FINAL REPORT PROGRAM LEFE

Program LEFE-CHAT	Project Title: Towards a new characterization of organic aerosol formation in the atmosphere (NECTAR)	Years 2019 – 2021

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Context: Fine aerosol particles are ubiquitous in the atmosphere and have important impacts on climate change and air quality. Organic compounds represent the largest mass fraction of fine particulate matter, and their formation is not accurately predicted yet. One of the current limitations is the incomplete understanding of the contribution of oxygenated products to aerosol formation. This lack of understanding is caused by current instrumental limitations precluding the full characterization of the chemical composition and the processes forming aerosol particles.

Objectives / scientific questions: NECTAR aimed at developing novel online couplings consisting in interfacing a new generation of soft ionization systems (i.e., chemical ionization source) with a highly sensitive mass spectrometry technique, based on the Orbitrap technology. With these new methods, we were able to propose an unrivaled characterization of complex gaseous compounds, including the structure of organic condensable species

Main results: The developments realized in this study are based on the Orbitrap technology (i.e., very high mass resolving power: 140 000 at m/z 200). Hence, we developed and produced an 'in-house' interface, i.e., chemical ionization (CI) enabling coupling it to the Orbitrap mass analyzer. As a proof of concept, we analyzed gas-phase OVOC formed during the oxidation of two monoterpenes using nitrate-ion-based (NO_3^-) CI (Riva et al., 2019). We used this chemistry as it has been shown to be highly selective towards atmospheric reactive species such as HOMs. The ultra-high resolving power of the CI-Orbitrap allows unambiguous identification of all ions. The successful capabilities of this coupling opened new collaborations for our group: this system is now in use in 4 other research groups. Additionally, we deployed the instruments during 4 laboratory campaigns (Germany, Switzerland, and at the CERN) as well as one field campaign (Shanghai, 2019). In the initial study, we demonstrated the possibility of interfacing a CI inlet with an ultrahigh-resolution mass spectrometer. Further, by using the MS2 feature of the CI-Orbitrap (Figure 1), novel structural information about HOM was acquired (Riva et al., 2019; Tomaz et al., 2021). This greatly increases the information obtained compared to traditional TOF-based methods, and helped us to characterize the chemistry and, to a certain extent, the physicochemical properties (e.g., volatility) of the compounds of interest.

As atmospheric pressure interface time-of-flight mass spectrometry (CI-APi-TOF) is widely used in the field of atmospheric chemistry, a comparison of the performance in terms of the sensitivity, linearity, and versatility towards different ionization schemes of the newly developed CI-Orbitrap naturally followed. In collaboration with the Leibniz Institute for Tropospheric Research, the first side-by-side comparison between a CI-Orbitrap and CI-APi-TOF, using two different chemical ionization methods, i.e., acetate-ion-based (CH_3COO^-) and ammonium-ion-based ($n\text{-}C_3H_7NH_3^+$) schemes (Riva et al., 2020). Despite the wealth of studies using the Orbitrap technique, little is known about the capability of the Orbitrap in measuring compounds at very low concentrations. The abundance of the main OVOCs, generated from the oxidation of α-pinene, (e.g., $C_{10}H_{14,16}O_x$; $C_{20}H_{30,32}O_x$) and RO_2 radicals (e.g., $C_{10}H_{15,17}O_x$) at nominal masses M, (M + 1) and (M + 2), corresponding to their ^{13}C atom and ^{18}O atom fraction were used. We show that the Orbitrap provides a linear response to ion concentrations as low as ~ 1 ×10^6 molecules cm^{-3}. However, below these concentrations, the Orbitrap mass analyzer nonlinear response yields substantial uncertainties.

While the lack of linearity can be problematic to measure OVOC and organic radicals at atmospherically relevant concentrations, it appeared to be independent of the instrument and the type of reagent ions. This behavior indicates that this instrumental limitation might be overcome to retrieve the “correct” signal strength for peaks with the lowest signal intensity. Indeed, using all measurements from multiple experiments and reagent ions, a function named “sigmoidal correction function” based on a fitting algorithm using a characteristic sigmoidal shape was determined. Therefore, raw normalized signals (corrected for sampling losses) measured with the CI-Orbitrap can be corrected using this “sigmoidal correction function”. By applying this method, all the data were corrected, greatly helping to maintain the good agreement between both techniques. Overall, product signals measured by CI-Orbitrap and the CI-APi-TOF are mostly within a factor of 2 providing a good agreement between these two analytical techniques for concentration ranging from ~ 1×10^5 to 2×10^7 molecule cm^{-3}.

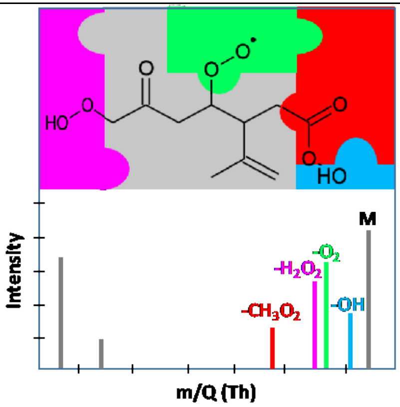

Figure 1.

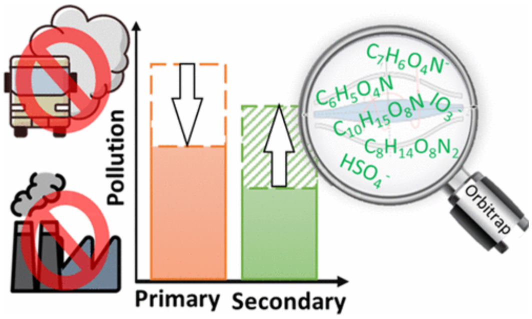

Figure 2.

While the newly developed instruments have demonstrated their unique capabilities to provide key information during laboratory experiments, it is important to deploy new technology during field campaigns to evaluate their performance in very complex systems. Hence the CI-Orbitrap was deployed during the EXPO 2019 in Shanghai (China). We investigated the influence of emission reduction on atmospheric gas-phase chemistry from the molecular level, based on in situ ambient measurement (Zhang et al., 2022). We concluded that the applied emission control was effective in diminishing primary pollution with 20% - 70% efficiency. The total intensity of secondary oxygenated products, however, did not show substantial change (15% decrease in the emission control period). Certain secondary products on contrary have shown an increase up to 50% ~ > 300% with the roared O3 level (> 80% increase). Nonetheless, with even stricter emission control, both O3 concentration and total secondary oxygenated products started to show a decreasing trend, suggesting the importance of strict mitigation strategies in controlling both primary and secondary pollutants towards a cleaner air.

Future of the project: Future developments to allow the chemical characterization of gas and particle phases using the CI-Orbitrap. It will be critical to study the dynamic and processes involved in the formation and growth of atmospheric particles.

Number of publications, communications, and theses

5 publications: Nature Communication (1) (https://doi.org/10.1038/s41467-020-20532-2); Analytical Chemistry (2) (https://doi.org/10.1021/acs.analchem.9b02093; https://doi.org/10.1021/acs.analchem.0c00111); Environmental Science & Technology (2) (https://doi.org/10.1021/acs.est.2c04587; https://doi.org/10.1021/acs.est.1c08346)

Data availablility

Data are available upon request.