in Figure 1(a)). The angle of the nozzle is controlled using a knob on the outer plate which is connected to the nozzle via a universal coupling joint and a mitre gear thread, and can be changed from 0^{o}-90^{o} (θ in Figure 1(a)).

Mass spectrometry measurements were made using an ion-trap mass spectrometer (Thermo Scientific LTQ Velos). The HESI-II probe was set to a spray voltage of -3.0 kV in negative ionisation mode. A water-methanol 1:1 mixture (Optima LC-MS grade solvents; Fisher Scientific) containing 0.05%

formic acid (90%, Breckland Scientific) was infused into the probe via syringe pump to generate the primary spray. Tandem MS experiments were performed using collision-induced dissociation (CID) by helium gas in the ion-trap using a normalised collision energy of 30%.

Aerosol production and classification

Aerosol analysed by EESI was produced in the laboratory using an aerosol flow tube system which is shown in Figure 1(b).

L-Tartaric acid (99%, Aldrich) aerosol was used for the initial characterisation measurements. This was produced from solutions between 1-500 mmol/L in water (HPLC grade, Rathbones) using a custom-built nebuliser. The nebuliser was supplied with N_2 (oxygen-free nitrogen, BOC) at 3 bar and had an output flow rate of 1.3 L/min. The aerosol was dried using a pair of silica diffusion driers to produce an aerosol with a relative humidity (RH) below 5%.

The reaction of oleic acid (99%, Sigma) aerosol with ozone was used as a simple proof-of-principle model to study the aging of organic aerosol using EESI. This aerosol was also produced using the nebuliser from a 0.5 mmol/L solution in ethanol, with an input pressure of 2.3 bar and an output flow rate of 1 L/min. The diffusion driers and charcoal denuder were employed to remove ethanol, although small amounts were detected in the MS analysis.

Ozone was produced by flowing synthetic air (Zero Grade, BOC) through a photolysis tube containing a 185 nm UV lamp (Appleton Woods) at 0.3 L/min. The oleic acid aerosol and ozone were mixed in a 5L aerosol flow tube. The concentration of ozone after mixing was around 40ppm,

determined using a UV photometric ozone analyser (Thermo Scientific model 49i). A charcoal denuder was used after the flow tube to remove any remaining ozone and gas-phase organic species.

Particles from the polydisperse aerosol generated by the nebuliser were size-selected prior to EESI analysis using a differential mobility analyser (DMA) (TSI model 3081). The sheath flow rate was set to 13 L/min and the voltage was varied manually to vary the particle size transmitted. The aerosol could be humidified using a permeable Gore-Tex tube with a variable water level. 0.3 L/min of the monodisperse particle output was counted using a condensation particle counter (CPC) (TSI model 3775) with the remaining 1 L/min introduced into the EESI chamber using the custom aerosol injector. Particle mass concentrations were calculated from the CPC number concentration by assuming an aerosol density from bulk literature values (1.8 g/cm^3 for tartaric acid, 0.9 g/cm^3 for oleic acid) and varied between 0.2-600 μg/m^3.

Results and Discussion

EESI source optimisation

The EESI source was built in-house and optimised to give the best combination of sensitivity and signal stability for organic aerosol measurements. The following parameters were tested: Angle and position of the aerosol nozzle (θ, x and y, Figure 1(a)), and the sheath gas flow rate and solvent infusion flow rate of the ESI probe. The aerosol flow was held constant at 1 L/min.

It was found that maximum sensitivity was obtained when the aerosol nozzle was directed at the tip of the solvent electrospray capillary. However, this also increased the level of sample carry-over observed after the aerosol flow was switched off, probably due to particle deposition on the tip. θ was set to 40^{o} for typical operating conditions (aerosol concentration 3-600 $\mu g/m^3$) so that the aerosol intersected the primary spray away from the capillary and hence sample carry-over was minimised. For the sensitive tandem MS experiments with concentrations less than 2 $\mu g/m^3$, θ was set to 55^{o}. Typical values of x and y were 9 mm and 2 mm.

