4th Imeko TC19 Symposium on Environmental Instrumentation and Measurements
Protecting Environment, Climate Changes and Pollution Control
June 3-4, 2013, Lecce, Italy

APPLICATION OF XPS SURFACE ANALYSIS FOR CHARACTERIZATION OF SIZE-SEGREGATED PARTICULATE MATTER FROM A URBAN BACKGROUND SITE IN LECCE

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Abstract: Application of X-ray Photoelectron Spectroscopy (XPS) to chemical surface analysis of Particulate Matter (PM) is not yet a routine method in aerosol characterisation. Nonetheless, in the last years the interest towards the potentialities of this technique for PM analysis has rapidly grown. Surface chemical composition plays an important role in determining the optical properties of aerosol and its reactivity. In this communication we present an XPS surface study of different size fractions of PM, suitably collected using a 10-stage MOUDI-II impactor. Results were compared with chemical analysis of water soluble ions and water soluble carbon in the bulk of the collected particles. Elemental % (conc. > 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. Surface and bulk analyses relevant to size fractions characteristic of coarse and accumulation modes will be reported, considering also a particular case of sea spray accompanied to an intrusion of Saharan Dust.

Keywords: MOUDI impactor, XPS, size segregated aerosol, particle surface composition.

1. INTRODUCTION

Heterogeneous atmospheric reactions take place on the surface of particles. Therefore, the determination of surface composition of atmospheric aerosol is an extremely important task because the surface of particles contains chemical species responsible for particle growth as well as potentially toxic compounds [1,2]. Moreover, surface chemistry together with nanostructure are important features 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 [3,4]. In particular, particle modification in terms of composition and structure may lead to multiple evolution pathways. There are many methods and instruments available for studying different properties of the surface of airborne particulate matter, ranging from morphology to elemental composition [5-9].

The use of X-ray Photoelectron Spectroscopy (XPS) for chemical surface analysis of airborne particulate is not a routine method in aerosol characterisation. However, in the last years there has been an increase of interest in applying this surface analytical technique to study the atmospheric particulate. There are several advantages related to the possibility of element identification, their distribution and quantification on particle surface, and of chemical speciation. In particular XPS can provide chemical (speciation) information on the surface of a solid without any particular sample preparation. Moreover, XPS is capable of analysing even insulating samples without any pre-treatment. Additionally, its sensitivity allows detection of surface elements at 0.1-1% atomic percentage (depending on the element) and distinction among the main oxygen-based carbon functional groups and as well as among different oxidation states for other species is also possible [1]. On the other hand, it should be pointed out that XPS allows the characterisation of a near surface region of ~ 10-15 nm for solid materials. It is clear, however, that surface values slightly differ from bulk ones only for chemically homogeneous samples. More often it should be considered that values are averaged over escape depth of the photoelectrons.

It is also worth mentioning the determination of particle surface composition as a function of the average aerodynamic diameters [10] in order to correlate the growth processes involved in the formation of the aerosol [11-13]. Moreover, the aerosol particle size distribution is one of the key variables involved in the analysis of radiative aerosol effects, and, numerous works have examined the spatio-temporal characteristics of particle size distributions with respect to the distribution of anthropogenic sources [14]. Actually, only a few, but significant works are based on XPS studies to correlate surface chemical composition of aerosol particles as sampled on filters and size-segregation thereby giving information on surface properties as function

of particle size. There have been reported different practical applications of this technique for analyses of both "coarse" and "fine" fractions of aerosol [2,13,15-16], even as a complement to scanning electron microscopy coupled with X-ray microanalysis (SEM/EDX) [17-18]. On the other hand, only few XPS studies have been reported on the variation of surface chemistry of aerosol particles as a function of different size classes, ranging between few nm to some hundreds of nm. In fact, most of these works have been applied to the main PM size fractions, PM10, PM2.5 e PM1 [8,13] and little attention has been given to this issue. Differences in chemical composition according to size have been considered for artificially generated aerosol [6] and for atmospheric particles in the diameter range 0.1-20 μm, collected in an industrial area [5].

