



AEROSOL MASS SPECTROMETER MEASUREMENTS IN A HEAVY FUEL OIL –FIRED HEATING STATION IN HELSINKI

Sanna Saarikoski^{*A}, Samara Carbone^A, Anna Frey^A, Liisa Pirjola^B Topi Rönkkö^C and
Risto Hillamo^A

A) Finnish Meteorological Institute

B) Metropolia University of Applied Sciences

C) Department of Physics, Tampere University of Technology

* Corresponding author, Sanna.Saarikoski@fmi.fi

ABSTRACT

The particle emissions of energy production were investigated in a heavy fuel oil –fired heating station in Helsinki, Finland. The instrumentation included a sampling system and after that a versatile measurement setup with real-time aerosol particle instruments. Chemical composition, mass concentration, number- and mass size distribution, and volatility properties of emitted particles were studied. This paper focuses on the chemical characterization of submicron aerosol particles that were measured with an Aerodyne Soot Particle Aerosol Mass Spectrometer (SP-AMS). SP-AMS is able to measure real-time sulfate, nitrate, ammonium, chloride, organic matter, black carbon and elemental composition including some metals.

The heating station was operated with 30 MW (half power) and 47 MW (full power). In half power conditions, majority of the particle mass was composed of sulfate (63% of mass) and trace elements (25% of mass) whereas only 4 and 0.7% of the mass consisted of organics and black carbon, respectively. In full power conditions, the total particle mass concentration was little bit smaller than in half power conditions. With full power, elements comprised slightly larger and sulfate slightly smaller portion of the particle mass than with half power. The contributions of organic and black carbon were almost the same with half and full power.

Volatility characteristics of the particles emitted from the heavy fuel oil combustion in half power conditions were determined using a thermodenuder (TD) before the SP-AMS. Seven temperature steps were used for TD: 50, 75, 100, 125, 150, 200 and 250 °C. Mass and sulfate concentrations decreased as TD temperature was increased, however, the concentration of organics did not change clearly with increasing temperature. This might indicate that there were heavier organic compounds in particles that were not volatile even in the temperature of 250 °C. Thus, the evaporation behavior of submicron particles was based on other components than organics (e.g. sulfate).

Keywords: Aerosol mass spectrometer; heavy fuel oil combustion; particle chemistry



1 Introduction

Submicron particles (PM_{10}) are important from the environmental point of view because their lifetime in the atmosphere is long. Submicron particles have climate impacts but they are also harmful to human health as they pass deep to the respiratory system and even directly to the cardiovascular system. Harmfulness of particles depends not only on the particle size but also on their chemical composition. From the energy production point of view, submicron particles are most difficult to remove from the flue gas.

2 Experimental

The particle emissions of energy production were investigated in a heavy fuel oil –fired heating station in Helsinki, Finland. The heating station was operated with 30 MW (half power) and 47 MW (full power). Flue gas was sampled using a FPS-4000 sampling system, consisting of two stage dilution, after which the chemical composition, mass concentration, number- and mass size distribution, and the volatility properties of emitted particles were studied with a versatile set-up of real-time instruments.

This paper focuses on the chemical characterization of submicron aerosol particles using the Aerodyne Soot Particle Aerosol Mass Spectrometer (SP-AMS; Onasch et al., 2012). SP-AMS is a combination of two well-characterized instruments: Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (DeCarlo et al., 2006) and Single Particle Soot Photometer (e.g. Subramanian et al., 2010). SP-AMS consists of particle sampling inlet, particle sizing chamber and particle composition detection section. Aerosol inlet samples submicron particles into the AMS through an aerodynamic lens forming a narrow particle beam. The beam is transmitted into the detection chamber, in which non-refractory components are flash vaporized upon impact on hot surface under high vacuum. After that the components are ionized by electron impact ionization and the ions are detected by a mass spectrometer. In the SP-AMS, there is an additional intracavity Nd:YAG laser (1064 nm) that vaporizes refractory particles, specifically laser-light absorbing refractory black carbon particles and metals or elements, that are not detected in a standard AMS. In addition to black carbon and metals/elements, SP-AMS is able to measure inorganic components, sulfate, nitrate, ammonium and chloride, and organic matter. The volatility of particles emitted from the heavy fuel oil combustion was determined using a thermodenuder (TD, manufactured by Dekati Inc.) with the SP-AMS. In the TD, the diluted aerosol sample was heated and after that, led into the denuder where the cooled inner wall was covered with active charcoal to collect evaporated compounds.

