

A microscopic and Synchrotron-based characterization of urban particulate matter (PM₁₀–PM_{2.5} and PM_{2.5}) from Athens atmosphere, Greece

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ABSTRACT

Urban particulate matter (PM₁₀–PM_{2.5} and PM_{2.5}) from Athens (Greece) atmosphere, primarily investigated by SEM-EDS, was further studied in the FLUO and SUL-X beamlines of ANKA Synchrotron facility (KIT, Germany). The SR μ -XRF study showed both geological (e.g. Ca–Ti, Ca–K and Ca–Sr–K–Rb) and anthropogenic particles exhibiting heavy metal combinations such as Fe–Co, Fe–Co–Cu–V and Zn–V. It was also revealed that very hazardous metalloids and heavy metals, namely As and Pb, are concentrated in isolated respirable (PM_{2.5}) microparticles. It was attempted to investigate the oxidation state of As by means of μ -XANES. The As K-edge XANES spectrum of the sample shows a main peak at about 11.874 keV which matches adequately with the As(V) reference spectrum but part of the As seems to have a lower oxidation state (most probably As(III)). This is the first non-bulk study with regard to the partitioning and solid-state speciation of hazardous chemical elements in urban atmospheric microparticles from greater Athens area, rated as an alpha-world city with a population of ca. 4 million people.

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1. Introduction

The greater Athens area, the capital of Greece, is a continuously growing alpha-world city (ca. 4 million people) in the Attica province with serious air-pollution problems. The photochemical cloud, containing a variety of anthropogenic molecules, such as SO₂, which is a hazard to both living organisms and valuable objects, appeared in late 70's as noted by Lalas et al. [1]. Nowadays, almost 40 years later, the Athenian “νέφος” (smog) still remains and measurements for certain gaseous pollutants (SO₂, NO₂, O₃ and CO) are reported on daily basis by the Greek government and particularly by the Ministry for the Environment, Energy and Climate Change. At the same time, the concentration of particulate matter (PM), in $\mu\text{g}/\text{m}^3$, and specifically of PM₁₀ (thoracic fraction), is also reported. There are no certain daily reports for the dangerous PM_{2.5}, representing the respirable fraction, which also should be monitored according to Greek law (Greek Government Gazette (ΦΕΚ) 125A/2002). Concerning the chemical composition of PM, principally towards heavy metals, there are sporadic annual governmental reports, after 2001 referring to the bulk concentrations of Pb in PM₁₀, although according to the Greek law, the concentrations of this pollutant should be

reported on a 3-month basis. Additionally, there are only few brief reports released to the public concerning the bulk concentration of Ni, As and Cd. However, according to European parliament regulations (Directive 2004/107/EC) the above hazardous elements, as well as Hg, have to be seriously monitored in urban atmospheric air. The regulation was adopted by the Greek Legislation in 2007 (ΦΕΚ920B/2007) demanding installation of measurement stations by the Ministry for the Environment and relevant actions in order to decrease the concentrations of As, Cd and Ni in the lowest permissible levels after 31st of December 2012. The recommended analytical methods, according to Appendix V of this law, include AAS and ICP-MS, which are typical bulk techniques, while there is no indication about methods revealing the partitioning (elemental combinations) and solid-state speciation of hazardous chemical elements (determination of oxidation state, e.g. As(III) and/or As(V), Cr(III) and/or Cr(VI), etc.) despite the great toxicity differences. Since 1988, the time that the first study on hazardous metalloids and heavy metals in Athens PM was published by Valaoras et al. [2], almost only bulk analytical data have been presented in the literature [3–11]. In a recent paper by Karageorgos and Rapsomanikis [12] PIXE was used but obviously without a proton microbeam which could provide elemental partitioning information. In addition, Dall'Osto and Harrison [13] implied that current air-quality standards for Athens, as well as for many other European cities, are wrongly based only on particle-size measurements because particles with different constituents may potentially elicit different

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health effects. The above authors gave the first approach to the problem of heavy metals (Cr, Fe, Pb) partitioning in single particles using an aerosol time-of-flight mass spectrometer (ATOFMS). Concerning the speciation of elements in Athens urban particulate matter, it is worth noting the work by Valavanidis et al. [14] who focused on Fe(II) and Fe(III) determination using, however, chemical extraction and not a direct solid-state spectroscopic method. In spite of this, none of the previous authors attempted to resolve the speciation of certain hazardous elements, such as As which is classified as number one in the EPA priority list of hazardous substances, most likely due to technical difficulties and the current absence of relevant Greek and European legislation. Nevertheless, the authorities and the scientific community should draw more attention to the detailed chemical characterization of particulate matter because Athens continues to show very high levels of PM and mainly of PM_{2.5}, together with Bucharest among 22 major European cities, a fact that could cause a significant increase in morbidity and mortality [15]. Finally, it should be mentioned that Synchrotron-based spectroscopic techniques, showing advantageous analytical capabilities in μ -scale, have never been used before the present study for the characterization of urban atmospheric particles from greater Athens area and any other city in Greece.

