Analysis of organic aerosols collected on filters by Aerosol Mass Spectrometry for source identification

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Abstract

Aerosol mass spectrometers (AMS) are powerful tools in the analysis of the chemical composition of airborne particles, particularly organic aerosols which are gaining increasing attention. However, the advantages of AMS in providing on-line data can be outweighed by the difficulties involved in its use in field measurements at multiple sites. In contrast to the on-line measurement by AMS, a method which involves sample collection on filters followed by subsequent analysis by AMS could significantly broaden the scope of AMS application. We report the application of such an approach to field studies at multiple sites. An AMS was deployed at 5 urban schools to determine the sources of the organic aerosols at the schools directly. PM\textsubscript{1} aerosols were also collected on filters at these and 20 other urban schools. The filters were extracted with water and the extract run through a nebulizer to
generate the aerosols, which were analysed by an AMS. The mass spectra
from the samples collected on filters at the 5 schools were found to have
excellent correlations with those obtained directly by AMS, with $r^2$ ranging
from 0.89 to 0.98. Filter recoveries varied between the schools from 40 -
115%, possibly indicating that this method provides qualitative rather than
quantitative information. The stability of the organic aerosols on Teflon filters
was demonstrated by analysing samples stored for up to two years.

Application of the procedure to the remaining 20 schools showed that
secondary organic aerosols were the main source of aerosols at the majority
of the schools. Overall, this procedure provides accurate representation of the
mass spectra of ambient organic aerosols and could facilitate rapid data
acquisition at multiple sites where AMS could not be deployed for logistical
reasons.

**Keywords**

Organic Aerosols, Aerosol Mass Spectrometry, Source, Filter samples

**1.0 Introduction**

One of the more significant advancements in aerosol science in the past 20
years has been the development of aerosol mass spectrometers [1]. These
instruments allow the chemical composition of airborne particles to be
determined at higher temporal resolutions than traditional filter-based
chemical analytical methods [2]. The Aerodyne Aerosol Mass Spectrometer
(AMS), one of the more widely used types of these instruments measures
quantitatively the chemical composition of the near-refractory particles with an
aerodynamic diameter less than 1 µm (PM$_1$). Recent attention has focused on
the organic fraction as measured by the AMS, as it is frequently the largest
Further simplification of the organic fraction into two main components based upon key mass to charge ratio (m/z) ions in the mass spectrum is possible: hydrocarbon-like organic aerosols (HOA) and oxygenated organic aerosols (OOA). The HOA component is characteristic of primary organic aerosols while the OOA can be considered as a surrogate for secondary organic aerosols [4, 5], thus the AMS offers insights into the origin of ambient organic aerosols.

The chemical composition information and high time resolution offered by the AMS can however be outweighed by the numerous difficulties in field measurements with an AMS, including the transportation, set-up, maintenance and the need for adequate housing of the instrument. By comparison, filter based sampling is relatively easy and an inexpensive method to perform in the field, and the filters can be easily stored. Therefore a procedure that can allow for the analysis of filter samples obtained from the field by an AMS back in the laboratory, would improve the scope and application of the AMS markedly, particularly for sampling across many sites during one project.

Preliminary results from an AMS studies of filter samples extracted by water was described previously [6]. Based on these promising results we thus undertook a comprehensive study to test and validate this approach using samples at multiple sites where an AMS directly measured the ambient OA. In the current study, PM1 filter samples were collected at 25 urban schools whereas an AMS sampled at five of the 25 schools. For the remaining 20
schools, the filter extraction method was applied retrospectively to the PM$_1$
filter samples in order to determine the water soluble organic aerosols mass
spectra at these schools. Based on the determined mass spectrum, the
source of the organic aerosols was investigated at each school to determine
the contributions of primary and secondary sources.

2.0 Method

2.1 Sampling Sites

This paper utilises TOF-AMS measurements and PM$_1$ filter samples that were
collected as a part of a larger study investigating the effect of ultrafine
particles from traffic emissions on children’s health, known as UPTECH
(www.ilaqh.qut.edu.au/Misc/UPTECH%20Home.htm). The twenty-five schools
selected are referred to as S01 to S25 and were in different suburbs of the
Brisbane Metropolitan area. The schools that participated were not near any
major pollution sources apart from traffic emissions. Measurements at the
schools were conducted from October 2010 to August 2012. More details of
the school sites and sampling conditions at the AMS schools can be found in
Crilley et al [7].

2.2 AMS field operation
An Aerodyne compact Time-Of-Flight Aerosol Mass Spectrometer (TOF-AMS)
was used for this work and a description of the instrument and its operation
has been given previously [8, 9]. The TOF-AMS was available to run at only 5
schools, S01, S04, S11, S12 and S25, which will be referred to as the “AMS
schools” throughout the paper, with the remaining schools referred to as “non-
AMS schools”. A full description of the TOF-AMS field operation is available in
In brief, the TOF-AMS was housed in a vacant classroom within the school and sampled continuously with a five-minute interval for two to three weeks at each school. Ambient outdoor air was sampled at a sampling height of about 1.5 m.