3 Results

The results from the SP-AMS measurements are presented in Figure 1. On the first day, February 9, 2011, the measurements were performed in full power conditions and on the second day, February 10, 2011, with half power. SP-AMS measured sulfate, nitrate, ammonium, chloride, organic matter, black carbon and elemental composition, including some metals, using an averaging time of 2 minutes. Fast measurements enabled the testing of several measurement conditions (thermodenuder) only in a matter of few hours.

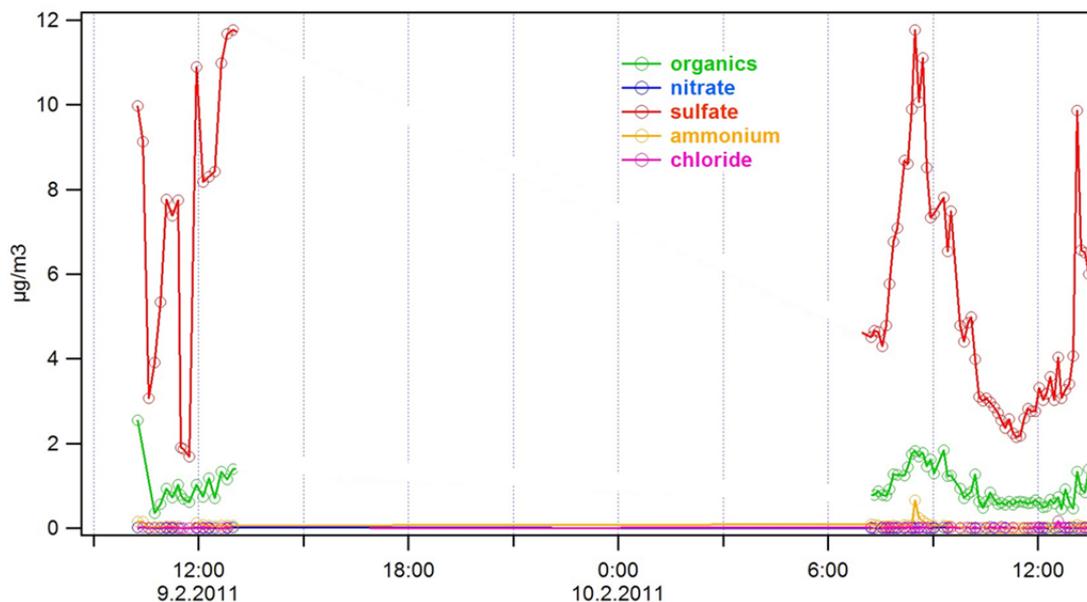


Figure 1. Real-time measurement of particle emissions from heavy fuel oil combustion with the Soot Particle Mass Spectrometer. Data was collected only when the oil burner was operating.

Regarding the chemical composition of particles, the majority of the particle mass was composed of inorganic components in half power conditions (Figure 2). The most abundant compounds were sulfate (63% of mass) and trace elements (25% of mass), e.g. potassium, calcium, sodium, magnesium, aluminum, vanadium, iron and nickel. There was only a small amount of carbonaceous species in the particles with 4% of the mass consisting of organic compounds and 0.7% of black carbon. In full power conditions, the total particle mass concentration was little bit smaller than in half power conditions. With full power, elements comprised larger (35%) and sulfate slightly smaller (61%) portion of the particle mass than with half power. The contributions of organic and black carbon were almost equal with half and full power.

