Aerosol Science and Technology, 41:865–872, 2007
Copyright © American Association for Aerosol Research
ISSN: 0278-6826 print / 1521-7388 online
DOI: 10.1080/02786820701501899

Technical Note: Description and Use of the New Jump Mass Spectrum Mode of Operation for the Aerodyne Quadrupole Aerosol Mass Spectrometers (Q-AMS)

J. Crosier,[1] J. L. Jimenez,[2] J. D. Allan,[1] K. N. Bower,[1] P. I. Williams,[1]
M. R. Alfarra,[3] M. R. Canagaratna,[4] J. T. Jayne,[4] D. R. Worsnop,[4] and H. Coe[1]
[1]*SEAES, University of Manchester, UK*
[2]*CIRES and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, USA*
[3]*Paul Scherrer Institute, Villigen, Switzerland*
[4]*Aerodyne Research, Inc., Billerica, Massachusetts, USA*

A new mode of operation for the Aerodyne Quadrupole Aerosol Mass Spectrometer (Q-AMS) has been developed and used to improve the detection limits and time resolution of the instrument. The Jump Mass Spectrum (JMS) mode works by stepping through a small number of specific user defined positions within the mass spectrum, increasing the time spent scanning specific *m/z's*. The JMS mode is conceptually similar to the "Selected Ion Monitoring" mode of some commercial quadrupole-based instrumentation and can be used for direct quantification when the fragmentation pattern is known. The JMS mode can also be used to augment the standard Q-AMS operation in Mass Spectrum mode when the fragmentation pattern is not known, improving the effective signal-to-noise ratio (SNR) and in turn the detection limits and time resolution. A decrease in detection limits for the Q-AMS by factors of 4.6, 3.9, 1.3, and 3.5 for nitrate, sulphate, total organics, and *m/z* 43 mass loadings respectively was achieved for 1 minute sampling (20 s in each of the three Q-AMS modes, monitoring 10 *m/z* in JMS mode). Although the benefit to the SNR of the total organic mass concentration measured by the Q-AMS is smaller, sensitivity to organic fragments which can act as markers for various sources and processes (such as fresh primary anthropogenic emissions, aged secondary organics, and biomass burning aerosol), is greatly increased by the JMS mode. Example data from applications that benefit from this technique are presented, including an aircraft platform and in smog chamber experiments, alongside high time-resolution, ground-based data.

1. INTRODUCTION

The Aerodyne Quadrupole Aerosol Mass Spectrometer (Q-AMS (Jayne et al. 2000)) has been deployed in many field and laboratory experiments to provide quantitative, high time resolution (typically 5 minute) information on the size-resolved chemical composition of sub-micron non-refractory (NR-PM_1) aerosols (Canagaratna et al. 2007). The principle of operation is to focus particles onto a vaporizer (approx 550°C) under high vacuum using an aerodynamic lens (Zhang et al. 2002, 2004), where they flash vaporize on the hot vaporizer surface. Particle vapors are ionized using 70 eV electron impact (EI) ionization, and the ions are analyzed using standard quadrupole mass spectrometry with an electron multiplier detector. Only particles that readily vaporize in a few seconds at or below the vaporizer temperature are measured by the Q-AMS, meaning sea-salt, black carbon, and mineral species cannot be detected under normal operating conditions. The operating pressure in the Q-AMS detection region is around 10^{-7} Torr.

The Q-AMS was originally designed to operate in two modes (Jimenez et al. 2003), Mass Spectrum (MS) and Particle Time-of-Flight (PToF). In MS mode the mass spectrometer continuously scans the mass-to-charge ratio (m/z) and measures the ion current at each point in the spectrum, usually in the range of 0–300 m/z. A total mass spectrum is recorded for the sample that enters the instrument, and also for the instrument background

---

Received 9 November 2006; accepted 8 June 2007.

We wish to acknowledge the Natural Environment Research Council (NERC) funding for CityFlux under grant NE/B504865/1, and for AMPEP under grant NER/T/S/2002/00152. J. Crosier was supported by an NERC studentship NER/S/A/2003/11441. The NERC National Centre for Atmospheric Science (NCAS) Universities Facility for Atmospheric Measurements (UFAM) supported the maintenance of the QAMS. NCAS also supported the data interpretation methods employed through the Composition Directorate. We also acknowledge U. Baltensperger and A. Prevot of the Paul Scherrer Institute for the smog chamber data. The data acquisition software for the JMS mode was developed with funding from NASA (grant NNG04GA67G) and ONR (grant N00244-04-P-0425) to J.L. Jimenez. We kindly thank the anonymous reviewers for their helpful suggestions for improving the paper.

Address correspondence to J. Crosier, School of Earth Atmospheric and Environmental Science, Sackville Street Building, University of Manchester, P.O. Box 88, Manchester, M60 1QD, UK. E-mail: j.crosier@manchester.ac.uk

with no sample, by the use of a movable beam blocker (referred to as the chopper) that can be used to block the particle and molecular beam generated by the aerodynamic lens. The background spectra are subtracted from the total spectra to yield mass spectra resulting from the sample beam only. In the Q-AMS the quadrupole mass spectrometer is scanned at 1 m/z per millisecond (ms) and the signal is sampled at 5 MHz and co-averaged by a factor of 250 into equidistant points in the scan at 0.05 m/z intervals. This means any point in a single MS scan represents a time average of 0.05 ms.

