TXRF analysis of ultrafine atmospheric particles from mobile sources

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Particulate emission from ground transportation has two types of sources: exhaust from fuel combustion and non-end-of-pipe emissions like tire debris, brake wear or road abrasion. The nanosize particles are formed by a complicated set of processes like the production of nanometer clusters from vapour phase, the growth of these clusters to detectable sizes and their simultaneous removal by coagulation with the pre-existing aerosol particle population. The ultrafine fraction (PM_1) having highest health impact is difficult to characterize as individual particles since the mass of one particle is very small compared to the sensitivity of EPMA. Other techniques are either too cumbersome or need extremely long sampling time for routine analysis. A special impactor developed for submicron size particle collection results in optimal sample geometry for very efficient TXRF excitation of nanoscopic sampled masses. The sampling time has to be adjusted to the aerosol content at remote or urban areas; it can take one or just a few minutes. Contamination free field sampling and sample storage is crucial part of the method. This unique technique is enabling the observation of fast changing emissions and plumes. Typical application is study of ignition or engine start-up. The impact of micro and mesoscale meteorological variations and mixing can also be investigated.

Submicron fraction of roadside and airport aerosol were analyzed for total elemental composition in the size fractions, as well as for the chemical state of major elements (C, N, S) and trace metals (Cu, Zn) that are typical indicators of brake and tire erosion. XAFS in conjunction with TXRF detection mode was used in order to derive the chemical environment of the selected elements. Two characteristic peaks of C, elemental carbon and carbonate show very different ratios in the size fractions depending on traffic load and distance from road. In accordance with transmission electron microscopy observations the ratio of elemental carbon peak related to soot is decreasing with particle diameter. TXRF-XAFS can not only determine the oxidation state of S but also distinguish the cations connected to sulphate. The size distribution of metal concentrations depends basically on the particle formation processes. Pb and Zn originating from combustion are in the small size fractions, after aging of the particles chemical state of Zn is sulphate and nitrate. Ultrafine particles from traffic contain Cu typically as sulphate.