Advantages of XPS application in PM analytical surface characterisation may be summarised as: 1. surface chemical composition in terms of atomic percent of elements (hetero-elements) different from carbon, as for example Si, S, Na, N, Cl and heavy metals that could be characteristic markers of different sources [1, 5, 19-20]; 2.classification of different functional groups, as for example C-OH, C=O and COOH, based on C1s signal and identified by their relative peak position (Binding Energy, BE) and determination of their relative concentration [1,6]; 3. differentiation of the carbon bonding states between Csp2 and Csp3 which have distinctive BEs, expressed as Csp2/Csp3 content [12, 20-22].

This work will aim at the systematic evaluation of surface chemical composition of different size-segregated particulate matter (PM) samples using XPS and as this is related to the composition of the bulk in terms of soluble ions and carbon content. Results will be used to put in evidence the dependence of the surface composition on the particles size. The chemical information (element quantitative distribution and speciation) of the surface has contributed, in a complementary way on bulk chemical composition, to the recognition of aerosol different sources (including secondary sources) incrementing the knowledge on the mechanisms involved in atmospheric heterogeneous processes.

2. EXPERIMENTAL APPARATUS

XPS spectra were recorded using a Leybold LHS10 upgraded by a PHOIBOS 100 Analyzer/Detector system (SPECS, Berlin, Germany) equipped with a twin anode (Mg K•/Al K•) non-monochromatized source (operating at 140 W). Survey spectra (FRR, B = 30) and detailed spectra (FAT, E_0= 50 eV) for C1s, O1s, S2p, Si2p, N1s, Cl2p, Na1s, Ca2p, Mg2p, and some other metals as for example Fe2p, Cr2p, etc. were collected at 1 and 0.1 eV step intervals, respectively. High-resolution spectra were referenced to the C 1s main component binding energy of the adventitious hydrocarbon at 285.0 eV. For comparison, XPS spectra of Al foil samples were also collected. In all XPS experiments the acquisition of survey scan spectra allowed the identification of elements present on the surface of samples. Afterwards, high resolution (HR) XP spectra of the identified elements has been recorded in the corresponding spectral regions. In this way it has been evaluated the chemical composition of the single sample, thus estimating possible differences between different analysed samples.

The samples analysed have been collected [23] 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 particles have been examined by XPS (size 10 mm x 7mm). The other part of the substrate of the same sample was 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.

3. RESULTS AND DISCUSSION

3.1. XPS Analysis of size-segregated PM

The example reported here referred to a series sampled for 48 h at 30 l/min in March 2011 between the 15th and the 17th. It represented a typical case of sea spray accompanied to an intrusion of Saharan Dust (SD) correlated to a large scale transport from the SW direction. Figure 1 showed the mass size distribution characterised by an accumulation mode (mass median diameter, MMD = 0.37 ± 0.07 μm) which accounts for 15% of PM10 and a coarse mode (MMD = 3.0 ± 0.2 μm) which represents 85% of PM10.

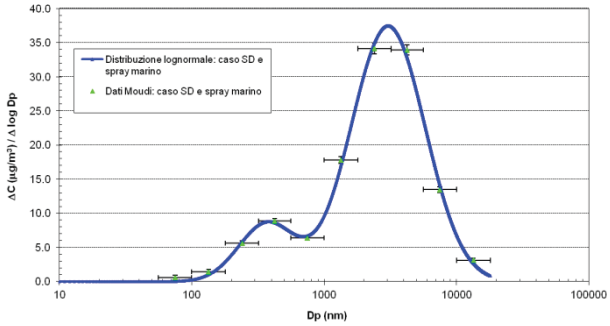

Figure 1. Mass size distribution characterised by an accumulation mode (mass median diameter, MMD=0.37±0.07 μm) which accounts for 15% of PM10 and a coarse mode (MMD=3.0 ± 0.2 μm) which represents 85% of PM10. The blue curve is a fit with two lognormal distributions.