In PToF mode, a single m/z setting is continuously monitored by the quadrupole mass spectrometer while a packet of particles is allowed to pass through the chopper via one of two opposite facing slits in the chopper disc (each slit usually having 2% duty cycle), which rotates at approximately 65 Hz resulting in 130 particle size scans per second. Due to the supersonic expansion into vacuum at the exit of the aerodynamic lens in the Q-AMS, particles obtain a size dependent velocity in the instrument (Jayne et al. 2000). The signal as a function of time in PToF mode can be calibrated to provide size-resolved chemical information, with the sizing metric being vacuum aerodynamic diameter (DeCarlo et al. 2004). Usually around 10–15 m/z settings are monitored in PToF. Each m/z is monitored for 300 ms (approximately 40 chopper cycles) before the quadrupole voltages are adjusted to monitor the next m/z. The exact point in the spectrum monitored is predicted to lie in the centre of the plateau (in signal) of the peak produced by a given integer m/z and is determined by a previous m/z calibration.

Aerosol composition information is derived from the entire mass spectrum obtained in the MS mode of operation using the deconvolution technique of Allan et al. (2004). However, inorganic aerosol species typically fragment into only a few distinct fragments (Allan et al. 2004). Even for the case of organic species, which yield many ion fragments, Zhang et al. (2005) developed a technique for the Q-AMS to extract Hydrocarbon-like and Oxygenated Organic Aerosol (HOA and OOA) particle components from the Q-AMS data taken in urban environments, based on the total organic mass spectra and key m/z markers. One algorithm used in this technique bases HOA on the signal resulting from m/z 57 which is frequently dominated by an alkyl fragment ($C_4H_9^+$), and OOA based on the m/z 44 signal (CO_2^+) which occurs when poly/di-carboxylic acid functional groups and other oxygenated species decompose on the vaporizer. m/z 60 from levoglucosan is a tracer for at least some types of biomass burning aerosols (Schneider et al. 2006).Therefore improvements in signal to noise of a few key m/z's in the mass spectrum can potentially lead to increases in instrument sensitivity.

The high time resolution of the Q-AMS has been one of its leading assets. While Q-AMS data is usually measured with a time resolution on the order of minutes, MS and PToF data with time resolutions of a few seconds have been obtained during vehicle chase studies that sampled high exhaust aerosol concentrations (Canagaratna et al. 2004). Other important applications, such as eddy covariance flux measurements or aircraft measurements that are typically carried out at 100 m/s, require high time resolution under low aerosol concentration conditions. This paper presents a method that allows the Q-AMS to sample at higher time resolution, while maintaining a high signal-to-noise and a high quality data product for key mass fragments and chemical species.

2. JMS MODE DESCRIPTION

The JMS mode of operation allows higher signal to noise measurements to be acquired by the Q-AMS than the MS mode of operation. The JMS mode improvements are obtained by increasing the sample time on a few (typically around 10) important m/z's, instead of scanning the entire mass spectrum (as in MS mode). The increased signal to noise data from the JMS mode allows fast processes to be monitored. Quantitative mass loadings can be derived from the JMS data alone when the fragmentation pattern is known or can be determined from the data, while the JMS mode works best in conjunction with MS mode when the pattern is not known. Any time spent sampling in JMS mode results in a reduction in sample time for MS and PToF modes which may also be in use. This means the use of the JMS mode results in lower signal to noise data for the MS and PToF modes. However as we demonstrate later in the text, when JMS is used in conjunction with MS mode an increase in the overall mass concentration sensitivity results due to the increase in sample time for key mass fragments which contain the majority of the information.

In JMS mode the signal of specific key masses is measured in the chopper open (total signal) and chopper closed (background signal), as in MS mode; i.e., the slit chopper (which reduces the signal by approx a factor of 25 relative to MS mode to provide particle size measurement) is not used as in the PToF mode. The JMS scan works on a basic 60 ms cycle (see Figure 1), with an initial 2 ms settling time where signal is rejected while the DC and RF voltage circuits of the quadrupole reach stable values. A 1 ms scan of an entire m/z (defined by an m/z calibration performed at the start of the averaging period) is then conducted. Next the midpoint of the m/z plateau in the middle of the peak of the integer m/z is then monitored for the remaining 57 ms. The cycle is repeated for each m/z selected by the user. After a predetermined time period (usually 3 s), the chopper switches position from open (closed) to closed (open) and the background (sample) is measured. This continues until the predefined averaging time in JMS mode (typically 10 s) is reached, at which point the software switches to the next mode. After an average time (typically 1–5 min) the average open and closed signal strengths for each m/z are saved to disc. This results in high signal-to-noise information in both the total and background signals, which can be subtracted and processed. The average spectrum from the 1 ms scans of each m/z monitored in JMS mode is also saved to disk.

For example if the Q-AMS were set to sample for 12 s running in only MS mode (from 0–300 m/z) the average of 40 individual spectra would be acquired. Each individual point in