The sheath gas flow rate of the ESI probe was varied between 0.3-1.3 L/min by varying the supplied N_2 pressure. Below 0.3 L/min a stable solvent spray could not be obtained on the hour-long timescale of the EESI experiments. The most stable spray was obtained around 0.8 L/min, with higher and lower flow rates leading to more inter-scan variability and larger long-term drifts in the intensities of background signals from the solvent. Consequently, 0.8 L/min was selected for typical operating conditions (aerosol concentration 3-600 $\mu g/m^3$). However, at 0.3 L/min, the EESI source was most sensitive to low concentrations of aerosol presumably because more of the incoming particles intersect the spray rather than being carried away by the sheath gas. For detecting low concentrations of aerosol, specifically the sensitive tandem MS experiments with concentrations less than 2 $\mu g/m^3$, the lower sheath flow (0.3 L/min) was used.

The methanol/water/formic acid solvent mixture was infused into the HESI-II probe between 5-20 μL/min while N_2 from the probe's sheath and aerosol from the injector nozzle was being delivered to the source. The spray stability was poor at 5 μL/min, perhaps due to the additional gas flow from the injector nozzle in the source. At high flow rates of 10 μL/min and above, a stable spray was obtained but no difference in spray stability and sensitivity could be identified in the range 10-20 μL/min. 10 μL/min was selected to enable a longer acquisition time without refilling the syringe; coupled with a 2.5 mL syringe, this enabled continuous acquisition for over 4 hours. This will be useful for future experiments using the EESI source, such as monitoring changes in the composition of aerosol from a large atmospheric simulation chamber.

Characterising the optimised EESI source

The optimised EESI-MS setup enabled sensitive, reproducible measurements of organic compounds in aerosol particles on long timescales. Figure 2 shows a time series where size-selected oleic acid aerosol (100 nm) was introduced into the EESI source. The MS signal corresponding to deprotonated oleic acid was closely correlated in time and intensity with the concentration of aerosol delivered to the source, as seen in Figure 2. The MS signal responded rapidly to changes in concentration, reaching a stable intensity within a matter of seconds. Increasing the aerosol concentration produced a proportional increase in the signal. Measurements of a constant aerosol source over hour-long timescales gave rise to a stable MS signal (<10% root-mean-square deviation) with negligible long-term drifts in intensity.

Sample carry-over, where a significant signal remains after the addition of new material has stopped, has been reported as a concern in other EESI experiments[25]. However, it is not problematic here due to the optimised operating conditions; low aerosol concentrations could be used and the nozzle

geometry minimised particle deposition onto the electrospray capillary and MS inlet. The signal falls back to near-baseline levels within a minute of switching aerosol for N_2 gas in the nozzle.

Quantification with EESI

We tested the EESI source with a range of particle concentrations and diameters to test if the extraction mechanism was dependent on particle mass, surface area or other parameters. Tartaric acid particles (<5% RH) with diameters in the range 50-250 nm were size-selected from a polydisperse aerosol distribution, using a fixed voltage on the DMA, and directed into the source. A first approximation for the total mass and surface area of the DMA's aerosol ouput can be made by counting the particles using a CPC and assuming a monodisperse aerosol. Tartaric acid aerosols do not effloresce and hence we assumed that they are spherical particles even at low RH. Therefore we used the aerosol's electrical mobility diameter to calculate the particle volume and then the bulk tartaric acid density to convert to a particle mass.

However assuming a monodisperse aerosol neglects the transmission of larger particles bearing multiple charges. To account for this, the full polydisperse aerosol size distribution was measured using the SMPS and so the number of particles at multiples of the selected mobility diameter could be determined. Using the equilibrium charge distributions from Wiedensohler[30] the fraction of doubly and triply charged particles contributing to the CPC number concentration could be estimated to give corrected mass and surface area values.

Figure 3 shows a calibration curve for tartaric acid particles with diameters between 70-200 nm after the multiple charge correction procedure. The total aerosol signal is dependent only on the mass of aerosol and is independent of particle size. This again points to a mechanism where particles are fully dissolved in the spray regardless of size. Large particles leave no undissolved "core". Presumably

above a certain particle diameter such a phenomenon will occur, but it appears that this is unlikely to be problematic for sub-micrometer aerosols.

