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Atmospheric
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Discussions

Interactive comment on "Single particle characterization using a light scattering module coupled to a time-of-flight aerosol mass spectrometer" *by* E. S. Cross et al.

Anonymous Referee #1

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Review of Cross, et al. Part 2

Q) p. 21344: they state particle For example, Fig. 10 shows that most of the ambient particles measured at T1 contained ammonium nitrate.

This should be re-worded to state more accurately: most of the ambient non-refractory particles with a prompt ion signal (23% of the total) measured at T1 contained ammonium nitrate.

R) p. 21345: they state This observation is strongly supported by the single particle mass spectra reported by Moffet et al. (2008a) for ATOFMS results obtained at the T0

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site. Nearly all classified single particle types reported exhibit both NO2 and NO3 ions (see Fig. 2 in Moffet et al., 2008a).

Importantly, many of these nitrate-containing particles detected with the ATOFMS by Moffet et al. contained NaNO3 and not just ammonium nitrate which the AMS claims is most of the nitrate mass. One must exercise caution when interpreting the nitrate concentrations detected by the AMS–when it is stated most of the nitrate is in the form of ammonium nitrate, the authors mean most of the non-refractory nitrate that produces a prompt ion signal is in the form of ammonium nitrate which makes sense since this is the most common non-refractory form of nitrate. However, the AMS is not detecting sodium nitrate which was significant during certain periods in Mexico City, even in the submicron particles.

S) p. 21353: “In such cases, the Pb signal was approximately 100 times smaller than the chloride signal. Care must be taken when interpreting AMS measurements of heavy metals and further characterization of the ionization efficiency of metal species must be done before quantitative information is reported. Nevertheless, on a qualitative basis, these observations suggest that only some of the chloride events at T1 were correlated with Pb, and that when present, lead constituted a relatively minor component of the total particle mass. Lower concentrations of Pb containing particles were also measured at the T1 site relative to the T0 site by Moreno et al. (2008).”

If the AMS cannot measure most of the Pb mass (what is the volatilization temp and limit of detection of the AMS for the different Pb salts?), it isn't appropriate it represents a small % of the mass. The AMS did detect Pb with Cl in almost 1/2 of the events–the question arises, since it is not easily detectable with the AMS, what % of the Pb events were below the AMS detection limits? It would be worthwhile to report the AMS detection limits for Pb. How high a % would have to exist in a single PbCl3 particle for the AMS to detect lead? Also, most of the Pb particles were highly non-spherical. Wouldn't these be missed due to particle bounce issues such as reported for ammonium sulfate?

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T) p. 21354: "Murphy emphasizes the importance of understanding the chemical detection sensitivity of single particle mass spectrometers. Calibration experiments indicate that the PALMS and ATOFMS instruments are 12 times more sensitive to metal species than detection of NH4NO3 or HNO3. Therefore, when measuring single particles with any Pb content, it is possible to over-estimate the mass contribution of the metal species to the total particle composition with laser-ablation single particle mass spectrometers."

Provide the reference which shows this factor of 12. It is likely the PALMS and ATOFMS have different detection efficiencies since they use different LDI wavelengths. There is no paper that shows the detection efficiency for both instruments for metals vs. NH4NO3 and HNO3. Most/all single particle mass spec reports of Pb have reported # fractions and not attempted to report mass contributions as this final sentence implies. Without knowing the mass fraction of Pb in a single particle, it would be difficult to do this. For that matter, it is unclear if the AMS can provide such info given the fact that many forms of Pb could be refractory. What is the sensitivity of the AMS towards Pb in the various salt forms?

U) p. 21354: “Our single particle measurements at T1 suggest that the predominant form of chloride in the single particles was ammonium chloride.”

Can the authors estimate the fraction of the total chloride the AMS detects? Have they derived calibration curves for Cl in various salt forms? The chloride signals shown in Figure 8-10 are extremely small. It is likely the AMS only detects a small fraction of the total Cl since most of the Cl in the form of NaCl, KCl, PbCl, and ZnCl would not be vaporized in the AMS. Also, because the shape of the metal-chloride particles were needle-like (Moffet, ES&T, 2008), it is likely the AMS didn’t detect these particles as part of the 23% for which they acquired a prompt ion signal. Again, it would be more appropriate to state "the predominant form of non-refractory chloride in the 23% of particles which underwent prompt vaporization (23%) was ammonium chloride".

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Also, on p. 21354: “Examination of all single particles measured during the high chloride particle events show that no particles had effective densities greater than 1.8 g/cm3.”

This must be re-worded. No particles that produced prompt ion signals in the AMS had effective densities greater than 1.8. It is highly likely given the non-spherical nature (see Moffet ES&T, 2008) of these metal-chloride particles, that they were not detected in the AMS as part of the 23% analyzed. However, they could have been part of the other 77% that were not analyzed.

V) P. 21355: “The mass spectrum shows that this particle was predominately NH4Cl combined with some NH4NO3 and very little organic. Based on these observations, we conclude that a significant fraction of the particulate chloride measured with the LS-ToF-AMS at T1 was in the form of NH4Cl.”