2.3 Filter sampling method

PM$_1$ filters were collected at all of the 25 schools and the filter set-up was housed within a trailer at a site that was assumed to give the best overall exposure. This site was never more than 150 m from the classroom housing the TOF-AMS at the corresponding school. Filters were collected using a PM$_1$ cyclone, with the required flow rate for the cyclone maintained by critical orifices. Four filters were collected at each school, over a sampling interval of 24 hours (8 am till 8 am the following morning), Monday till Friday with a typical sample volume of 8.2 m$^3$. Samples were collected on 47 mm, 0.2 µm pore size Teflon filters (Whatman) and the sampling inlets were approximately 3 m off the ground. At the schools where the TOF-AMS sampled, the distance between the TOF-AMS classroom and filter sampling site varied from 50 to 150 m. The filter sampling and TOF-AMS measurements were conducted concurrently at the schools. After sampling, the filters were placed in a Petri dish, sealed in a plastic ziplock bag and stored for analysis.

2.4 Filter extraction and analysis method

Extraction of the water soluble organic aerosols (WSOA) from the PM$_1$ filter samples and subsequent analysis by TOF-AMS was conducted at the International Laboratory for Air Quality and Health, Queensland University of
Technology. In the extraction method employed in this study, the filters were submerged in 25 ml of Milli-Q water (18.2 MΩ cm) and ultrasonicated for 45 minutes. To ensure enough particle mass was extracted for subsequent analysis on the TOF-AMS, the four filters collected at each school were extracted individually, one after the other into one solution. The filter extract solution was run through a nebulizer to generate the aerosols and then dried over silica, prior to being introduced into the TOF-AMS. For the analysis of the filter extract solution, the TOF-AMS was operated using the same settings employed during the school measurements, except that the sampling interval was reduced from 5 minutes to 1 minute.

2.5 Quality Control

Routine calibration of the ionization efficiency for the TOF-AMS was conducted according to the standard protocols [9-11] in both the schools and in laboratory for the filter testing. Using the method set out in Zhang et al [12], the detection limit for the organic fraction was calculated for the filter MS analysis to be on average 78 ± 23 ng m⁻³. This was comparable with the average detection limit for organics observed by Zhang et al [12] and previous sampling of ambient air at the AMS schools [7].

2.6 Data Analysis

TOF-AMS data was processed and analysed using Squirrel v1.51 in IGOR Pro v6.22. In this study only the organic fraction mass spectrum was compared. For the validation of the filter extraction method, only TOF-AMS data that corresponded to the filter sampling times were used. The average
organic mass spectrum (MS) calculated from these times will be referred to as the ambient MS throughout the paper. At each of the 5 schools where a TOF-AMS was deployed the ambient MS was correlated to the average mass spectrum from the filter extract solution, which will be referred to as the filter MS. For every filter MS the m/z 15, 29 and 31 ions were found to be outliers as they were at least an order of magnitude higher than in the ambient MS and were subsequently removed.

Pearson’s correlation coefficients and associated errors were calculated using SPSS v19. Errors for the correlation coefficients were calculated by bootstrapping analysis at a 95% confidence interval using 1000 bootstrap samples. All correlations reported for the comparison of ambient and filter MS were found to be significant below a 0.01 level.

Standard mass spectral profiles of the different OA components, HOA, SV-OOA, LV-OOA and BBOA are given in Ng et al [13] based upon the analysis of 15 urban datasets. These spectra have been used as reference spectra in this study for comparison with the filter MS for identifying the main source of the OA. There have been several m/z ions which have been shown to be key ions in the analysis of ambient organic aerosol (OA) and these include the m/z 44 and 57 ions [13]. The m/z 44 and 57 ions have been shown to be tracer ions for oxygenated OA (OOA) and hydrocarbon-like OA (HOA), respectively. OOA is considered as a surrogate for secondary OA, while the HOA is similar to vehicle emissions [4, 5]. Thus the m/z 44 and 57 ions are used as tracer
ions for secondary OA and vehicle emissions in this study for determining the sources at the schools.

One way of comparing the OA from different sites is to plot the $f_{43}$ and $f_{44}$ ratios. The $f_{43}$ and $f_{44}$ ratio refer to the ratio of the m/z 43 and 44 ions, respectively, to the total organic mass. OA has been shown to occupy a defined triangle space within this plot, and can give information on the degree of oxidation of the OA. HOA components have an $f_{44}$ that is less than 0.05 and so are found along the base of the triangle. OOA has a higher $f_{44}$ ratio and thus can be used to show the degree of oxidation of the OOA, so that the more oxidised and hence more aged OA are found closer to the top of the triangle.