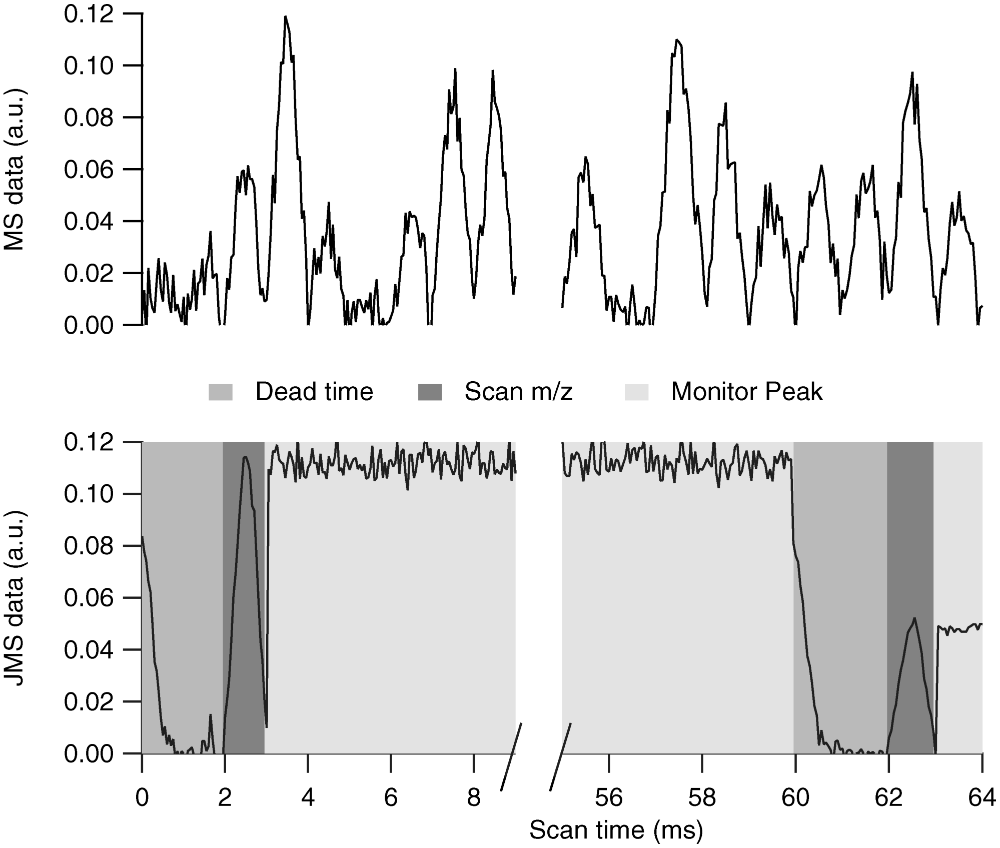

FIG. 1. Schematic of the JMS and MS modes of operation.

the spectra would be a result of 2 ms of sample time. In offline data processing the MS signal is averaged over a 0.45 m/z interval to generate a single value (referred to as the "stick" value) which represents the average signal for entire m/z. This means 9 points from the averaged spectrum are themselves averaged to create each stick value. Each stick value (which are used in the mass loading calculations) in this example of 12 s MS sample is a result of 18 ms of sample time. If the Q-AMS were set to sample again for 12 s, but with 6 s in MS mode and 6 s in JMS mode (monitoring 10 m/z's), each stick in the MS spectrum results from 9 ms of sample time, but the JMS data at key m/z's results from 570 ms of sample time. The duty cycles for a given m/z in MS and JMS mode will be 0.15% and 9.5%, respectively. It is this large increase in sample time that drives the significant improvement in SNR for the JMS mode. However, for the m/z's not scanned in JMS mode, there is a decrease in sample time from 18 ms to 9 ms. If sampling were to include PToF data as well, there would be an associated reduction in sample time for each m/z in this mode as well.

Ion counting statistics determine the errors associated with both the MS and JMS ion signals, and are described by Equation (1) (Allan et al. 2003), demonstrating an inverse proportionality between the noise in the difference signal (ΔI_d) and the square root of the scan time (t_s). In Equation (1) I_o and I_c represent the total (chopper open) and background (chopper blocked) signals, and α (which has a value of approx. 1.2) represents the additional noise originating from the variability of the single ion signal detected by the electron multiplier. For the example above (0–300 m/z MS scans and 10 JMS m/z's, with each mode sampling for 50% of the averaging period) there would be an overall reduction in ion-counting noise by a factor of approximately 8 for the 10 m/z's scanned in JMS mode. An associated increase in noise in the 290 m/z's not scanned in JMS mode of 1.4 is a result of the trade-off made. Under normal sampling conditions the Q-AMS is also run in PToF mode. Therefore running in JMS mode also results in a decrease in PToF mode acquisition time, and thus sensitivity.

$$\Delta I_d = \alpha \frac{\sqrt{I_o + I_c}}{\sqrt{t_s}} \qquad [1]$$

For each selected m/z, the JMS signal is measured while the quadrupole mass spectrometer is set to monitor a single point in the spectrum. The point monitored is in the centre of the m/z signal plateau as determined by an m/z calibration over the entire MS mode range (0–300 m/z). However, the MS mode data is an average over a large proportion of the plateau. Due to this systematic difference between the two data types, the JMS signal is typically scaled to the corresponding MS signal taken over the same measurement period.

Under normal operation of the Q-AMS, JMS mode is run in tandem with MS mode to allow the calculation of these scaling factors. The scaling factor is calculated using an error weighted least distance fit on the JMS and MS data at the specified m/z's, and can be verified in principle using the 1 ms scan (Figure 1). The scaling factor remains constant as the location of the JMS scan in m/z space is always the same, unless tuning parameters within the quadrupole or control software are changed. Therefore only a single scaling factor is needed for most campaigns. The scaling factor is typically in the range of 0.8–1.3, and varies as a function of m/z. Following normalization, the JMS signals are imported into the full mass spectra obtained in MS mode. These new data for specific m/z channels are processed in place of the original MS-derived data using the "fragmentation table" approach of Allan et al. (2004) to generate mass concentrations of species including total organics, nitrate, sulphate, and ammonium.

3. FOURIER ANALYSIS OF JMS IMPROVEMENTS

In order to characterize the benefit of the JMS mode of operation Q-AMS mass concentration time series using MS data with and without JMS improvements were analyzed using Fast Fourier Transforms (FFT). The FFT (Press et al. 1992) provides information on the signal at different sampling frequencies within a time series.