It would be appropriate to add the caveat that it is possible these NH4NO3/NH4Cl particles contained other refractory metal and salt species (NaCl and KCl); with the AMS alone, you cannot tell. Such mixtures are actually shown in the Moffet Milagro paper for T0 chloride-containing particles. Since the AMS is only detecting ammonium chloride particles, they should explicitly mention for the non-mass spectrometry expert that this is a chemical bias of the AMS and they would miss detecting the NaNO3, KCl, NaCl, and Pb and Zn-chloride-nitrate particles detected by other instruments (i.e. single particle mass spectrometry, electron microscopy and STXM). It is likely the AMS missed these other types because they were dry and irregularly shaped (i.e. needles) as well as refractory at 600 degrees. Also, was this period an appropriate one (i.e. proper transport conditions) where the ATOFMS T0 results should be compared with the AMS T1 results? This should be discussed. It would be interesting to use the light scattering signal to more fully explore the densities of these inorganic particles that are detectable.

Also, since the PILS was sampling during this same period, it would be interesting to

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see if they also conclude most of the chloride was in the form of ammonium chloride. How much of the chloride detected by the PILS-IC does the AMS detect? This gets back to the question of what is the detection limit for chloride by the AMS when it is in the form of NaCl, KCl, or metal-chlorides vs. NH4Cl?

W) p. 21356: “Using the single particle detection capabilities of this instrument, the detection efficiency of the AMS was quantitatively determined.”

This statement makes it sound like there was one detection efficiency when in fact the AMS showed a strong size dependence which varied significantly over the course of the study (as shown by the scatter in Fig 3). Thus, it would be more informative to state (and show) the detection "efficiencies" of the AMS and how they changed over the 75 hour sampling period. The average value is misleading as it has been reported to change from 0.25 to 1 over the course of one ambient study. It also changes as a function of size as shown in Figure 2. The light scattering module offers the ability to monitor CE over time which could be a powerful addition and helpful in advancing the quantitative ability of the AMS.

X) p. 21356: Prompt particles made up 23% of the total number and 59% of the total mass. Delayed particles made up 26% of the total number and 38% of the total mass. Null particles made up 51% of the 10 total number and 3% of the total mass. The study shows that the mass content of particles undergoing prompt vaporization is reliably measured. Detailed analysis was preformed for this class of particles.

This should be re-worded to state: "59% of the total mass detectable by the AMS" or it is extremely misleading.

Y) p. 21356–conclusion 7. From 09:00–12:00 LT all particles within the ambient ensemble, including HOA particles originating from local traffic sources, were coated with NH4NO3 due to…

Again, they state "all particles within the ambient ensemble," but this is not accurate.

Summary

In summary, there are some very useful findings in this paper. The weakest part of the paper is how the authors use an extremely limited subset of particles (23%) to draw overall conclusions about the Mexico City atmosphere. It is shown that the 23% is biased towards smaller sizes and most likely biased towards a specific chemistry (spherical non-refractory species); however these facts are lost in some parts of this paper where key conclusions are drawn. It would be useful, since this is the first time these detection biases are shown, to do a more complete analysis of the effect of only detecting 23% of the particles on the overall quantitative potential of the AMS technique. Does it or doesn't it affect the ensemble mass analysis and if so why or why not? One could use other aerosol chemistry analysis methods at the same location to better understand periods when the CE is lowest vs. highest, etc.

Organics analysis by single particle mass spectrometry (examples)

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17(8): 851-859.

Quantification papers by single particle mass spectrometry (examples)

Bhave, P. V., J. O. Allen, et al. (2002). "A field-based approach for determining ATOFMS instrument sensitivities to ammonium and nitrate." Environmental Science & Technology 36(22): 4868-4879. Cziczo, D. J., D. S. Thomson, et al. (2001). "Ablation, flux, and atmospheric implications of meteors inferred from stratospheric aerosol." Science 291(5509): 1772-1775. Fergenson, D. P., X.-H. Song, et al. (2001). "Quantification of ATOFMS Data by Multivariate Methods." Analytical Chemistry 73(15): 3535-3541. Liu, D. Y., K. A. Prather, et al. (2000). "Variations in the size and chemical composition of nitrate-containing particles in Riverside, CA." Aerosol Science and Technology 33(1-2): 71-86. Mahadevan, R., D. Lee, et al. (2002). "Measurement of condensed-phase reaction kinetics in the aerosol phase using single particle mass spectrometry." Journal of Physical Chemistry A 106(46): 11083-11092. Park, K., D. Lee, et al. (2005). "Size-resolved kinetic measurements of aluminum nanoparticle oxidation with single particle mass spectrometry." Journal of Physical Chemistry B 109(15): 7290-7299. Qin, X. Y., P. V. Bhave, et al. (2006). "Comparison of two methods for obtaining quantitative mass concentrations from aerosol time-of-flight mass spectrometry measurements." Analytical Chemistry 78(17): 6169-6178. Spencer, M. T. and K. A. Prather (2006). "Using ATOFMS to determine OC/EC mass fractions in particles." Aerosol Science and Technology 40(8): 585-594. Zelenyuk, A., D. Imre, et al. (2008). "Simultaneous measurements of individual ambient particle size, composition, effective density, and hygroscopicity." Analytical Chemistry 80(5): 1401-1407. Zelenyuk, A., J. Yang, et al. (2008). ""Depth-profiling" and quantitative characterization of the size, composition, shape, density, and morphology of fine particles with SPLAT, a single-particle mass spectrometer." Journal of Physical Chemistry A 112(4): 669-677. Zhao, W., P. K. Hopke, et al. (2005). "Predicting bulk ambient aerosol compositions from ATOFMS data with ART-2a and multivariate analysis." Analytica Chimica Acta

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