3.0 Results and Discussion

3.1 Validation of the filter extraction method

In Figure 1, the ambient and filter mass spectra for each school are given, along with the Pearson’s correlation coefficient between the filter and ambient MS. Excellent agreements between the ambient and filter MS was found with the Pearson’s correlation coefficient ranging from 0.89 to 0.98, a similar result to El Haddad et al [6], thus indicating that the OA was successfully extracted from the filters. One negative aspect of the filter MS was the low concentration of fragments above m/z 60, suggesting that the large organic compounds may not have been extracted completely. S01 and S04 were found to have slightly lower correlations than the other three schools. The precise reasons for this observation are currently unknown. However it is probably due to the fact that the OA at these schools were less oxidized and therefore less water-soluble.
S01 and S04 were sampled in November 2010 and March 2011, respectively and were analysed on the AMS in November 2012, which demonstrates the stability of WSOA sampled on Teflon filters. Therefore, this technique can be applied to samples collected over two years ago. Provided the filter are stored below 25°C and away from sources of contamination a true representation of the MS of the WSOA can still be obtained.

Figure 1

Filter recoveries varied between the schools from 40-115%. Teflon filters that were used for the sampling may have contributed to the variable recoveries, as Teflon repels water, thus inhibiting the extraction. However, the filter MS from these schools still showed the overall character of the ambient MS and are therefore representative of the ambient OA at the schools indicating that it is a good qualitative method. To further compare the filter MS and ambient MS, the correlations were determined between key m/z ions, 43, 44 and 57. The filter and ambient \( f_{43} \), \( f_{44} \) and \( f_{57} \) ratios, gave Pearson’s correlation coefficient scores of 0.84 ± 0.49, 0.94 ± 0.04 and 0.89 ± 0.25, respectively at a significant level of 0.05. Though there was a large error associated with the \( f_{43} \) ratio, the values from the ambient and filter MS were within 10% of each other at all 5 schools. As the m/z 43 and 57 ions are associated more with fragments from HOA than the more oxidized OOA [13], the likely cause of the large errors was that the HOA is less water soluble. Overall, the high correlations coefficients found for these key tracer ions indicate that this
3.2 Comparison of sources at the schools

As the filter extraction and analysis method produced good qualitative results it was applied to the filters from the remaining 20 schools. The filter MS results from all the schools are summarized in Table 1; with example filter MS from selected schools representative of the three observed OA types shown in Figure 2. In the Supporting Information, Figure S1-3, the filter MS for the additional schools are given. To aid in the comparison of the OA at each school, the $f_{43}$ and $f_{44}$ ratios were plotted as shown in Figure 3. In Figure 3 there are three clusters of schools, separated based upon the $f_{44}$ ratio and therefore source of the OA. From Figure 3, the OA at the AMS schools was found to be either SV-OOA or LV-OOA at S01, S04 and S11, S12, S25, respectively in agreement with the results from Crilley et al [7]. When the AMS and non-AMS schools were found to have a similar type of organic MS, the MS agreed well by visual inspection, having similar prominent ions.

Table 1

3.2.1 Hydrocarbon-like organic aerosols

The schools with a $f_{44}$ ratio less than 0.05 which included S03, S06-8 and S14 (Table 1) were in the HOA region of Figure 3 [14]. These schools had a filter MS that were similar to the HOA standard spectra from Ng et al [13] because
the strongest peaks are the m/z 41 and 43 ions; confirming the HOA nature of
the OA. From Table 1, the schools in the HOA region also had the highest $f_{57}$
ratios, with the exception of S14. This is as expected, as the m/z 57 ion has
been shown to be a tracer ion for HOA [13] and further confirms the source
identification. At S14 the m/z 43 and 57 ion peaks did not have the same
intensity as the m/z 41 and 55 ion peaks (Figure S2), as would be expected
for HOA [13]. Therefore at S14 another primary source of OA was dominant,
and was likely to be cooking OA (COA), as previous studies have shown that
the intensity of the m/z 55 is much stronger than that of the m/z 57 ion in the
MS for COA [16, 17].

