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Complementary online aerosol mass spectrometry and offline FT-IR spectroscopy measurements: Prospects and challenges for the analysis of anthropogenic aerosol particle emissions



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HIGHLIGHTS

- Organic aerosol particle types are studied using HR-ToF-AMS and FT-IR spectroscopy.
- Correlations of AMS fragment ions and functional groups are shown.
- Some AMS fragment ions are validated as rather specific markers.
- The prospects and challenges of this integrative analytical approach are discussed.

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ABSTRACT

The aerosol mass spectrometer (AMS) is well established in investigating highly time-resolved dynamics of submicron aerosol chemical composition including organic aerosol (OA). However, interpretation of mass spectra on molecular level is limited due to strong fragmentation of organic substances and potential reactions inside the AMS ion chamber. Results from complementary filter-based FT-IR absorption measurements were used to explain features in high-resolution AMS mass spectra of different types of OA (e.g. cooking OA, cigarette smoking OA, wood burning OA). Using this approach some AMS fragment ions were validated in this study as appropriate and rather specific markers for a certain class of organic compounds for all particle types under investigation. These markers can therefore be used to get deeper insights in the chemical composition of OA based on AMS mass spectra in upcoming studies. However, the specificity of other fragment ions such as $C_2H_4O_2^+$ (m/z 60.02114) remains ambiguous. In such cases, complementary FT-IR measurements allow the interpretation of highly time-resolved AMS mass spectra at the level of molecular functional groups. Furthermore, this study discusses the challenges in reducing inorganic interferences (e.g. from water and ammonium salts) in FT-IR spectra of atmospheric aerosols to decrease spectral uncertainties for better comparisons and, thus, to get more robust results.

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1. Introduction

The chemical and physical characteristics of aerosol particles determine their impact on atmospheric processes, marine and

terrestrial ecosystems (Paytan et al., 2009; Després et al., 2012), the technosphere in urban areas (Faber et al., 2012) as well as on human health (Dockery, 2009). Especially the organic aerosol (OA) fraction is subject to intensive research due to its complex nature and high abundance in submicron particulate matter (PM₁) (Fuzzi et al., 2015).

The aerosol mass spectrometer (AMS) has been well established in characterizing urban, marine and continental non-refractory PM₁ with high temporal resolution during the last decade (e.g. Zorn et al., 2008; Ng et al., 2011). It is capable to measure emission dynamics and processes with high temporal resolution while

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differentiating several types of OA (e.g. Faber et al., 2013). Using statistical tools (Zhang et al., 2011), the contribution of different fragment ions to the total mass of certain types of organic atmospheric aerosols is quantified. Nevertheless, AMS mass spectra of OA are not very specific due to strong fragmentation resulting from flash vaporization and electron ionization. Furthermore, organic aerosol components can undergo oxidation, dehydration and/or decarboxylation reactions inside the AMS ionization chamber (Canagaratna et al., 2015). The capability to draw conclusions from AMS mass spectra on the chemical composition of OA is therefore critical. Liu et al. (2012) found very similar AMS mass spectra for several types of secondary OA whereas complementary FT-IR and mass spectrometric (electrospray, ESI, and atmospheric pressure chemical ionization, APCI) measurements revealed clear chemical differences for these particle types. In addition, inorganics such as carbonates can significantly interfere with OA mass spectra (Faber et al., 2015). Some mass spectral markers have been observed to be associated with a certain class of organic compounds and thus a certain type of OA (e.g. Schneider et al., 2011; Canagaratna et al., 2015). Nevertheless, transferability to other organic particle types remains unclear.

Fourier transform-infrared spectroscopy (FT-IR) has been applied as an alternative (Dillner and Takahama, 2015; Ruthenburg et al., 2014) or complementary (Russell et al., 2009; Kidd et al., 2014; Liu et al., 2012) offline technique for the identification and quantitation of functional groups within OA in several laboratory and field studies. Using appropriate calibrations specific absorption signals can be converted to number of moles of functional groups. FT-IR analyses of atmospheric aerosols are performed mostly on particles sampled onto filters or impaction substrates. Major limitations of this approach are potential chemical artefacts during sampling and storage. In addition, filter sampling is typically performed over several hours (e.g. Hawkins et al., 2010) resulting in a low temporal resolution of the subsequent FT-IR measurements. Highly dynamic temporal structures are typically not reflected in the data. Ambient mass concentrations of OA can finally be calculated from the FT-IR absorption spectra of functional groups based on the ratio of the IR beam area and the total sample area on the substrate and the sampled air volume.