The University of Manchester Q-AMS was deployed during July 2005 as part of the CityFlux (Emission, Transport and Chemical Processing of Pollutants within Cities) field campaign. The instrument sampled ambient aerosol though an inlet on the roof of the University of Manchester Sackville Street Building, which is situated approximately 30 m above street level (Williams et al. 2000). CityFlux was designed to investigate particle fluxes from Manchester City Centre and thus required highly time resolved measurements. For this reason the Q-AMS was run for 14 days with 1 minute averaging intervals with the JMS mode in addition to the usual MS and PToF modes, to allow a comparison of the high speed aerosol data with similar resolution trace gas measurements. The sample time in each of the three modes was 20 s out of every minute, with 0–300 m/z MS scans, and 12 m/z's in JMS and PToF mode. Approximately 2 s of dead time was attributed to each 20 s scans for all modes of operation to accounts for chopper movements, and data acquisition duty cycles of 85% and 65% were measured for MS and JMS mode, respectively.

The FFT of the MS and JMS nitrate, sulphate, total organic, and m/z 43 organic concentrations from CityFlux are shown in Figure 2 as Magnitude Squared (defined as Power) versus frequency. The data is processed by importing m/z's 30, 46, 48, 43, 44, 55, and 57, which are mainly due to the following ions: NO^+, NO_2^+, SO^+, $C_2H_3O^+$ and $C_3H_7^+$, CO_2^+, $C_3H_3O^+$ and $C_4H_7^+$, $C_3H_5O^+$, and $C_4H_9^+$ (DeCarlo et al. 2006). The remaining 5 m/z's scanned were used to monitor other species not considered in this analysis. Attempts to increase ammonium signal to noise using the JMS mode were unsuccessful due to large background noise at interfering water and air peaks in the spectrum. However making the assumption of charge balance (which can be verified using measured ammonium, nitrate, and sulphate) an improved estimate of ammonium can be calculated based on a charge balance on the JMS improved sulphate and nitrate mass concentrations. While this may not be an acceptable assumption in some environments, its validity can typically be verified using MS mode data (Zhang et al. 2007).

The region of constant power at high frequency in the power spectra (representing the variance (Stull 1988)) shown in Figure 2 associated with high frequency random noise ("white noise," with approx. the same power at all frequencies) in the instrument is visibly lower for the JMS data by approximately a factor of 10 for all species except total organic mass. The lowering of the white noise level in the power spectrum for the JMS data means that signal becomes resolvable above the noise at higher frequencies of sampling when JMS data is used. Noise in the power spectra can be estimated using Equation (2) (Stull 1988) which states the standard deviation is proportional to the square root of the area under the power spectrum between a and b, where a and b only contain high frequency noise (taken as 7×10^{-3} and 8×10^{-3} Hz, respectively, for these data). The reduction in noise of the measurement can be predicted by taking the ratio of the integrated areas of the MS and JMS power spectra.

$$\sigma_X \propto \sqrt{\int_a^b P_X(\upsilon)d\upsilon} \qquad [2]$$

The relative reduction in the standard deviation was determined to be 4.6, 3.0, 1.3, and 3.5 for nitrate, sulphate, total organics, and m/z 43, respectively, using the power spectrum analysis. The largest reduction in standard deviation was found for nitrate, as the two major ions produced (NO^+ and NO_2^+) were both sampled in JMS mode. A reduction in sulphate noise was found, but this is not as large as the nitrate reduction, as only one m/z was sampled for sulphate, which has typically 4 major fragments. A smaller reduction in the noise of the total organic signal is found. Assuming the organic signal is made up of signal from 0.45 m/z for each m/z scanned, and from 250 peaks in the mass spectra, each data point in the MS organic time series has a total sample time of 5.74 s, whereas with the additional use of the JMS data the total sample time increases to 9.44 s. However this MS mode scan time for the organics is not a fair representation of the noise levels as a majority of the organic signal is found in only a small fraction of the peaks, depending on the specific species under study. When compared to the increase in sample time for a species such as nitrate (from 0.054 s in MS mode to 3.01 s in JMS mode) it is clear where this reduction in signal to noise comes from. A reduction in the noise of organics at m/z 43 was found to be significant, consistent with a large increase in scan time. However, using this technique the improvement was not as large as that for the inorganic species. This could be a result of natural variability in the organic aerosol

