Aerosol Mass Spectrometry: The next generation of aerosol analysis

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Importance of Aerosols

Individually, tiny atmospheric particles have very little significance. Taken as a whole, however, aerosols have been shown to affect human health, visibility, acid deposition, and global climate change. Each of these aspects are influenced by the properties of aerosols, whether it be particle size, composition, or life time. From aggregates of soot to carcinogenic aromatic hydrocarbons, more research must be done to better understand these airborne particles.

Techniques of Aerosol Analysis

The leading methods of aerosol analysis have relied on filtering air over a given amount of time and later extracting the sample for chemical analysis: often gas-chromatography mass spectrometry (GC/MS). In filter-based studies, only 5-15% of the particles collected are eluted and speciated (Canagartna et al 2007). Filters are used for particles larger than a specific size, but no other information is given about particle size.

The recently developed Aerosol Mass Spectrometer (AMS) is field-deployable and provides instant high-resolution, time-of-flight (PTOF), real-time mass spectra, with virtually no loss of material.

Figure 1: An example of a filtering device used to take 24 hour samples in the field.

Aerosol Mass Spectrometer: The Basics

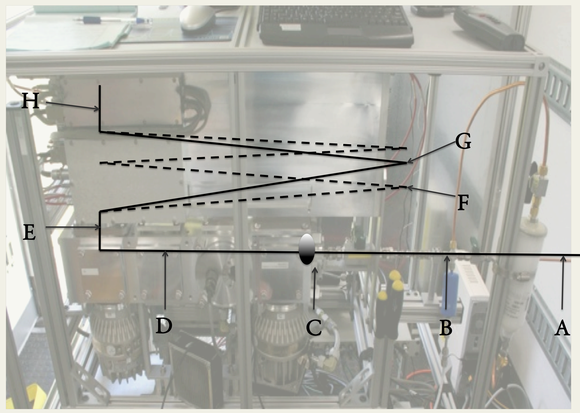


Figure 2 : The basics of the AMS. The air sample enters through the particle inlet (A) and is focused when passed through the aerodynamic lens (B). The chopper (C) segments the air stream; the aerosols are separated by size in the PToF region (D) . The particles are then evaporated and their vapors ionized (E) and sent through either the W (F) or V (G) mode. The time spent in each mode corresponds to a specific m/z (mass per charge) ratio, which is detected (H) and immediately reported on a monitor, resulting in a mass spectrum.

An Emission Study with AMS

Introduction

There are several thousand components in the diesel exhaust particles, including hydrocarbons, aromatics, and oxygenates (Akiyama 2006). Diesel emissions are usually a mixture of lubricant oil and diesel fuel emissions but dominated in most circumstances by the lubricant oil (Canagaratna et al. 2004). Differences arise when different engines are used as well as under different driving cycles (Akiyama 2006, Canagaratna et al. 2004). Dominant components include branched alkanes, cycloalkanes, and aromatics (including carcinogenic PAHs). In ambient air measurements using the AMS, it is easy to find the organic "signature" of fuels, especially in urban areas (Canagaratna et al. 2004). Biodiesel (especially new algae-derived biodiesel has been shown to be a viable future alternative to foreign oil. In this study, we obtained mass spectra from regular petroleum-based diesel and four types of biodiesel under controlled conditions.

Methods

Using a John Deere 4024T engine, we used four types of biodiesel: soy, canola, and two other fuels made to represent two common types of algae-based biodiesels. Not yet commercially available, algae biodiesel has been shown to contain more unsaturated fatty acids – a unique characteristic to algae-derived biofuels (Hossain et al. 2008). Algae 1 represents biodiesel with many of these fatty acids (similar to the fuel derived from *Nannochloropsis Oculata)*, while Algae 2 contains less fatty acids (to represent *L. Galbana)* All fuels were run for 80 minutes, half at 50% loading and half at 75% loading, in 20 minute intervals. Blends (20% biodiesel, 80% diesel) were also tested for each of the biofuels.

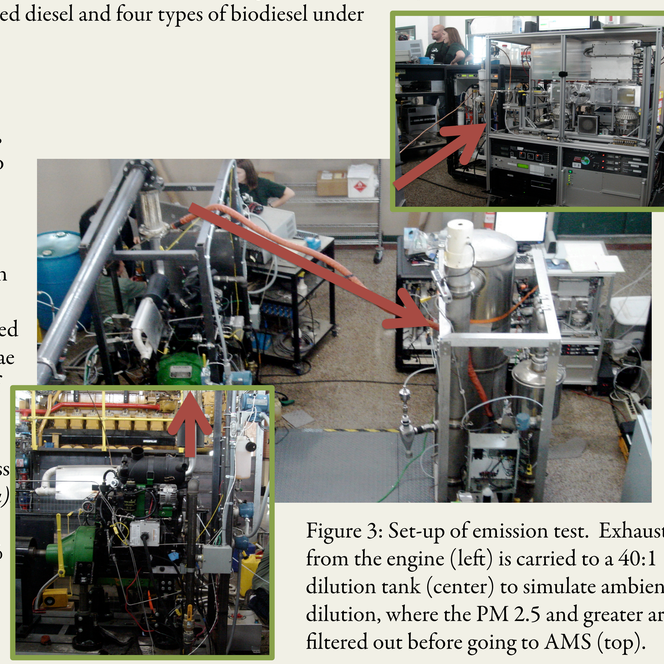


Figure 3: Set-up of emission test. Exhaust from the engine (left) is carried to a 40:1 dilution tank (center) to simulate ambient dilution, where the PM 2.5 and greater are filtered out before going to AMS (top).