Measurements mostly focused on lower aerosol concentrations below 100 μg/m^3. This range is typical for laboratory atmospheric chamber studies (although such particles will contain many compounds and hence the concentrations of individual species will be lower). The few higher concentrations demonstrate that the technique has a linear dynamic range over the entire concentration range tested (3-600 μg/m^3). This represents the first quantification of an aerosol component using an online ESI technique; the data suggest that EESI-MS could be used in a semi-quantitative fashion for known analytes down to a concentration of a few μg/m^3. Authors describing the related AESI technique were unable to quantify particle components in its current configuration owing to instabilities in the mass analyser used.[27]

The charge correction procedure described above was applied to all of the data points in the 70, 100 and 200 nm series in Figure 4. Explicit charge correction was not performed as described above for all of the data points in the 150nm series due to the time consuming requirement of measuring full aerosol size distributions for each nebuliser solution concentration (i.e. each data point). Instead, size distributions for most concentrations were interpolated from four solution concentrations which were explicitly corrected. The interpolation procedure appears to have been successful and the 150nm data show good agreement with the other diameters. The fractions of multiply charged particles contributing to the CPC number count in figure 6 was also estimated using this interpolation method.

Previous studies have indicated that EESI is capable of analysing samples with complex matrices which suffer large ion suppression and loss of detector sensitivity using direct infusion ESI techniques.[20,31] Here, we further minimise possible ion-suppression phenomena by employing

relatively low analyte concentrations; this means that the availability of primary spray droplets to dissolve and ionise the aerosol particles should not be a limiting factor in analyte ion formation. As a result, changes in the intensity of ions over time are likely to correlate with concentration changes of analytes in particles, as seen for a simple case in Figure 2. It should be noted, however, that our testing has been limited to particles composed of organic compounds and so the influence of a complex particle matrix (particularly the presence of inorganic salts) has not been assessed.

Tandem MS measurements

The data in Figure 3 have a constant background signal of 1.2×10^4 counts at m/z 149 which has been subtracted. This signal appears to originate from the "pure" solvent used for the primary ESI spray and is observed even when no aerosol is added to the source. It presents a problem when analysing low aerosol concentrations because the signal from the aerosol analyte is comparable to the background; this ultimately determines the technique's limit of detection. The resolution and mass accuracy of the LTQ Velos mass spectrometer are not sufficient to assign the background peak to a particular compound, and indeed it seems likely that the signal may originate from a mixture of unresolved compounds in the solvent. Extensive cleaning of the HESI-II probe does not reduce this signal, suggesting it is not from tartaric acid particles deposited on the probe in previous experiments.

The way we overcome this issue, and hence reduce the limit of detection, is to perform tandem MS measurements on the combined aerosol and background ions which make up the observed m/z 149 signal. Briefly, tandem MS involves isolating ions in a small mass window (typically 1 m/z) from the full spectrum and discarding all ions which fall outside of this window. The remaining isolated ions are fragmented using a collision gas; different ions will have different characteristic fragmentation patterns depending on their molecular structure. By monitoring fragments unique to the analyte of interest it is possible to resolve them from background impurities which have the same parent ion m/z, but form different m/z fragments.

This principle is applied to tartaric acid aerosol in figure 5. Spectrum (a) shows the fragments formed from the tandem MS of the solvent background in the range m/z 148.5-149.5. Major fragments are observed at m/z 77, 105 and 121. When tartaric acid aerosol was added at a concentration of 1μg/m^3 (spectrum (b)), new peaks appear in the tandem MS spectrum at m/z 59, 87, 103 and 131. The molecular formulae of these peaks are assigned in (c) at a higher aerosol concentration (20μg/m^3) where they become the dominant peaks. They were confirmed as tartaric acid fragments by direct infusion of a tartaric acid standard solution into an ultrahigh resolution LTQ Orbitrap Velos mass spectrometer, where unambiguous molecular compositions could be assigned.