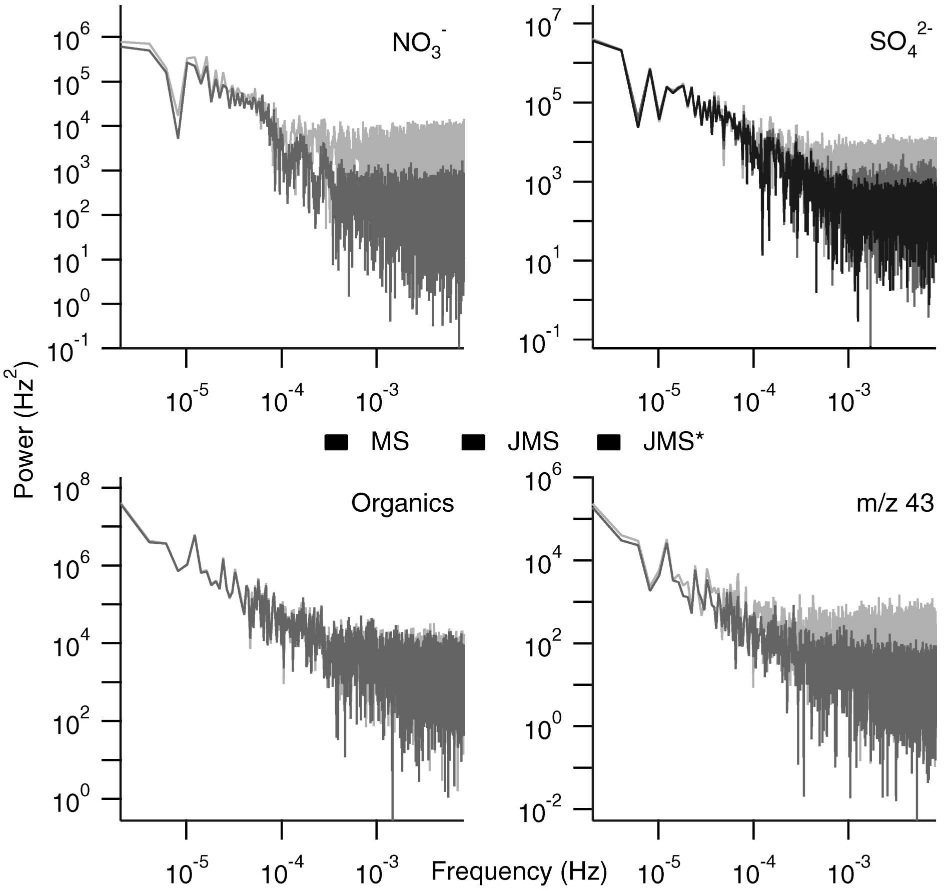

FIG. 2. Power Spectra (Magnitude Squared of the Fourier Transform) of different species using both the MS (light grey) and JMS (dark grey) data. Black spectra are sulphate data using only sulphate mass at m/z 48 JMS data and a scaling factor of 4.59.

at m/z 43 occurring on timescales shorter than sampling time due variations in primary organic concentrations brought about by inhomogeneities in traffic activity and street canyon air mixing, as reported by Zhang et al. (2005) . This would manifest itself in an apparent increase in instrumental noise and could explain the apparently low increase in signal to noise.

Figure 3 shows the normal MS-derived sulphate mass concentration with a modified JMS-derived sulphate concentration during CityFlux. Here, instead of simply importing the higher signal to noise JMS data and using this with the other standard MS data to calculate the total sulphate mass, only the mass concentration at m/z 48 is used, and scaled up to the total sulphate mass concentration using the expression $\mathrm{SO}_{4\mathrm{total}} = 4.59 \times \mathrm{SO}_{4\mathrm{m/z48}}$. This relationship was determined from linear regression of the data, forcing the intercept to equal zero. This can be done due to the predictable fragmentation pattern of sulphate and the small organic interference at this m/z (DeCarlo et al. 2006).The relative contribution of m/z 48 to total sulphate (i.e., the fragmentation of sulphate) is also shown in Figure 3 as a time series and is stable with no significant deviations. This is not the case for either nitrate or organics, as the fragmentation of these species is composition dependent, with ammonium nitrate and sodium nitrate producing significantly differing spectra (Alfarra 2004). An increased reduction in noise (from a factor of 3.03 to 3.90) is found when using only m/z 48 to calculate the total sulphate mass. This is demonstrated by the reduction in the white noise level in Figure 2 for the JMS* SO_4^{2-} spectra.

The predicted relative reduction in noise (using Equation [1] and the operation conditions of the Q-AMS during CityFlux) is approximately a factor of 6.35 per m/z. The improvement to the nitrate signal is the closest to the theoretical maximum, as all major fragments are scanned in JMS mode. Sulphate signals approach this limit but still have some degree of extra noise, whereas the organics at m/z 43 and total organics get progressively less benefit from the JMS mode.

Noise reduction never approaches the theoretical limit. However, the reduction in noise predicted by the use of Equation (2) applies over a specific frequency range of the power spectrum. This may not describe the overall reduction in standard deviation, as the FFT only provides information up to a maximum of half the original sample frequency, meaning the benefit to the one minute data cannot be assessed. Also, true variability in aerosol loadings over time intervals of twice the sampling

