

XPS analysis of size-segregated aerosol collected in an urban background site in Lecce (Italy)

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Surface chemical composition plays an important role in determining the optical properties of aerosol and its reactivity. Therefore, the determination of surface composition of atmospheric aerosol is an important task because the surface of particles is involved in particle growth/shrink and it may contain chemical species potentially toxic (Klejnowski et al. 2012). Moreover, surface chemistry is dependent on particle size and it is an important feature that may shed light on particulate origin, its reactivity and participation in heterogeneous reactions thus influencing the oxidation state, elemental composition, the formation of functional groups on the surface and the radiative properties that determine the climatic effects (Clarke and Kapustin, 2010). There are many methods and instruments available for studying different properties of the surface of airborne Particulate Matter (PM), ranging from morphology to elemental composition (Cory and Dillner, 2008). X-ray Photoelectron Spectroscopy (XPS) for the chemical surface analysis of PM is not yet a routine method in aerosol characterisation. Nonetheless, in the last years the interest towards the application of this has rapidly grown (Vander Wal et al. 2011). One of the main advantages of XPS relies on the possible identification, in terms of quantification and chemical speciation, of all the elements (except H and He) present on particle surface and segregated in ~10-15 nm depth.

In this work we present an XPS surface study of different size fractions of atmospheric particles. Samples were collected in a background site in Lecce (SE of Italy) in modality "size-segregated", using a 10 stages impactor (MOUDI II, 120R) with rotating collection plates having an inlet with a nominal cut-off at 18 μm and 10 stages with a 50% efficiency cut-off at 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.10 and 0.056 μm . The collection substrates were Al foils (47 mm in diameter) and only a fraction of collected samples were examined by XPS (size 10 mm x 7mm). The other part of the samples were analyzed by high-performance ion chromatography HPIC (Dionex DX600), for determining the content of the main soluble ions, and by catalytic combustion analysis and NDIR detection (Shimadzu TOC-5050 Analyzer) for water soluble organic (WSOC) and inorganic (WSIC) carbon, in the bulk of collected particles. Elemental % (concentrations > 0.1-1%) surface chemical composition was determined for each size fraction with particular attention to S (SO_4^{2-}), Na^+ , N (NH_4^+ , NO_3^- , organic nitrogen) and Cl. Detailed analysis of C1s XPS spectra allowed to distinguish

oxygen-containing groups such as carbonylic, carboxylic, and carbonate groups (e.g. Figure 1). In some cases different hybridisation carbon states $\text{Csp}^2/\text{Csp}^3$ associated to different bonds, probably produced during particle formation, were also discriminated. The average mass size distribution of collected aerosol showed a bimodal shape with an accumulation mode (centred at 0.35 μm) and a coarse mode (centred at 4.5 μm). This work will aim at the systematic evaluation of surface chemical composition of particles of different sizes in order to put in evidence the differences in the surface composition of the two aerosol modes. Further, surface composition will be compared to the water soluble chemical components observed in the bulk of collected aerosol.

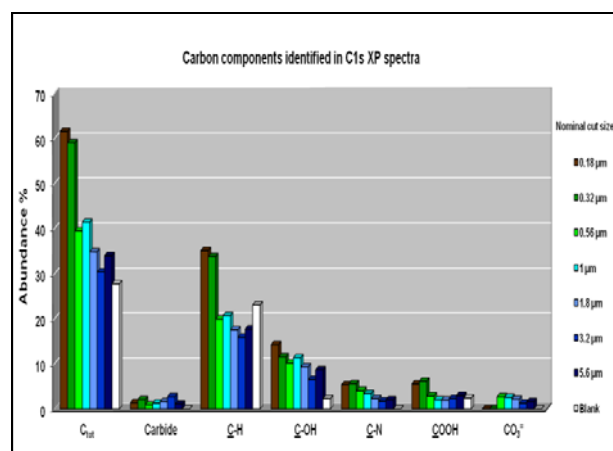


Figure 1. Size-segregated distribution of carbon components identified in C1s XP spectra. The indicated diameters are the geometric mean diameters of the stage analysed.

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