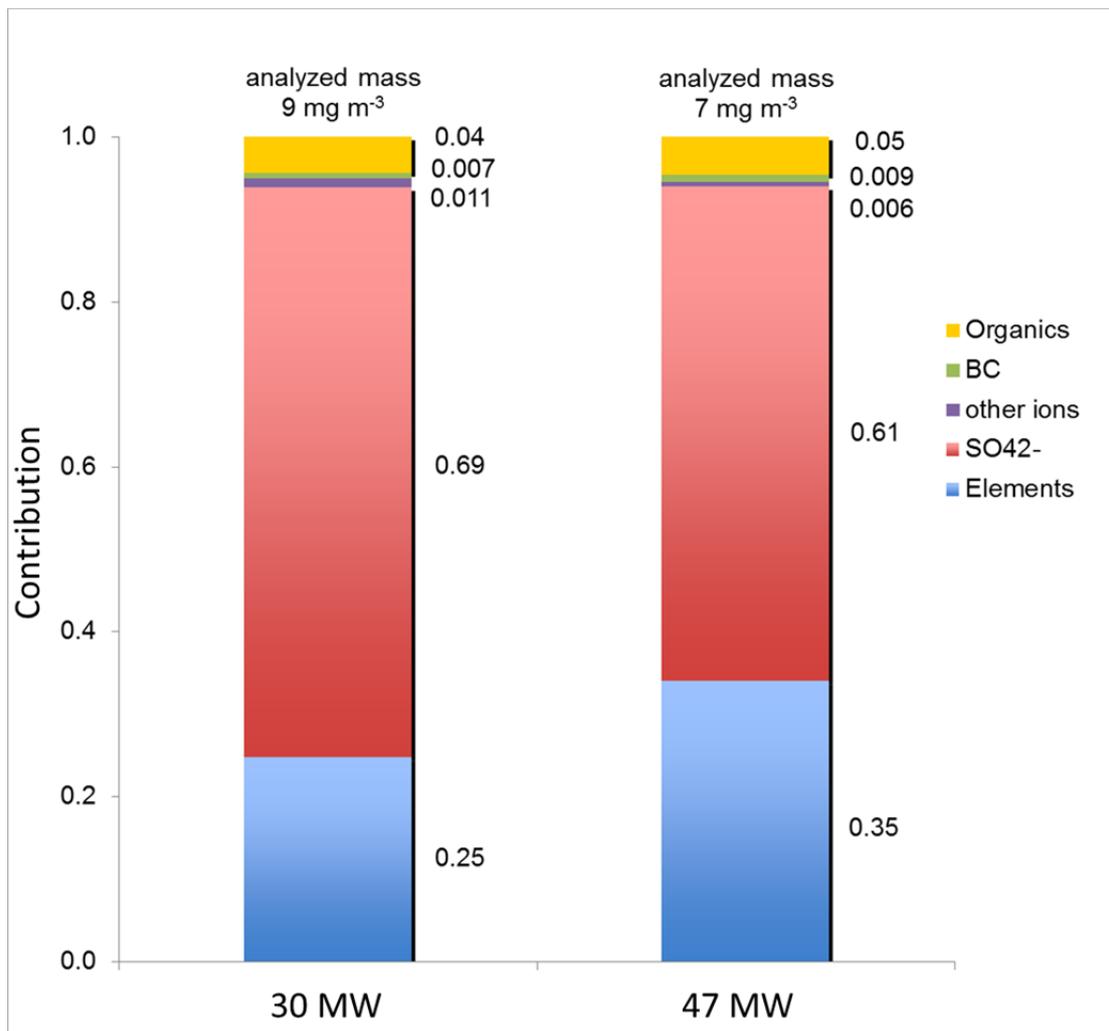


Figure 2. The contributions of elements, sulfate, other ions, black carbon and organics to chemically analyzed particle mass with half and full power. SP-AMS measurements without TD.

The average mass spectrum for the heavy fuel oil combustion particles with half power is shown in Figure 3a. It includes both organic and inorganic components. The mass spectrum only for organics is given in Figure 3b. For organics the highest signals were found for the fragments at m/z 29 ($C_2H_5^+$), 41 ($C_3H_5^+$), 43 ($C_3H_7^+$) and 55 ($C_4H_7^+$) and they had clear hydrocarbon pattern with the difference of 12 m/z 's. That suggests that organics were mostly made of hydrocarbons and it was only slightly oxidized. This is a consequence of the fact that the emissions were very fresh and had had no time to get oxidized. Figure 3c shows the advantage of the high resolution mass spectrum. It presents the separation of vanadium peak (V) at m/z 50.94 from the organic hydrocarbon fragment $C_4H_3^+$ at m/z 51.02 both displayed at the same m/z 51 if only the unit mass resolution data is available (like in Figure 3a).