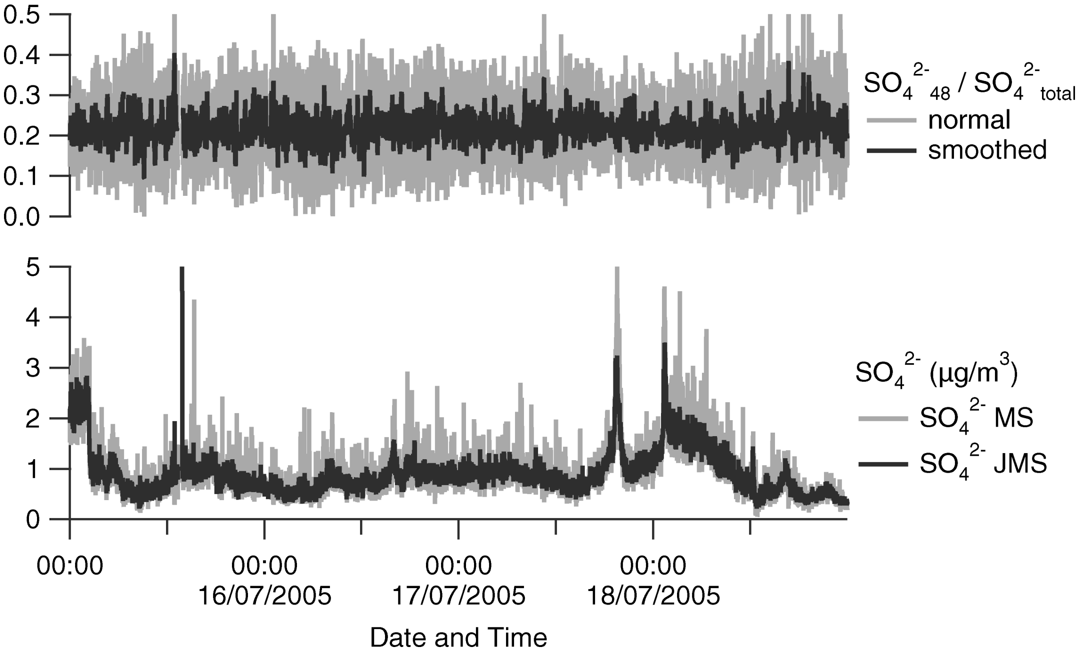

FIG. 3. Time series of sulphate in Manchester during the CityFlux project from MS data and predicted based on JMS derived sulphate at m/z 48. Also shown is the m/z 48 contribution to sulphate mass.

time or less would also result in an apparent increase in noise, reducing the apparent benefit of the JMS data.

4. JMS APPLICATIONS

The JMS mode of operation has been used extensively on the Q-AMS onboard the UK Facility for Airborne Atmospheric Measurements (FAAM), with the instrument measuring for over 200 hours collectively on research flights. Throughout spring/summer 2005 numerous research flights were conducted for the AMPEP project (Aircraft Measurement of Chemical Processing and Export Fluxes of Pollutants over the UK), which aimed at estimating the emission of pollutants in both the gas and particle phase from the UK. Figure 4 shows a 30-second averaged time series of nitrate mass concentrations enclosed within one standard deviation (as calculated in Allan et al. 2003),

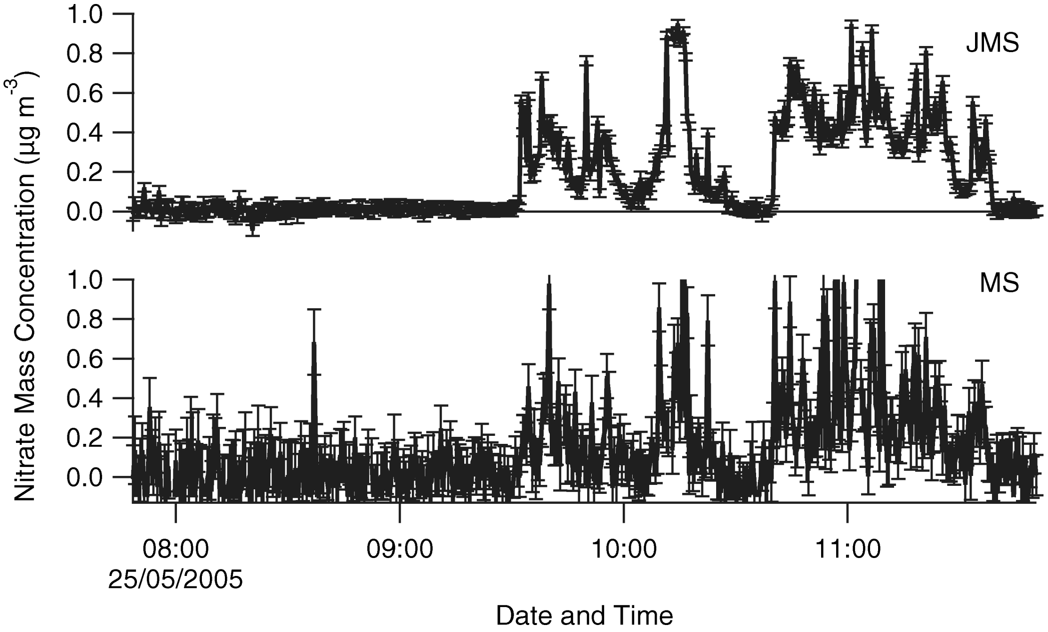

FIG. 4. Time series of 30-second nitrate mass concentrations from the FAAM aircraft during the AMPEP project using JMS data and MS data.