The marine contribution can be calculated, from water soluble ions concentrations, as Sea-Salt = Cl^- + 1.4468 Na^+ [24]. This sample was characterised by a contribution of sea-spray of 44% to the aerosol concentration in the coarse mode (stages S1-S5) and of 9% in the accumulation mode (stages S6-S10). These were significantly larger than the average contribution of sea spray calculated in the full measurement periods (21 samples collected in randomly chosen periods between February and October 2011), namely, 22% (±1%) in the coarse mode and 1.4% in the accumulation mode. XPS analysis performed on collected samples allowed to identify and to quantify the elements

present in the first few nm of surface (an example is reported in figure 2 as comparison between fraction with 1 µm nominal cut size and Al substrate as blank). It results that many elements may be quantified over blank level.

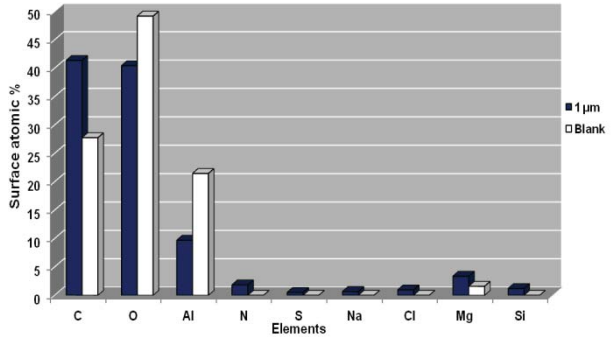

Figure 2. XPS elemental surface comparison between sample • (1 µm nominal cut size) and blank • (Al substrate).

Specific curve-fitting procedures applied to high resolution XPS signals allowed the chemical speciation of some particular elements (C, N, Cl, Na, Si, S) whose superficial abundance is greatly influenced by particle size. The presence of Si is especially remarkable in the coarse mode and it is an indicator of the presence of a significant dust contribution due to the intrusion of African dust.

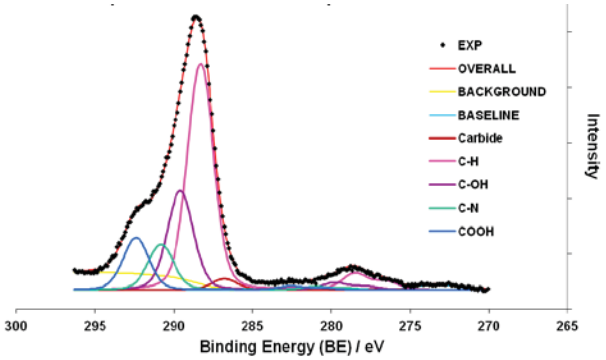

Figure 3. C1s XP spectrum relevant to 0.32 µm nominal cut size.

In figure 3 an example of C1s XP spectrum was reported showing different oxidation states. The detailed distribution of carbon species for all the samples along the series was presented in figure 4.

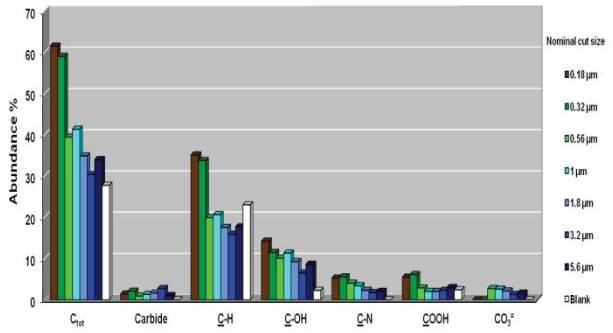

Figure 4. Carbon components identified in C1s XP spectra.

Bulk water-soluble carbon content is shown in figure 5. Carbonates may be associated to crustal contribution which is typical of the limestone composition of the soil of the Salentum peninsula (the area studied) [25]. Their presence was also confirmed by the bulk ionic balance obtained by High Performance Ion Chromatography [23]. Total surface carbon prevails in the accumulation mode and it is mainly present as organic. On the other hand, organic N may be ascribed to secondary aerosol due to combustion.