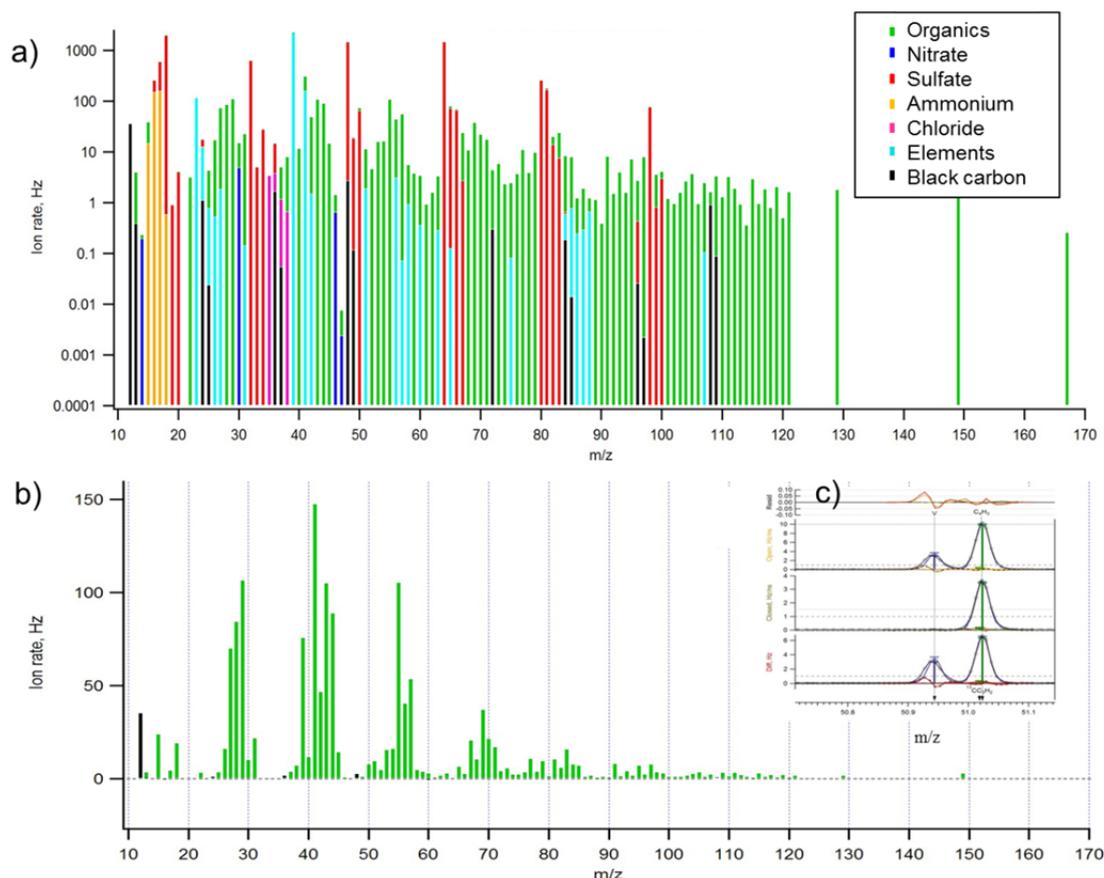


Figure 3. Mass spectra of particles from heavy fuel oil combustion. Total mass spectrum in logarithmic y-axis (a), mass spectrum of organics in linear y-axis (b), and the separation of metal component (vanadium) from hydrocarbon fragment (C₄H₃⁺) (c). SP-AMS measurements without TD.

Volatility characteristics of the particles emitted from the heavy fuel oil combustion were investigated by using a thermodenuder prior to the SP-AMS. TD was used in half power conditions with seven temperature steps: 50, 75, 100, 125, 150, 200 and 250 °C. Particle mass and sulfate concentrations decreased gradually as the TD temperature was increased (Figure 4), except for 150 °C which is an obvious outlier because of unknown reason. At 250 °C mass concentration was ~55% and sulfate concentration ~50% of that at 50 °C. The concentration of organics changed less than that of mass and sulfate with temperature. Organics decreased slightly when TD temperature was increased above 50 °C but in general the concentration had no clear dependence on temperature. The behavior of organics with TD indicated that organic compounds from heavy fuel oil combustion had rather low volatility as they did not evaporate significantly as the temperature was raised. The evaporation behavior of particles was based on the other components than organics (e.g. sulfate). Thermodenuder tests were not performed for full power conditions.