2. Experimental details

Urban particulate matter (PM₁₀–PM_{2.5} and PM_{2.5}) was collected in Athens atmosphere, in Autumn 2008, during non-rainy days without desert dust and/or other atmospheric episodes, using a Partisol®-Plus Model 2025 Sequential Air Sampler and a Partisol®-FRM Model 2000 PM_{2.5} Air Sampler (Rupprecht & Patashnick Co., Inc.) and appropriate quartz fibre filters. Thus, the materials investigated in the present study represent the “background” of Athens atmosphere (apparently clear) in respect of suspended solid microparticles. A part of the samples was initially subjected to Scanning Electron Microscopy examination (Jeol JSM-5600 SEM equipped with an Oxford EDS). The subsequent Synchrotron-radiation micro-X-ray Fluorescence study (SR μ -XRF), aiming to elemental mapping and elucidation of hazardous metalloids and heavy metals partitioning, was performed in the FLUO beamline of ANKA Synchrotron facility (KIT, Germany) using an excitation energy of 17.5 keV [16]. Special emphasis, besides V which is entirely associated to anthropogenic combustion emissions, was given to As and Pb which are always classified in the top five of the EPA priority list of hazardous substances. Certain microparticles of the respirable fraction (PM_{2.5}) showing As, were further studied in the SUL-X beamline of ANKA [17] by means of SR μ -XRF in combination with μ -XANES spectroscopy (As₂O₃ and As₂O₅ were used as reference materials of As(III) and As(V) whereas the spectra were processed by Athena software [18]).

3. Results and discussion

The initial SEM-EDS investigation of Athens urban particulate matter (the considered atmospheric “background”) showed an abundance of particles of various morphologies and chemical composition, especially in the case of PM₁₀–PM_{2.5} (coarse) fraction. The most characteristic particles of geological origin concern CaCO₃ (calcite) whereas hexahedral NaCl microcrystals, most probably from the effect of the sea, are also frequent. In addition, there are aggregates of PM₁₀–PM_{2.5} particles containing Ca–Mg–S–Cl, according to EDS spectra, which possibly correspond to natural mixed sulfate–chloride salts of alkaline earths. Phosphates of alkalis (Na–P in the EDS) are also present. On the other hand, the anthropogenic microparticles are predominantly represented by common spongy carbonaceous microspherulites, due to multiple

combustion sources, exhibiting an average diameter of ca. 20 μ m. The most common heavy metal in PM₁₀–PM_{2.5} is iron appearing in the form of single Fe oxide (Fe and O in the EDS spectra), Fe–Cr, and Fe–Cu microparticles (Fig. 1). More complex aggregates, of potential mixed natural and anthropogenic origin, consist of Fe–Cr–Cu–Mn–Ca. Iron itself is not considered to be toxic but when Fe-ions are released from urban particulate matter in aqueous media they can generate dangerous hydroxyl radicals (HO^{*}) [14]. In particular, Fe(II) is known as redox active and through reactive oxygen species (ROS) may cause DNA damage in the lung tissues. Soluble iron in Athens PM is mainly related to diesel exhaust particles (DEP) [14] and therefore to traffic pollution attributed principally to heavy vehicles. However, Fe–Cr and Fe–Cu particles should represent alloys and thus, in the present case, the availability of soluble Fe must be low. A microparticle composed of Cu–Zn was additionally detected in PM₁₀–PM_{2.5} as well as an isolated larger Sn particle (Fig. 1). Except tin, copper and zinc are heavy metals which are also considered to be anthropogenic and moreover the Cu:Zn ratio can be used to distinguish traffic and industrial emissions [19]. Concerning the PM_{2.5} fraction, which corresponds to respirable matter and subsequently is more important for health effects, the SEM-EDS investigation (Fig. 1) indicated microparticles containing only Fe and Fe–Mn (most likely Fe and Fe–Mn oxides) while there were no results for any other heavy metal and/or metalloid referred to previous bulk studies [3,5,9,10].