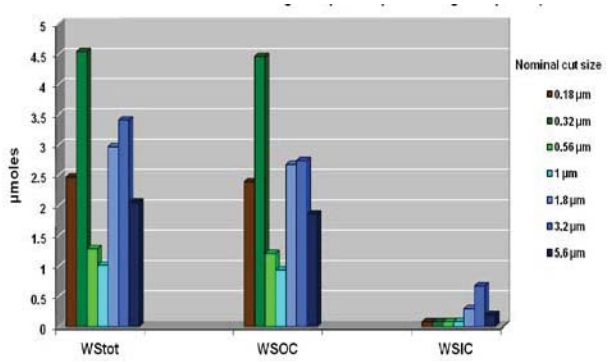

Figure 5. Water-soluble Carbon content: total (WStot), organic (WSOC) and inorganic (WSIC).

From figure 6 it is evident that ammonium was mainly present in the accumulation mode (in association with sulfate, not reported here) and nitrate was mainly present in the coarse mode. The presence of Na^+ and Cl^- was more evident in the coarse mode having a marine origin. Moreover, organic Na, likely as oxalates, may be identified in the fractions below 1µm (data not reported). In figure 7 it was reported the size-dependent concentrations of water soluble ammonium and non-sea-salt-sulfate in the bulk of aerosol, calculated as nss-SO_4^{2-}=SO_4^{2-} - 0.25Na^+ (being 0.25 the typical ratio SO_4^{2-} / Na^+ in sea water [26]). Figure 7 indicated that sulphate was mainly present as ammonium sulphate with a contribution of 56% to aerosol concentrations in the accumulation mode.

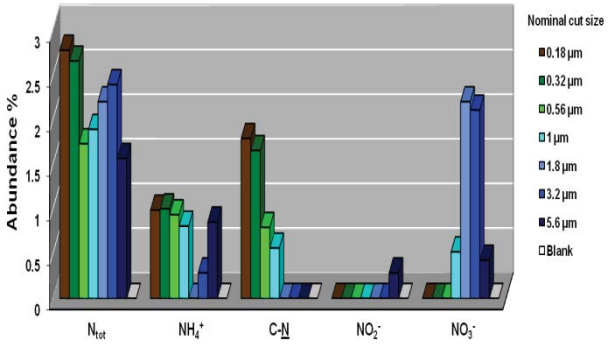

Figure 6. Nitrogen components identified in N1s XP spectra.

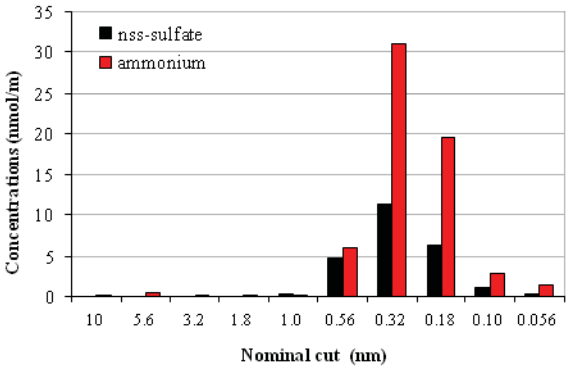

Figure 7. Size-dependent concentrations of water soluble non-sea-salt sulphate and of ammonium.

4. AKNOWDLEGMENTS

The financial contribution of the research laboratory network of the Apulia Region “Applied Innovation Technologies for Diagnosis and Conservation of Built Heritage (A.I.Te.C.H.)”, PO Puglia FESR 2007 – 2013, Asse I, Linea 1.2 - PO Puglia FSE 2007 – 2013 Asse IV, is gratefully acknowledged. Authors wish to thank Dr. C. Elefante (University of Salento) and Dr. F. M. Grasso (ISAC-CNR) for their help in setting-up the measurement campaign.

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