3.2.2 Oxygenated organic aerosols
Most of the schools had an $f_{44}$ ratio above 0.05 and are therefore in the OOA
region of the triangle plot (Figure 3) [14]. Of the schools in the OOA regions,
the distinction between SV-OOA and LV-OOA at the schools was not always
clear due to the oxidation levels of ambient OOA being a continuum.
However, a separation between SV-OOA and LV-OOA is present in Figure 3,
with the two groups of schools having distinct differences in the MS and are
separated based upon the level of oxidation. In the middle of the triangle plot
S01, S04, S13, S15, S18 and S20 have clustered with $f_{44}$ ratios between
0.067 – 0.099 (Table 1), and are within the region associated with SV-OOA
[14]. Also these schools had MS with prominent peaks at m/z 41, 43 and 44
(See Figures 1 and 2) and in this respect were more similar to the standard
SV-OOA MS from Ng et al [13], confirming the source identification. At S01
and S04 the WSOA MS was found to resemble the SV-OOA standard
spectra, for both the ambient and filter MS. These were similar to the filter MS
from the non-AMS schools, S13, S15, S18 and S20 and were characterized
by approximately equal intensities of the m/z 41, 43 and 44 ions. In our
previous work [7], we attributed the SV-OOA at S04 to slightly aged vehicle
emissions from nearby highways due to the similarities of the MS for aged
diesel exhaust obtained by Sage et al [18]. Therefore, slightly aged vehicle
emissions were likely to be a dominant source at S13, S15, S18 and S20.

The remaining schools which formed the third and largest cluster had $f_{44}$
ratios that were higher than the other two groups, ranging from 0.102 – 0.169
(Table 1). This group were in the LV-OOA region and the MS from these
schools (See Figures 1 and 2) had a strong m/z 44 ion peak intensity relative
to the other peaks, and were thus similar to the LV-OOA standard MS [13]
indicating a regional source of the OA at these schools [5,14]. At S11, S12
and S25 the LV-OOA MS were also consistent for the ambient and filter MS
as they were all within the LV-OOA region of the triangle plot (Figure 3). In
addition, the LV-OOA filters MS at the non-AMS schools (Table 1) were
similar to ambient MS from S11, S12 and S25, characterized by a strong m/z
44 ion concentration relative to other m/z ions. In Figure 3, the filter MS from
the non-AMS schools also fell within the LV-OOA region of Figure 3, however
these were generally separate from S11, S12 and S25, with the exception of
S05. These variations were likely as a result of differences in the regional OA
present during sampling at the AMS and non-AMS schools which is
conceivable as the sampling at the schools was undertaken at different times
of the year.
4.0 Conclusions

Overall, the simple procedure described in this paper, which involved water extraction of filter samples followed by analysis on a TOF-AMS has been shown to provide an accurate representation of the MS of ambient OA. Application of this procedure enabled the source of the OA to be distinguished between primary and secondary sources at the schools where a TOF-AMS was not deployed. Therefore this offers a simplified approach to field measurements at multiple sites and also extended the possible applications of TOF-AMS to locations where deployment is difficult. In addition, the current paper demonstrated the stability of the WSOA on Teflon filters, enabling the analysis of samples that were stored for up to two years. Possible future work should aim to improve the extraction method to enable more quantitative measurements and thus extending it to the other chemical species measured by an AMS.

Acknowledgments
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<table>
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<tr>
<th>School</th>
<th>( f_{44} )</th>
<th>( f_{57} )</th>
<th>Type of OA</th>
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</thead>
<tbody>
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<td>0.013</td>
<td>LV-OOA</td>
</tr>
<tr>
<td>S03</td>
<td>0.046</td>
<td>0.048</td>
<td>HOA</td>
</tr>
<tr>
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<tr>
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<td>0.050</td>
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</tr>
<tr>
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<td>HOA</td>
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<tr>
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<td>HOA</td>
</tr>
<tr>
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<td>0.105</td>
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<td>LV-OOA</td>
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<td>S24</td>
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<td>LV-OOA</td>
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Table 1: The filter MS values for \( f_{44} \) and \( f_{57} \) for the non-AMS schools and the type of OA based upon comparison to reference spectra.
Figure 1: Comparison of the ambient and filter mass spectra at the five AMS schools, with the Pearson’s correlations shown.
Figure 2: Filter MS from selected schools as examples of the different types of organic aerosols.
Figure 3: Plot of the $f_{44}$ vs $f_{43}$ ratios for the ambient and filter MS for the schools where the AMS was deployed and the filter MS from the remaining 20 schools.

References


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This supplementary information contains 3 figures.

**S02 (LV-OOA)**

**S09 (LV-OOA)**
S19 (LV-OOA)

S22 (LV-OOA)

S23 (LV-OOA)
Figure S1: Filter extract mass spectra at the schools where the water soluble organic aerosols were classified as LV-OOA.
Figure S2: Filter extract mass spectra at the schools where the water soluble organic aerosols were classified as HOA.
Figure S3: Filter extract mass spectra at the schools where the water soluble organic aerosols were classified as SV-OOA
Supplementary information for Analysis of organic aerosols collected on filters by Aerosol Mass Spectrometry

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Figure S3: Filter extract mass spectra at the schools where the water soluble organic aerosols were classified as SV-OOA