The signal from the most intense fragment peak from tartaric acid, m/z 103, is plotted as a function of tartaric acid aerosol mass concentration in figure 6. It varies linearly with concentration and extends the dynamic range of the EESI technique below 1 μg/m^3 for known analytes. The other assigned fragments also vary linearly with mass concentration. The error bars on the data correspond to the standard deviation of the scan-to-scan variability (which we believe arises primarily from variations in the primary ESI spray). For the lowest aerosol concentration tested, 0.22μg/m^3, the signal is 2.5 times the background signal from the solvent and is easily distinguished from the inter-scan variability. This probably represents an upper bound on the limit of detection for tartaric acid.

The limit of detection using this method will depend on the particular analyte under consideration due to differences in its ionisation probability and fragmentation pattern. However, it demonstrates that in general EESI-MS/MS will be highly sensitive to small changes in the concentration of analytes in particles and that detection limits in the sub-μg/m^3 range can be achieved.

Effect of aerosol phase and water content

To examine the extraction mechanism, we tested the impact of aerosol water content on the extraction efficiency of the EESI process. This was achieved by humidifying the dried aerosol after it was size-selected in the DMA, to ensure that the mass of analyte in the particles remained constant. Tartaric acid and maleic acid aerosols were tested, both of which are hygroscopic and in principle fully soluble in the primary spray. The two compounds exhibit different phase behaviour; maleic acid effloresces to form a crystalline solid during the drying process and deliquesces around 87% RH[32] – we use it to test extraction of solid soluble particles. Tartaric acid does not effloresce and a small amount of water, 10% by mass,[33] remains associated with the particle at low RH.

Figure xx*** shows the relative extraction efficiencies of maleic and tartaric acid aerosols (dry diameter 150 nm) as a function of relative humidity. The extraction efficiencies were calculated by scaling the observed MS signal to the mass of aerosol estimated from the number of particles detected by the CPC. This mass estimate is somewhat uncertain due to the presence of multiply charged particles. We found the loss of (positively charged) size-selected particles through the humidification setup to be large and strongly RH-dependent. It has been shown that particle losses are also size and charge dependent[34] so the contribution of large multiply-charged particles to the MS signal could not be accounted for.

Despite this uncertainty, the EESI mechanism is able to detect both solid and aqueous organic particles and there does not appear to be a systematic trend in the extraction efficiency as a function of liquid water content. We infer a mechanism where soluble solid particles are fully dissolved and extracted into the solvent spray. This finding will be important when analysing aerosols from chambers; evidence suggests that these may form amorphous solid phases as a result of aging processes[35].

It should be emphasized that the particles must be in principle soluble in the electrospray solvent to be detected using EESI. We do not expect to detect insoluble particles such as elemental carbon and mineral dust. However, we are unsure how mixed particles containing both soluble and insoluble fractions affect the EESI ionisation mechanism.

Chemistry of a model system – oleic acid oxidation

To test the applicability of EESI-MS to laboratory studies of aerosol aging, a proof-of-principle experiment involving the ozonolysis of oleic acid particles was conducted. Oleic acid aerosol is a well-characterised model system for organic aerosol in the atmosphere and its reaction products have been extensively studied in this group as well as others.[36–38]

Figure 7 shows mass spectra acquired using EESI of oleic acid aerosol at a concentration of 20 $\mu g/m^3$, before and after ozonolysis. The spectra shown are background subtracted; a "solvent background" spectrum was acquired by flowing pure N_2 through the aerosol nozzle, and this was subtracted from the raw aerosol spectra. The unoxidised oleic acid particles show only one major peak in the negative mode, at m/z 281, which is deprotonated oleic acid (OA). The peak at m/z 327 corresponds to a non-covalent adduct between oleic acid and ethanol, suggesting that there is a small amount of ethanol remaining in the particles originating from the particle generation process.

