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Characterization of Organic Matter in PM_{2.5} sampled on different filter by FTIR and Electrospray ATR-FTIR

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Atmospheric particulate matter (PM) is composed of up to 90% of organic matter [1]. Chemical characterization of PM organic fraction can be achieved by transmission mode Fourier transform infrared spectroscopy (TM-FTIR). FTIR is fast and inexpensive for qualitative and quantitative analysis of functional groups (FG) [2]. However, the applicability of TM-FTIR strongly depends on the filter support properties onto which particles are collected. Indeed, Teflon filters may negatively affect the effectiveness of the technique because of the symmetric and asymmetric stretching of -CF₂ bonds covering the spectral range of 1100-1300 cm⁻¹, and the polymeric matrix causes diffusion of the incident radiation leading to baseline distortion in the 1500 - 4000 cm⁻¹ region. Additionally, high loads of NH₄NO₃ cause the "Christiansen peak effects" - refractive index of the samples matches that of the surrounding medium - which produces an anomalous transmittance of radiation and a distorted absorbance [3]. Moreover, FTIR analysis cannot be directly applied on quartz filters (QF) due to their strong IR absorbance that prevents the radiation source to cross the filter.

In order to overcome these drawbacks, we applied attenuated total reflectance - Fourier transform infrared (ATR-FTIR) spectroscopy on solvent extracts of PM_{2.5} directly transferred onto a ZnSe crystal employing electrospray (ES). The ES-ATR-FTIR technique is characterized by a rapid solvent evaporation favouring the formation of thin films [4]. This enables us to improve the sensitivity and efficiency of the technique obtaining transmission-mode-like spectra of methanol extracted samples characterized by a high solvent/analyte ratio.

In this work, 403 samples of atmospheric PM_{2.5} collected in Zürich-Kaserne site from March 2016 to April 2017 are analyzed using TM-FTIR. The spectra were initially employed to evaluate the FGs composition of PM_{2.5} and the fraction of organic matter (OM) which resulted into an average of 40-50%. Successively, PM_{2.5} co-sampled on QF filters from Zürich-Kaserne site were analysed by ES-ATR-FTIR. The technique was performed on a reduced number of representative samples selected from clusters with different FGs profile. The ES-ATR-FTIR spectra of ambient samples were collected and compared to those obtained by TM-FTIR on Teflon filters. While the OM/OC for each

cluster is comparable to the OM/OC estimated from the Teflon filters, both OM and OC estimates of ATR mode are 40% of the transmission estimates due to the extraction limitation.

Further insights on the PM chemical composition are explored by applying non-negative matrix factorization (NMF) to ATR spectra. Through NMF analysis, inorganic and organic spectral features and their relative contributions are identified and quantified over the year and indicating the contribution of biogenic sources in summer and residential wood burning in winter.

In conclusion, ES-ATR-FTIR enables the acquisition of spectra of PM_{2.5} samples without interference of supporting material. Additionally, further insights on the PM chemical composition due to extended accessible spectral region are discussed.

Bibliography

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