By combining both techniques, Russell et al. (2009) were able to associate several peaks in AMS mass spectra with certain functional groups (e.g. alkanes, alcoholic OH, carboxylic OH) in FT-IR spectra of a few types of typical tropospheric organic aerosols. However, the relative contribution of several fragment ions to a certain m/z which can vary significantly for different types of organic aerosol reveals unclear due to the low mass resolution (unit mass resolution, UMR) of their AMS. For the investigation of atmospheric PM, recent studies combined therefore FT-IR spectroscopy with high-resolution AMS which is capable to distinguish between different fragment ions of the same nominal mass. These studies mainly focused on the quantification of oxidation levels of the organic matter (e.g. Frossard et al., 2014) or on comparing groups of ions from HR AMS measurements with molecular functional groups (Chen et al., 2016). However, no studies on the suitability of individual fragment ions in high-resolution AMS mass spectroscopy as tracers for FT-IR functional groups for different particle types were found in the literature.

For this reason, we extended the approach of Russell et al. (2009) by using high-resolution time-of-flight (HR-ToF)-JAMS data to correlate signals from individual fragment ions in AMS mass spectra with those from selected organic functional groups in FT-IR absorption spectra. In addition, we used aerosol particle types from several emission sources for this study. We also investigated interferences from inorganics when analyzing OA filters by FT-IR. Strategies to remove inorganic interferences in typical continental

and marine aerosols have been described by e.g. Gilardoni et al. (2007) as well as Frossard and Russell (2012). However, when measuring in close proximity to sources, PM_{10} may contain further very specific inorganics such as metals (Faber et al., 2013) and carbonates (Faber et al., 2015) which differ significantly from those of the typical tropospheric aerosol. We therefore discuss possible strategies to overcome interferences of inorganics in the FT-IR spectra of organic aerosol samples from several anthropogenic emission sources.

2. Experimental

2.1. Sampling of aerosol particles

Extending the work of Russell et al. (2009), different aerosol particles types from several anthropogenic emission sources in the urban environment including cigarette smoking, wood burning, cooking (potato frying, barbecuing, nebulized oil), and pyrotechnical devices have been addressed in this study. They were investigated using the mobile aerosol research laboratory (MoLa) which is equipped with numerous instruments for online gas and particle analyses (Drewnick et al., 2012). For this study, a home-made PM_{10} filter sampling system was implemented in MoLa.

PTFE filters (pore size: 1.2 μm ; Sartorius, Germany) were used as sampling substrates due to their insignificant adsorption of water and volatile organic compounds (Ruthenburg et al., 2014) which has been verified by analyzing back-up filters. The sampling time varied from 30 min to 5 h depending on aerosol loadings. The filters have been stored at $-22\text{ }^{\circ}C$ in sealed polystyrene petri dishes and were allowed to warm in a desiccator prior to analysis.

Laboratory standards for the univariate calibration of the FT-IR analysis by correlating absorbance values at specific wave numbers to moles of functional groups were prepared by atomizing aqueous solutions of glutaric acid (for carboxylic OH-groups), levoglucosan (for alcoholic OH-groups), and sodium lauryl sulfate (for CH_3 , CH_2) and sampling the respective aerosols onto filters. Molecules associated with these four functional groups typically represent about 80% of the total organic mass in tropospheric PM_{10} (Russell et al., 2009) and are therefore of high atmospheric relevance (Liu et al., 2012). Filter deposits have been calculated from particle number size distributions (Scanning Mobility Particle Sizer, SMPS Model 3936, TSI, Inc., USA), measured during sampling, specific density and molecular weights of the compounds, sampling time and flow rate, and the number of functional groups per molecule, respectively.

The calibration has been positively validated by FT-IR analysis of citric acid and leucine reference samples. Qualitative filter samples of ammonium sulfate, ammonium nitrate, iron nitrate, and sea salt have been prepared the same way.

2.2. Aerosol mass spectrometry

A thermal desorption aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Res., Inc., USA; DeCarlo et al., 2006) operated in V-mode (mass resolution $R = m/\Delta m$: 2 100 for m/z 200) was used to analyze the chemical composition of the non-refractory PM_{10} with a temporal resolution of 1 min. The principles of AMS data analysis have been described in detail by Canagaratna et al. (2007). Mass concentrations of the AMS species were determined as described by Faber et al. (2013). The uncertainty of the mass concentration of individual ions introduced by the fitting procedure was assumed to be 10% (Canagaratna et al., 2015).

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