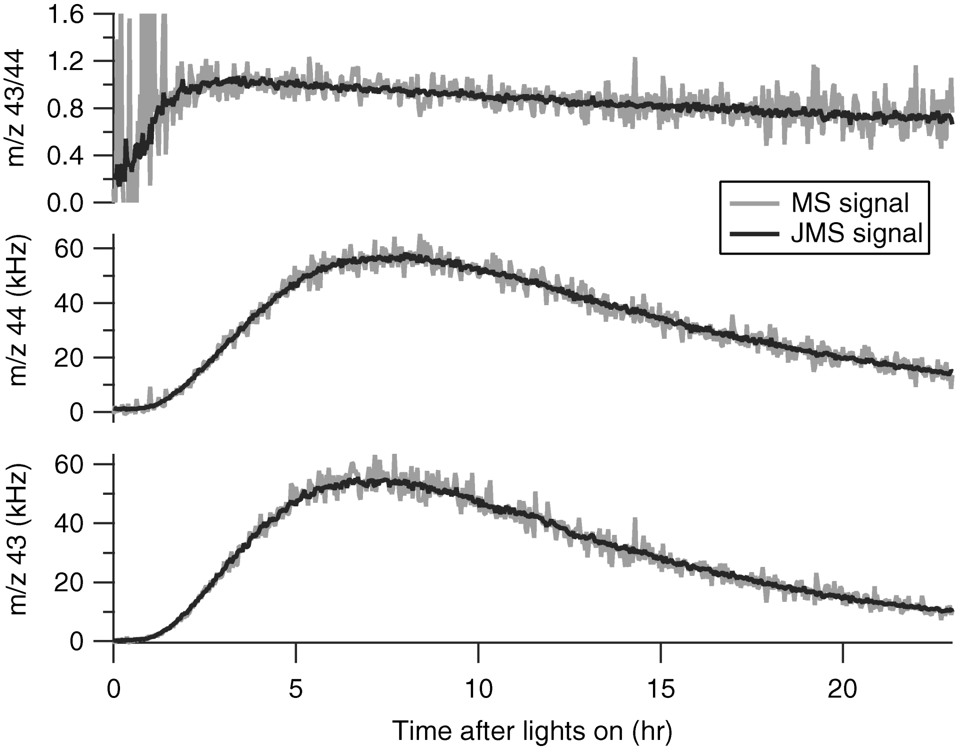

FIG. 5. Smog chamber data from alpha-pinene photooxidation. Time series of the m/z 43 to 44 ratio for both MS and JMS data, as well as time series for both m/z 43 and 44.

calculated using the MS and JMS optimized (m/z 30, 46) data, respectively, on AMPEP flight B097 on 25th May 2005. It appears that the JMS mode improves the temporal signal of the nitrate mass concentration, resulting from a reduction in noise (this can be seen in the time series 08:00–09:30, with nitrate levels below detection limits). This results in key structures within the data becoming increasingly resolved. The relative reduction in noise (measured as the relative reduction in standard deviation of the nitrate signal for the initial period of near zero nitrate mass) was found to be a factor of 5.81. This approaches the maximum benefit possible (assuming 85% and 65% data acquisition duty cycle for 10 seconds of MS and JMS data respectively, with 0–300 m/z scans at 1 m/z per ms, and JMS scans for 9 m/z's using the 60 ms JMS cycle), which is 7.33. For aircraft flux inventory work such as that carried out during AMPEP, this increase in signal to noise is crucial, as in addition to improving the absolute accuracy of the measurements, the resulting improvements to the spatial resolution are vital for identification of sources. The two time trends are also of the same order, meaning that the scaling factor technique adopted did not introduce measurement artefacts. Also the estimated errors in the 30-second JMS nitrate data from the aircraft are much smaller than the magnitudes of the plumes, whereas the errors in the standard MS data are much larger, which results in the loss of some information.

The JMS mode of operation is not only useful in aircraft studies, but in any highly dynamic laboratory studies such as chamber studies of Secondary Organic Aerosol (SOA) formation. Figure 5 shows MS and JMS Q-AMS time series for m/z's 43 and 44 (the latter corrected for gas-phase CO_2) taken during an alpha-pinene photooxidation experiment at the Paul Scherrer Institute (PSI, Villigen, Switzerland) smog chamber at 2-minute averaging times. Not only is there an increase in the signal to noise of the JMS data, the high temporal information allows insight into possible chemical changes in the aerosol. For example also plotted in Figure 5 is the ratio of m/z 43 ($C_2H_3O^+$ and $C_3H_7^+$) and 44 (CO_2^+). The time trend of this ratio when calculated from MS data is very noisy and shows little information at the start of the experiment, however a clear trend in JMS data can be resolved at the start of the experiment that may allow insight into the processes involved in SOA formation. Without such high temporally resolved and sensitive measurements, this important information would not be available. A relative reduction in the standard deviation of the signals in the presence of no aerosol mass was found to be 6.0 for both m/z's (the theoretical improvement is calculated to be a factor of 6.35).

5. CONCLUSIONS

A new mode of operation for the Q-AMS is demonstrated and is found to increase the sensitivity to inorganic species that typically break into few fragments upon vaporization/ionization in the instrument, or species such as sulphate which fragment in a predictable manner. The same is true for key organic fragments that can be used as characteristic markers. However, the benefit to the total organic signal is limited due to the large number of peaks associated with the organic mass spectra. The relative increase in sensitivity is related to the relative dwell time in the MS and JMS modes of operation, and also the number of m/z scanned in the JMS mode. Assumptions about the fragmentation of sulphate can lead to increases in signal-to-noise to the overall sulphate signal. Improvements to nitrate (both m/z 30 and 46 due to composition-related variation in fragmentation) and sulphate (m/z 48 or 64) are easily achieved using the JMS mode, which can prove useful in situations where highly time resolved measurements are needed, such as in-situ cloud activation and droplet nuclei composition measurements. Improvements to non-refractory chloride measured by the Q-AMS could also be achieved due to the small number of fragments produced (typically at m/z 35 and 36) but are not investigated here.

When combined with standard Q-AMS operation in MS mode, a decrease in detection limit for the Q-AMS by a factor of 4.5, 3.9, 1.3, and 3.5 for nitrate, sulphate, total organics, and m/z 43 mass loadings was achieved for 1 minute time interval (20 s in each of the three Q-AMS mode, monitoring 10 m/z in JMS mode) was calculated using Fourier analysis. These are somewhat lower than the value predicted by the increase in sample times. This could be due to natural variability and particle counting statistic appearing as noise in the FFT power spectrum. Also, the noise improvements from an FFT can only be determined at frequencies less than half the sample frequency. Noise improvements calculated from zero particle filter runs showed improvements closer to the theoretical predictions.

Important information on organic functionality can be obtained with high time resolution at low concentrations using the JMS mode as demonstrated using the data from the PSI smog chamber. However a reduction in signal to noise for the PToF size distributions means that careful consideration of mode operating times should be undertaken for each experiment (DeCarlo et al. 2006). Also, the low flowrate into the Q-AMS (typically 1.4 cm^3 s^{-1}) means that particle counting statistics limit the maximum time resolution of the instrument in many environments.