By contrast, a variety of oxidation products can be observed in the oleic acid particles processed by ozone (40 ppm, 3 minute reaction time) and the major peaks can be assigned to known reaction products. Oleic acid is an 18-carbon fatty acid containing a single double bond and so ozonolysis via a Criegee intermediate mechanism leads to the formation of four 9-carbon primary reaction products. This chemistry has been characterised in detail elsewhere.[36–38] The peaks at m/z 157, 171 and 187 correspond to three of the primary oxidation products; nonanoic acid (NA), 9-oxonoanoic acid (ON)

and azaleic acid (AA) respectively. The fourth product, nonanal, has a high vapour pressure and so partitions out of the particle and into the gas phase. Since a charcoal denuder was used in this experiment to remove unreacted ozone and volatile organic compounds, nonanal was not observed here. Unreacted OA can be seen as a consequence of the short residence time of the aerosol in the flow tube reactor. Adducts of OA and the major products with ethanol can again be seen.

A number of the smaller peaks can also be assigned. The ozonolysis mechanism discussed above involves the formation of a Criegee intermediate (CI), a highly reactive biradical species. A possible fate of the CI is to react with the primary reaction products or unreacted oleic acid to form high molecular weight oligomer chains. The peak at m/z 375 is consistent with a CI adding to AA to form a covalently-bonded dimer. Measurements at higher aerosol concentrations (100 $\mu g/m^3$) reveal a variety of dimers, trimers and higher oligomers which were reported and characterised in detail using offline analysis methods.[36,37,39]

Implications

The new extractive electrospray ionisation (EESI-MS) source developed and thoroughly characterised here offers a number of advantages for the online characterisation of organic aerosol composition. EESI produces intact molecular ions with little fragmentation because of the "soft" extraction and ionisation process. Hence, characterisation of the molecular composition of highly complex mixtures such as aerosols is simpler than for other online techniques. This will enable the elucidation of aerosol reaction mechanisms in unprecedented detail with high time resolution.

New insight into the EESI extraction mechanism will help to better quantify processes occurring in aerosols. We demonstrated that the dynamic range for quantification of the method covers more than three orders of magnitude (0.2-600 $\mu g/m^3$) which will enable the analysis of particle composition

under ambient conditions. Particle concentration changes were detected on the timescale of seconds and the technique shows promise for characterising the time evolution of aerosol composition in real time. Future work will attempt to understand the mechanisms and reaction kinetics occurring in particles by monitoring changes in the composition of aerosols in laboratory flow tube and chamber studies.

Acknowledgements

Financial support by the UK Natural Environment Research Council (NERC) is greatly acknowledged.

