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AMS Collection Efficiencies of dry smog chamber aerosols, dependence on $(NH_4)_2SO_4$, NH_4NO_3 and SOA fractions

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The Aerodyne Aerosol Mass Spectrometer (AMS) measures the average chemical composition of non-refractory species, i.e. particulate matter which vaporizes when impacted on a surface heated to 600 C. The instrument provides quantitative data on-line with time resolution down to seconds (dependent on mass loading). This is accomplished through mass spectrometric measurements subsequent to aerodynamic lens focusing. Each particle type (with respect to shape, size and composition) has associated collection efficiency (CE) which data analysis needs to take into account in order to yield quantitative results.

CE is a collective name for any effect on instrument sensitivity associated with particle sampling, and was given by Huffman *et al* (2005) as

$$CE(d_{va})=E_L(d_{va})*E_s(d_{va})*E_b(d_{va})$$

The expression above emphasizes three particle properties which may bias the sampling; lens transmission (E_L), non-spherical shape (E_S), bouncing from the vaporizer plate (E_b), and their possible dependence on size. E_L and E_S are close to unity for most ambient accumulation mode particles, making E_B the main contributor to uncertainty in quantification.

This study is a summary of CE estimates from inter comparison with other aerosol instrumentation (primarily Scanning Mobility Particle Sizer, SMPS, and Aerosol Particle Mass analyzer- Differential mobility Analyzer, APM-DMA) on data from two light duty vehicle exhaust ageing campaigns. The experiments were performed by nebulizing $(NH_4)_2SO_4$ and injecting it into a 6 m^3 smog chamber, mixing with real exhaust or precursor species and irradiating the chamber with UV-light under dry (RH~5%) conditions (Nordin et al 2011). This typically resulted in condensation of SOA and/or NH_4NO_3 (NH_3 forms in the oxidation catalyst of the vehicle), a process which was monitored for approximately 5 hours. These internally mixed aerosols spanned a wide range of chemical compositions, from pure seeds to particles dominated by either condensate, enabling investigation of the effects of these proportions on CE.

Figure 1 below illustrates one of the experiments were NH_4NO_3 and SOA condense onto $(NH_4)_2SO_4$ seeds. In the two hours plotted, the particles transform from salt cores lightly coated with organic matter (this coating occurred while injecting the exhaust) to heavily coated (approximately 50% SOA, 30% NH_4NO_3, and 20% $(NH_4)_2SO_4$) particles. During this process, the ratio of reported AMS/SMPS mass increases from 0.23 to 0.37. This is in agreement with ambient observations, where dry aerosols dominated by $(NH_4)_2SO_4$ typically is found to have E_B=0.25 while dried SOA gives E_B=0.5.

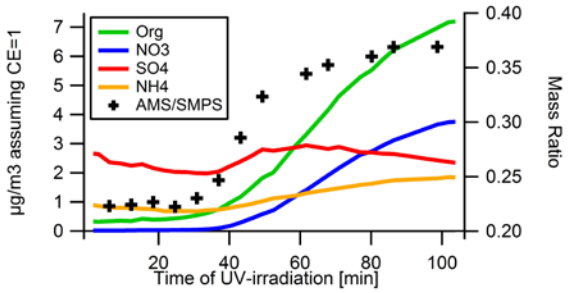

Figure 1. Chemical composition during an exhaust ageing experiment. The increase in AMS/SMPS mass ratio is likely due to an increase in E_b of the sampled aerosol. The time trace of SO_4 supports this.

Although the increasing ratio illustrated above is mainly due to increasing E_b, it should be noted that other aspects of instrumental response (in both instruments) also may affect the ratio. E_B is believed to be an effect of particle phase (Matthew et al 2008). Ambient AMS measurements usually employ a dried sampling line (to reduce interference from gaseous and particulate water), which may perturb the phase of the sampled particles. Since these experiments were performed under dry conditions, this effect is presumably captured here.

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