REFERENCES

Alfarra, M. R., Insights Into Atmospheric Organic Aerosols Using An Aerosol Mass Spectrometer, PHD thesis, submitted to the University of Manchester, 2004.

Allan, J. D., Delia, A. E., Coe, H., Bower, K. N., Alfarra, M. R., Jimenez, J. L., Middlebrook, A. M., Drewnick, F., Onasch, T. B., Canagaratna, M. R., Jayne, J. T., and Worsnop, D. R. (2004). A Generalised Method for the Extraction of ChemicallyResolved Mass Spectra from Aerodyne Aerosol Mass Spectrometer Data, *J. Aerosol Sci.* 35(7):909–922.

Allan, J. D., Jimenez, J. L., Williams, P. I., Alfarra, M. R., Bower, K. N., Jayne, J. T., Coe, H., and Worsnop, D. R. (2003). Quantitative Sampling Using an Aerodyne Aerosol Mass Spectrometer—1. Techniques of Data Interpretation and Error Analysis, *J. Geophys. Res.-Atmospheres* 108(D3):4090.

Canagaratna, M. R., Jayne, J. T., Ghertner, D. A., Herndon, S., Shi, Q., Jimenez, J. L., Silva, P. J., Williams, P., Lanni, T., Drewnick, F., Demerjian, K. L., Kolb, C. E., and Worsnop, D. R. (2004). Chase Studies of Particulate Emissions from In-Use New York City Vehicles, *Aerosol Sci. Technol.* 38(6):555–573.

Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q., Onasch, T. B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L. R., Trimborn, A. M., Northway, M. J., DeCarlo, P. F., Kolb, C. E., Davidovits, P., and Worsnop, D. R. (2007). Chemical and Microphysical Characterization of Ambient Aerosols with the Aerodyne Aerosol Mass Spectrometer, *Mass Spectrom. Rev.* 26(2):185–222.

DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L. (2006). Field-Deployable, High-Resolution, Time-of-Flight Aerosol Mass Spectrometer, *Anal. Chem.* 78(24):8281–8289.

DeCarlo, P. F., Slowik, J. G., Worsnop, D. R., Davidovits, P., and Jimenez, J. L. (2004). Particle Morphology and Density Characterization by Combined Mobility and Aerodynamic Diameter Measurements. Part 1: Theory, *Aerosol Sci. Technol.* 38(12):1185–1205.

Jayne, J. T., Leard, D. C., Zhang, X. F., Davidovits, P., Smith, K. A., Kolb, C. E., and Worsnop, D. R. (2000). Development of an Aerosol Mass Spectrometer for Size and Composition Analysis of Submicron Particles, *Aerosol Sci. Technol.* 33(1–2):49–70.

Jimenez, J. L., Jayne, J. T., Shi, Q., Kolb, C. E., Worsnop, D. R., Yourshaw, I., Seinfeld, J. H., Flagan, R. C., Zhang, X. F., Smith, K. A., Morris, J. W., and Davidovits, P. (2003). Ambient Aerosol Sampling Using the Aerodyne Aerosol Mass Spectrometer, *J. Geophys. Res.—Atmospheres* 108(D7):8425.

Press, W. H., Flannery, B. P., Teukolsky, S. A., and Vetterling, W. T. (1992). *Numerical Recipes in C: The Art of Scientific Computing*, Cambridge University Press, Cambridge.

Schneider, J., Weimer, S., Drewnick, F., Borrmann, S., Helas, G., Gwaze, P., Schmid, O., Andreae, M. O., and Kirchner, U. (2006). Mass Spectrometric Analysis and Aerodynamic Properties of Various Types of Combustion-Related Aerosol Particles, *Intl. J. Mass Spectrom.* 258(1–3):37–49.

Stull, R. B. (1988). *An Introduction to Boundary Layer Meteorology*, Kluwer Academic Publishers, Dordrecht.

Williams, P. I., Gallagher, M. W., Choularton, T. W., Coe, H., Bower, K. N., and McFiggans, G. (2000). Aerosol Development and Interaction in an Urban Plume, *Aerosol Sci. Technol.* 32(2):120–126.

Zhang, Q., Alfarra, M. R., Worsnop, D. R., Allan, J. D., Coe, H., Canagaratna, M. R., and Jimenez, J. L. (2005). Deconvolution and Quantification of Hydrocarbon-Like and Oxygenated Organic Aerosols Based on Aerosol Mass Spectrometry, *Environ. Sci. Technol.* 39(13):4938–4952.

Zhang, Q., Jimenez, J. L., Worsnop, D. R., and Canagaratna, M. R. (2007). A Case Study of Urban Particle Acidity and its Effect on Secondary Organic Aerosol, *Environ. Sci. Technol.* 41(9):3213–3219.

Zhang, X. F., Smith, K. A., Worsnop, D. R., Jimenez, J., Jayne, J. T., and Kolb, C. E. (2002). A Numerical Characterization of Particle Beam Collimation by an Aerodynamic Lens-Nozzle System: Part I. An Individual Lens or Nozzle, *Aerosol Sci. Technol.* 36(5):617–631.

Zhang, X. F., Smith, K. A., Worsnop, D. R., Jimenez, J. L., Jayne, J. T., Kolb, C. E., Morris, J., and Davidovits, P. (2004). Numerical Characterization of Particle Beam Collimation: Part II—Integrated Aerodynamic-Lens-Nozzle System, *Aerosol Sci. Technol.* 38(6):619–638.