INTRODUCTION

Atmospheric aerosol particles comprise a complex mixture of volatile and semivolatile inorganic and organic compounds. The determination of organic compounds in aerosol particles is of great current interest owing to the potential effects of these compounds on human health, cloud formation and the climate in generally (Kulmala, 2004). Although different analytical techniques are nowadays available, the determination of atmospheric organic aerosol composition in sub 50 nm size range remains a challenging task. It includes the complexity of atmospheric aerosol particles within many different possible compounds (McMurry, 2000), the difficulty involved in sampling, and the trace-level concentrations of the compounds. Traditional way is to collect aerosol particles onto filters and remove the compounds from the filter by solvent extraction. One of the main analytical techniques for this kind of analysis has been gas chromatography followed by mass spectrometry (GC-MS) (Feng, 2007, Cincinelli, 2007).

There is growing evidence, moreover that smaller particles can react more rapidly than bigger particles. Many of the studies addressing the organic composition of aerosol particles deal with a mixture of particle sizes collected onto a single filter. However, only few studies have been carried out where nanoparticles of specific sizes been collected and analyzed to determine specific organic compounds. Various aerosol mass spectrometer set-ups have successfully been applied for the analysis of size-segregated organic aerosol particles. Although aerosol mass spectrometry methods are usually chemically non-separative, while they suitable for in situ analysis (Allan, 2006).

The aim of this work was to test our two-step laser desorption ionization aerosol mass spectrometer (Laser AMS) applicability for field measurements in boreal forest site. The idea was to measure particles between 10 and 50 nm and try to determine semi-quantitatively their chemical (organics) compositions. Parallel measurements were done with Aerodyne aerosol MS and with filter samples, collected for chromatographic analysis. The filter samples were used for identification and quantitation of selected organic compounds. Results obtained with these different methods were analyzed and compared. Possible correlations between the results from different techniques were studied with special data analysis software.
METHODS

All measurements were carried out parallel in boreal forest area at SMEAR 2 station in Hyytiälä, Finland, between September 23rd 2009 and October 15th 2009 continuously. All the samples were collected from the same inlet line 5 meters above ground, from the roof of the SMEAR 2 station cottage.

The aerosol mass spectrometer set-up has been presented elsewhere (Laitinen, 2009) and its applicability tested (Laitinen, 2010) in laboratory experiments. Only brief description of the system is given here. The unipolarly charged and size-separated particle flow from ambient air was directed to an oppositely charged polished stainless steel collection surface, which is part of the specially designed sampling valve. The collected sample was introduced to the high vacuum of the mass spectrometer (MS) by rotating the sampling valve. The sample was desorbed from the collection surface with an IR-laser (1064 nm wavelength) and ionized with UV-laser (193 nm wavelength). The ions were then diverted to the TOFMS, separated, and detected according to their m/z ratios.

All the AMS spectra were analyzed on-line and in-situ. Only data analysis was done at later time. The effective mass window (Laitinen, 2010) was varied between 0 to 400 amu in all measurements. The system was used for compound identification and semi-quantitative analysis. The samples were collected with +2.5 kV collection voltage while aerosol flow rate was set to 4 LPM and DMA sheath air flow to 10 LPM. All together 26 samples were collected and analyzed.

Two different types of particles were collected onto quartz filters parallel. One with the size separation (particle diameter set to 50 nm by using a DMA and a bipolar (Am^{2+}) charger) and one without size separation (total sample). Particle flow rate was set to 20 LPM in total sample and 4 LPM in DMA sample. The DMA sheath air flow was set to 10 LPM. The collection time for filters in both cases varied from one day to few days.

The filters were stored at the freezer and analyzed later on the lab. The compounds were removed from the filters with solvent (Acetonitrile:Methanol 50:50) extraction, vaporized with rotavapor to 1 ml and diluted to 5 ml with Methanol. Samples were then analyzed with different chromatographic techniques (LC-MS, GC-MS, GCxGC-MS) according to their chemical groups (Ruiz-Jimenez, 2010).

The data analysis was done by looking similarities on different techniques by using Dataminer program (Data Rangers 1.5.4). Data for different meteorological parameters were added for comparison. The data analysis started by first analyzing the Laser AMS data and then comparing it to all the other data sets.

DISCUSSION

Several ions were detected during the Laser AMS measurements. The ions were grouped as clusters (total of 13 clusters). Their exact masses were measured and some possible ions for most of the cases were suggested. Findings of these measured ions include: aliphatic hydrocarbons, different oxygenated hydrocarbons, aromatic hydrocarbons, oxygenated aromatics, alkyl substituted amine and black carbon. As an example, a spectrum is shown in Fig. 1, where black carbon and some aliphatic hydrocarbon fragments can be seen.
Correlations were found only between the Laser AMS and the filter samples. The best correlations between two different methods were found with 50 nm filter samples and laser AMS, while no correlations were recorded between the AMS and Laser AMS. During the whole measurement period 6 different measurement periods were compared (Laser AMS vs. 50 nm filter). The sampling times were generally longer for filters than with the Laser AMS and to get corresponding sampling times for the comparison some of the Laser AMS samples were added together. Totally 4 different correlation groups were found which one of them was anti-correlation (Fig. 2). In Fig 2 (on top), it can be seen that the ion 143 from laser AMS tend to behave totally opposite to octanal in filter samples. Meanwhile, good correlations were obtained for ion 44 (Laser AMS) and DPA, for ion 57 (laser AMS) with malonic and malic acids, and for ions 126, 140, 142 and 245 (Laser AMS) with maleic and pinonic acid. We tried to seek the reasons for the correlations from the EI mass spectra of the filter sample compounds. We checked the common ions for each compounds in filter samples from the NIST MS-library and compared those to ones that were present in the same correlation group, but we could not find enough matches to be sure what compounds Laser AMS ions represents. Only thing which somehow makes sense is that ion 44 is possibly produced from the DPA. Probable reason for the behavior of the ions and molecules is that the ionization techniques (EI vs. soft photo ionization) are so different that different spectra are then produced. Although, the ions and compounds which are on the same group tended to behave at the same way in these samples, which tells us that these compounds can be from the same source. Additionally, the mass window problem at the Laser AMS can affect to these results.
Figure 2. Correlations found between Laser AMS ions and compounds determined from the 50 nm filter samples. The upper one is anti-correlation between ion 143 and octanal, below that is correlation between ion 44 and dipropylamine, then ion 57 correlation for malonic and malic acids and on the bottom ions 126, 140, 142, 245 correlating with maleic and pinonic acid.

Some correlations were found between total filter samples and Laser AMS. There were totally 9 samples for correlation study. Ions 29 and 43 from Laser AMS seem to correlate with oleic acid, which is understandable, since EI fragmentation of oleic acid will produce those ions. Another correlation was found between the tridecanal and ion 44 in Laser AMS. This result cannot be explained by the ion formation because the ion 44 is not possible from the tridecanal molecule. It is just that these two items tend to behave similarly on the samples.

As a final conclusion: organic compounds were successfully determined from nanoscale ambient particles in boreal forest environment. Different instruments and methods were used for analysis. The chromatographic analysis of filter samples provided best identification of compounds, but the worst time resolution. Laser AMS showed its ability to analyze small nanoparticles in near real time with reasonable collection times. Main findings from particles ≤ 50 nm were black carbon, different hydrocarbons and some amino compounds found on Laser AMS. On the future measurements it is advisable to do all the measurements in same time frame and keep the instrument properties and particle sizes at more comparable range.

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REFERENCES


Ruiz-Jimenez et al. (2010), manuscript in preparation.