Figures

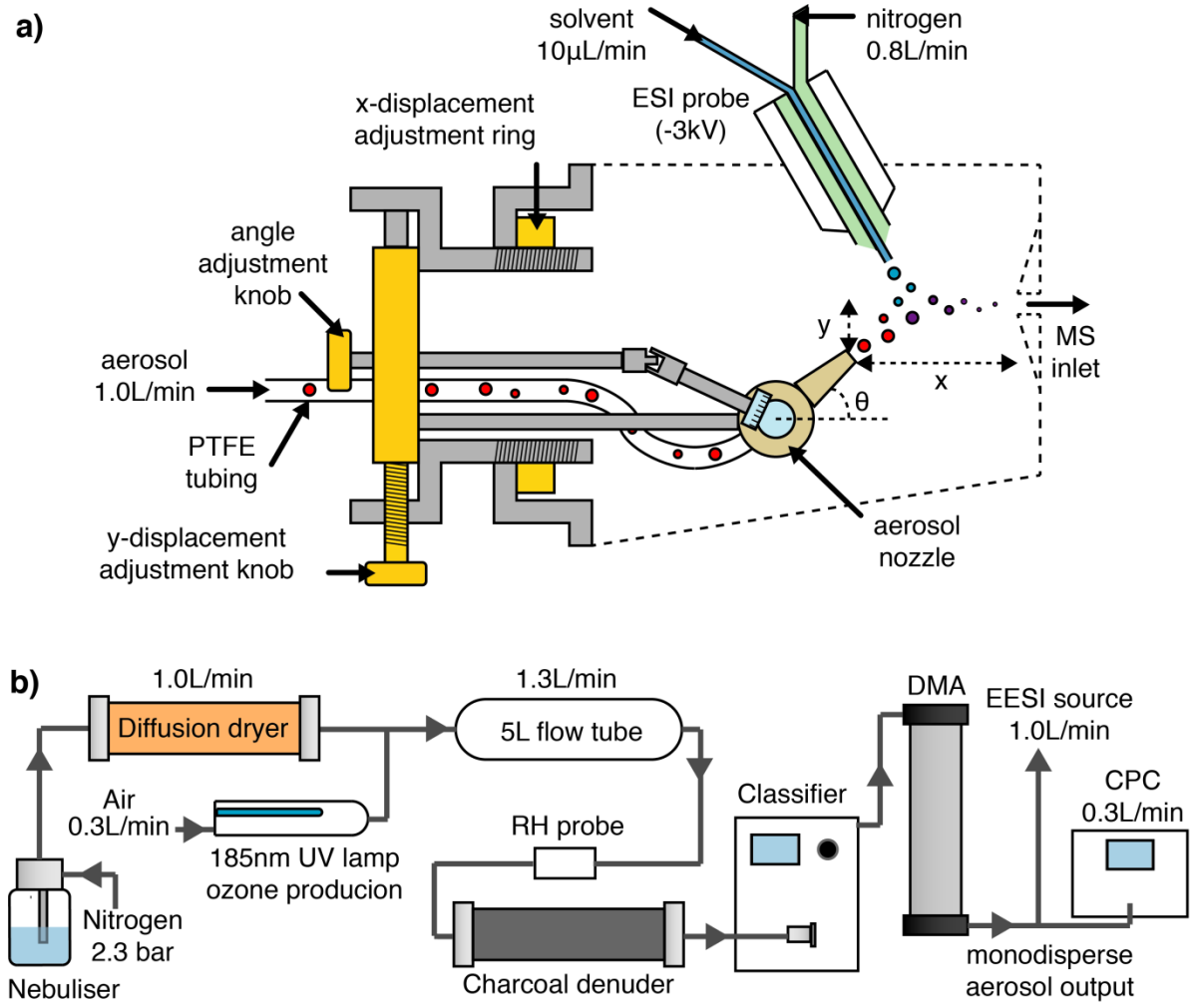

Figure 1: (a) Design for the custom-built Extractive Electrospray Ionisation source. The housing was adapted from a Thermo Ion Max API source (dotted line) fitted with an electrospray probe (HESI-II). The aerosol particles (red) are directed into a spray of charged solvent droplets (blue) where extraction and ionisation of the aerosol analytes occurs (purple) and the solvent evaporates to eject analyte ions into the gas phase. The geometric parameters x, y and θ can be optimised during source operation. (b) Schematic diagram of the aerosol flow tube and size-selection apparatus for the oxidation of oleic acid aerosol. For tartaric acid, the ozone lamp was not used and the nitrogen pressure for the nebuliser was increased to 3 bar to maintain a total flow rate of 1.3 L/min. DMA – differential mobility analyser, CPC – condensation particle counter.

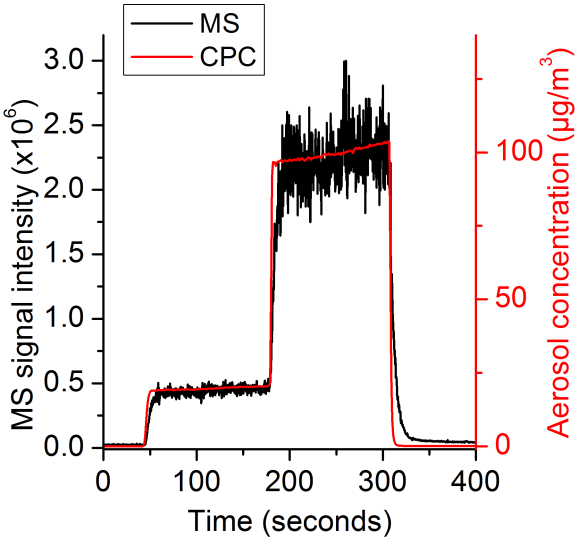

Figure 2: Red line: Time series of the mass concentration of oleic acid aerosol delivered to the EESI source, measured using a condensation particle counter (CPC). Black line: Time series of the MS signal at m/z 281 corresponding to deprotonated oleic acid in negative ionisation mode. All ion source parameters were held constant. The inter-scan noise scales approximately with the signal intensity. The signal/noise ratio (i.e. average/standard deviation) of the MS signal was 10.3 between 0-40 seconds, 14.3 between 80-160 seconds and 11.6 between 200-280 seconds.