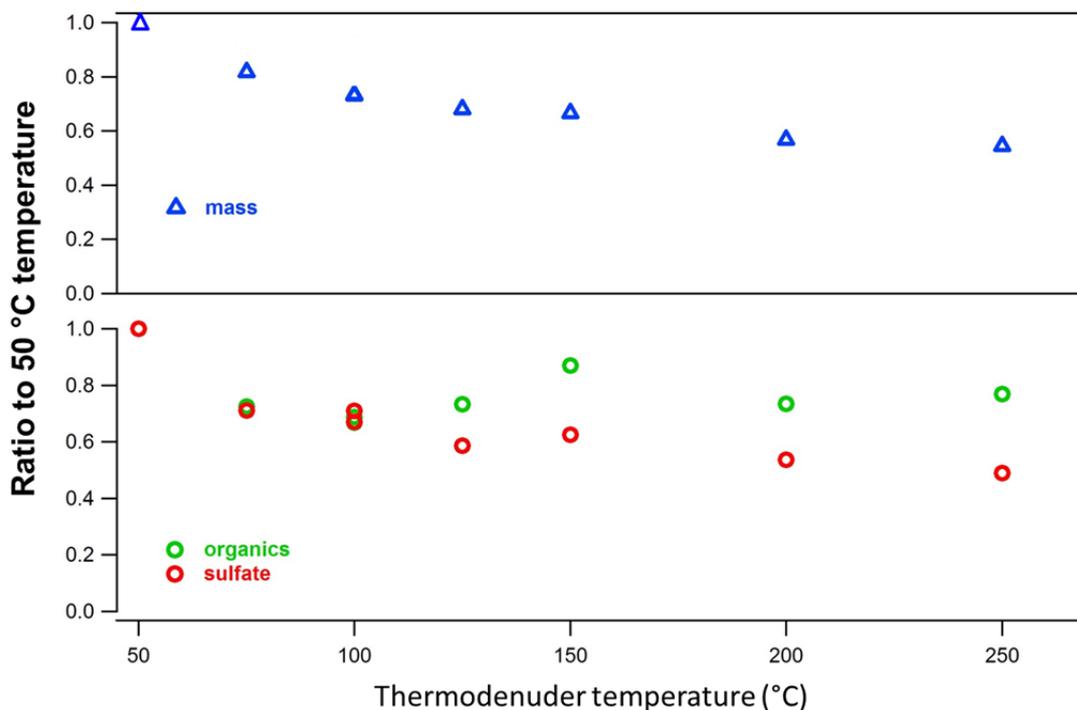


Figure 4. The dependence of mass, organics and sulfate concentrations on thermodenuder temperature. The 150 °C point is an obvious outlier.

4 Conclusions

This study demonstrated that the measurements with a soot particle aerosol mass spectrometer can provide a fast and comprehensive insight into the chemistry of the particles from the heavy oil fuel combustion. Even though the measurements were carried out within a few hours the SP-AMS gave a lot of new information about the chemistry of the particles as well as their volatility.

5 Acknowledgements

This work was supported by the Cluster for Energy and Environment (CLEEN Ltd) Measurement, Monitoring and Environmental Assessment (MMEA) Work package 4.5.2. Sanna Saarikoski acknowledges Academy of Finland for funding (Grant number 259016).

REFERENCES

- 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., Jimenez, J.L. 2006. Field-deployable, high-resolution, time-of-flight mass spectrometer. *Analytical Chemistry*, 78, 8281–8289.
- Onasch, T.B., Trimborn, A., Fortner, E.C., Jayne, J.T., Kok, G.L., Williams, L.R., Davidovits, P., Worsnop, D.R. 2012. Soot Particle Aerosol Mass Spectrometer: Development, Validation, and Initial Application. *Aerosol Science and Technology*, 46, 804-817.



International Flame Research Foundation
The Finnish and Swedish National Committees
Finnish – Swedish Flame Days 2013

Subramanian, R., Kok, G.L., Baumgardner, D., Clarke, A., Shinozuka, Y., Campos, T.L., Heizer, C.G., Stephens, B.B. 2010. Black carbon over Mexico: the effect of atmospheric transport on mixing state, mass absorption cross-section, and BC/CO ratios. *Atmospheric Chemistry and Physics*, 10, 219–237.