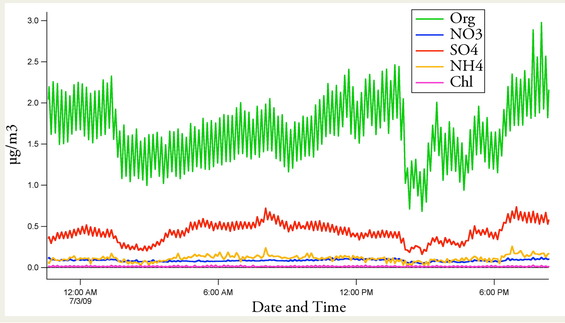
Ambient Air Sampling with AMS

Introduction

Many controlled studies have obtained mass spectra from burning different biomasses, fuels, and industrial emissions including those often found in the Rocky Mountains. These mass spectra can be used when looking at ambient air sampling to determine the effect that biomass burning has on ambient aerosols. In this experiment, the AMS was used to obtain a mass spectrum of the ambient aerosols in Rocky Mountain National Park, Colorado.

Methods

Using a mobile lab, we brought the AMS to Rocky Mountain National Park, to monitoring site ROMO1. The AMS sampled continuously for 1 week, with the exception of daily calibration (about 1 hour). Figure 4 (left): Mobile lab on site. Figure 5 (top right): Particle inlet outside of mobile lab. Figure 6 (right): Portion of Time Series obtained on site.



AMS Data

The following are examples of data acquired from the AMS. These data are from the emissions study.

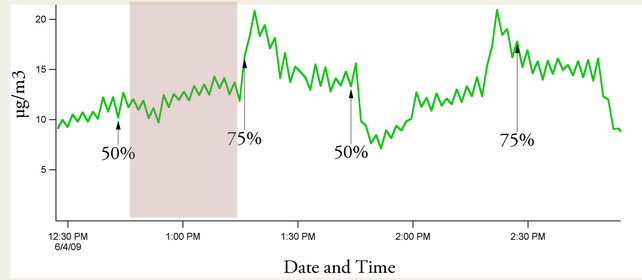


Figure 7: Example of time series obtained by AMS. Organic aerosol concentration of 20% Canola is shown, with engine loading.

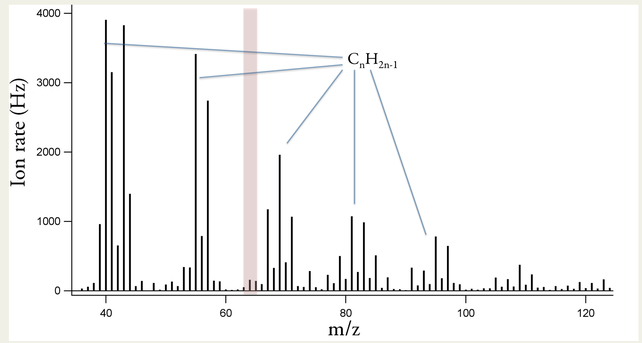


Figure 8: Example of average mass spectrum obtained by AMS. Total aerosol MS of 20% Canola is shown of highlighted area of Fig 7.

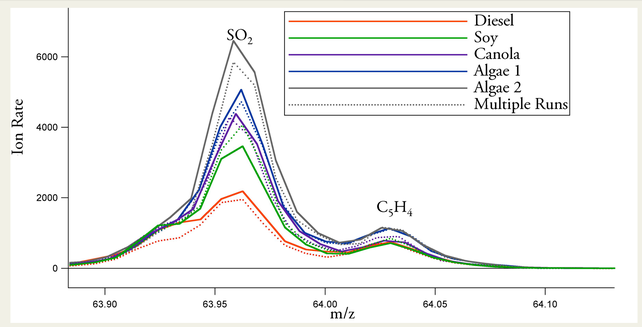


Figure 9: Example of high resolution MS. All 20% blends (and diesel) shown of highlighted area of Fig 8 (m/z = 64)

References

Akiyama, K, 2006: Gas chromatographic analysis and aerosol mass spectrometer mearsurement of diesel exhaust particles comoposition. *Talanta*, **70**, 178-181.

Canagaratna, M. R., J. T. Jayne, D. A. Ghertner, S. Herndon, Q. Shi, J. L. Jimenez, P. J. Silva, P. Williams, T. Lanni, F. Drewnick, K. L. Demerjian, C. E. Kolb, and D. R. Worsnop, 2004: Chase studies of particulate emissions from in-use New York city vehicles. *Aerosol Sci. and Tech.,* **38**. 555-573.

Canagaratna, M. R., J. T. Jayne, J. L. Jimenez, J. D. Allan, M. R. Alfarra, Q. Zang, T.B Onasch, F. Drewnick, H. Coe, A. Middlebrook, A. Delia, L. R. Williams, A. M. Trimbon, M. J. Northway, P. F. DeCarlo, C. E. Kolb, P. Davidovis, and D. R. Worsnop, 2007: Chemical and microphyisical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer. *Mass Spec. Review* **26**. 185-222.

Hossain S., A. Salleh, A. M. Boyce, P. Chowdhury, anad M. Naqiuddin, 2008: Biodiesel fuel production from algae as renewable energy. *American Journal of Biochem. and Biotech.*, **4**. 250-254.

Acknowledgments

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