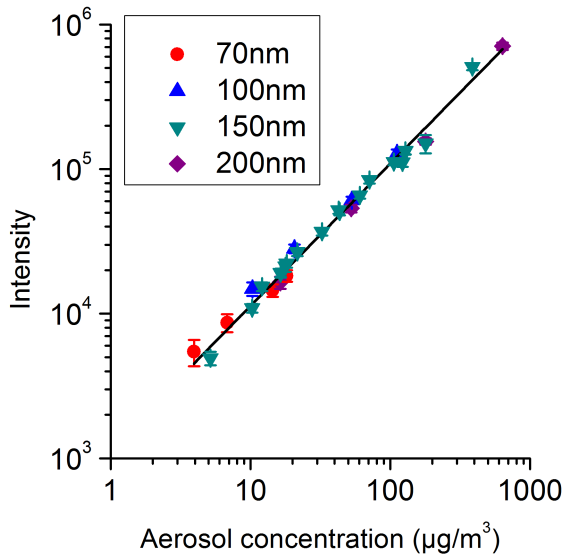

Figure 3: The signal intensity of tartaric acid (m/z 149), linearly correlated with the total particle mass concentration between 3-600µg/m^3. For each diameter, the particle concentration was varied by using different concentrations of tartaric acid solution in the nebuliser. Over the range of diameters between 70-200 nm the extraction efficiency is independent of particle size. The data were corrected to account for the transmission of multiply charged particles through the DMA and a background solvent signal of 1.2×10^4 counts was subtracted from all data points.

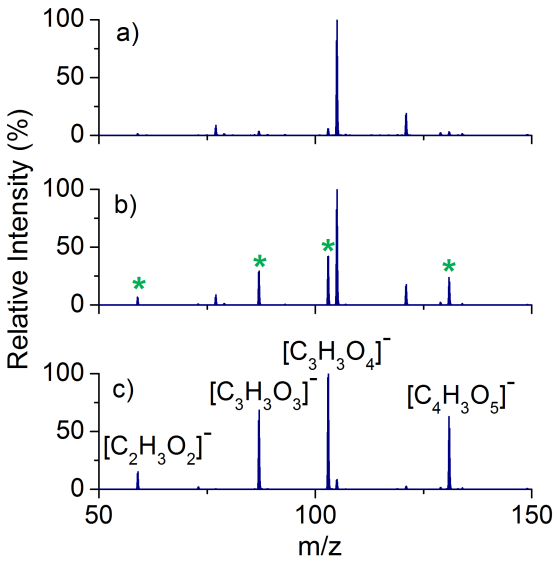

Figure 5: Mass spectra showing tandem MS fragmentation measurements on the m/z 149 peak. (a) solvent background without aerosol; (b) 1 µg/m^3 tartaric acid aerosol, where new fragments (*) appear at m/z 59, 87, 103 and 131 (c) 20 µg/m^3 aerosol, showing the fragments at correspondingly higher intensities relative to the background. Peak assignments in (c) were confirmed by direct infusion of a tartaric acid standard solution into an ultrahigh-resolution LTQ Orbitrap Velos mass spectrometer with sufficient mass accuracy and resolving power to unambiguously assign the molecular formulae of the ions.

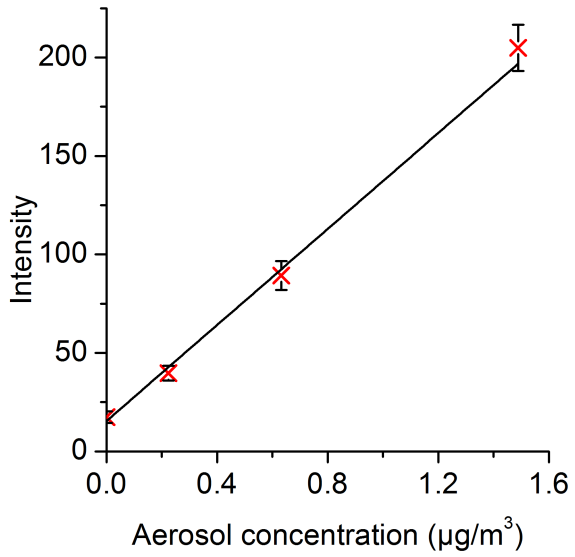

Figure 6: MS signal at m/z 103 for tandem MS fragmentation of the m/z 149 peak, as a function of tartaric acid aerosol concentration. m/z 103 was identified as the most intense fragment of the tartaric acid parent ion in figure 5. The m/z 149 ions were fragmented using collision induced dissociation (CID) in the ion trap of the mass spectrometer. The error bars represent the standard deviation of the average intensity of 100 scans.

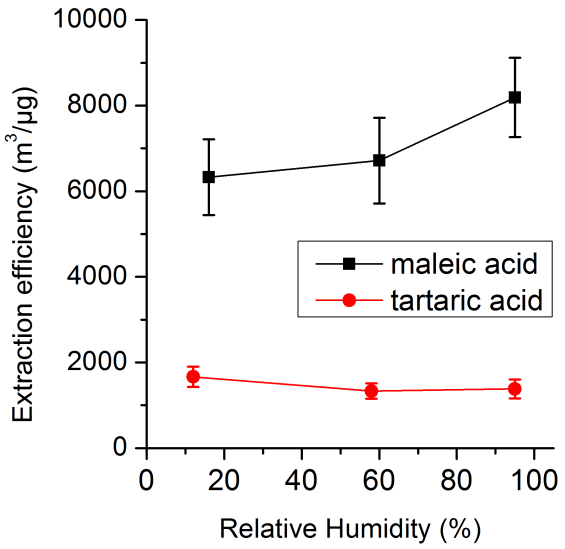

Figure 7***: Extraction of organic aerosol particles by EESI as a function of relative humidity. Extraction efficiency was calculated by dividing the MS intensity by the aerosol mass concentration estimated from the CPC. Within experimental uncertainty, there was no significant trend in the extraction efficiency as a function of relative humidity for either compound. Lines joining the data points are as a guide to the eye.

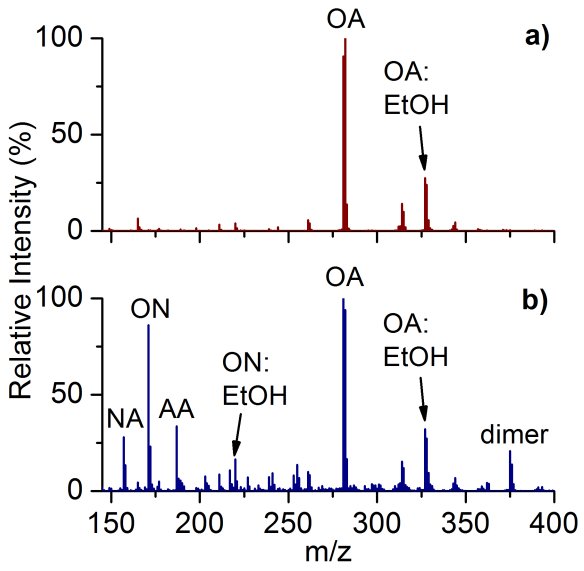

Figure 8***: Mass spectra between m/z 150-450 showing: (a) 20 µg/m^3 oleic acid aerosol nebulised from a 0.5 mM solution in ethanol. (b) 20 µg/m^3 aerosol oxidised by 40 ppm ozone for 3 minutes, showing the major reaction products and some unreacted oleic acid.

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