The SR μ -XRF study of PM₁₀–PM_{2.5} confirmed the existence of Ca-containing microparticles which could possibly be calcite (CaCO₃) due to the geology of Athens area (hills and surrounding mountains composed of limestone and marbles). However, the existence of non-geological Ca-compounds, such as Ca oxides, cannot be excluded. More microparticles of geological origin may be those containing K and Ca–Ti. Concerning the anthropogenic particles it was found that Fe–Cr microparticles, detected in few cases

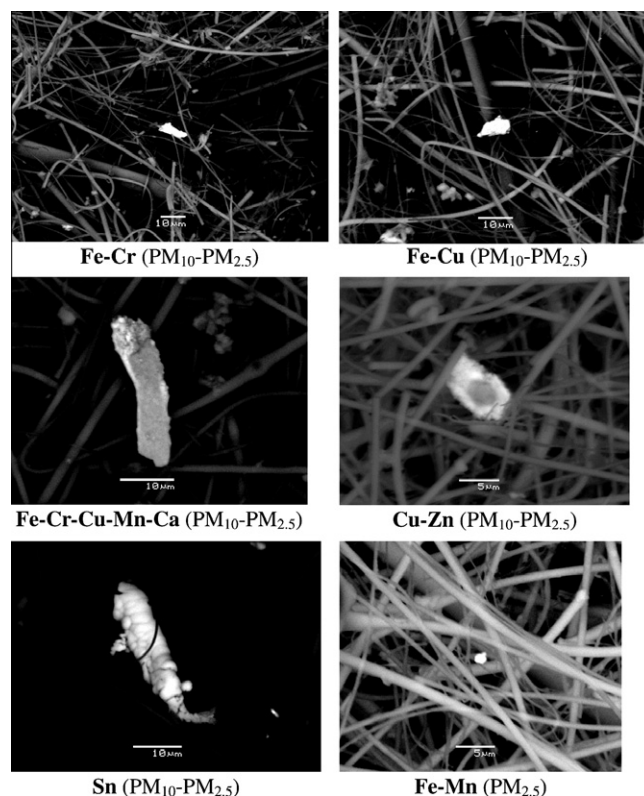


Fig. 1. Selected SEM-EDS data about urban particulate matter (PM₁₀–PM_{2.5} and PM_{2.5}) from Athens atmosphere, Greece, as deposited on quartz fiber filters.

by SEM-EDS, are in fact infrequent whereas Fe (Fe oxide) microparticles are indeed common containing supplementary Co (Fe–Co). The Fe–Cu microparticles, also recorded by SEM-EDS, contain additional Co and V (Fe–Cu–Co–V) and in some cases Ni (Fe–Cu–Co–V–Ni). Moreover, there are few microparticles of Fe–Co–Ni–Cr–Zn as well as notable cases of isolated Zn, Pb and As microparticles. It should be emphasized that Cu–Zn microparticles, except the one found by SEM-EDS, were not localized in the samples. It can be therefore stated that Cu and Zn are not generally correlated in Athens PM, in contrast to opposite arguments from previous bulk studies. As a conclusion, the most frequent elemental combinations concerns Fe–Co and Fe–Co–Cu–V. Copper and zinc (Cu–Zn) are also uncorrelated in the Athens PM_{2.5} whereas iron and cobalt (Fe–Co), again, commonly coexist in microparticles (Fig. 2). Additionally, there are Fe–Co–Cu microparticles, as in the case of PM₁₀–PM_{2.5}, but without V. Thus, the SR μ -XRF study revealed that vanadium, emitted by combustion of fossil fuels [20], shows a different behavior in the PM_{2.5}, respirable, fraction and is predominantly correlated to zinc (Zn–V, see Figs. 2 and 3). In some cases there are few particles containing Zn–V–Ti. Crude oils, and especially heavy crude oils, are rich in organically bound V, mainly in the form of vanadyl (VO²⁺)-porphyrin complexes [21]. As a consequence PM_{2.5} from oil combustion, examined by HRTEM/EELS techniques [22], were found to contain V oxides (mostly V₂O₅), sulfates (e.g. VOSO₄· χ H₂O), phosphates ((VO₂)₂P₂O₇) as well as various vanadates (such as CaV₃O₇ and Ni₃(VO₄)₂). On the other hand Zn, in the form of Zn-dithiophosphate, is a standard anti-wear and anti-oxidant oil additive [23]. The Zn–V microparticles detected in the present study could be mixed oxides and/or sulfates. However the presence of Zn vanadates (Zn₃(VO₄)₂· χ H₂O) cannot be excluded. In PM_{2.5} Cu (added as antioxidant) exists in isolated microparticles (Fig. 2) as well as in Cu–Cr–Fe (Fig. 3). The behavior of Ni in PM_{2.5} is also different, existing solely in a few microparticles. Manganese is partly related to Fe (as concluded complementary by SEM-EDS, see Fig. 1) and additionally to Co (Fe–Co–Mn) though there are many independent Mn-containing microparticles (Fig. 2). Besides natural Mn, the sources of anthropogenic Mn may numerous including the industrial activities and gasoline additives (methylcyclopentadienyl manganese tricarbonyl/MCMT, (CH₃C₅H₄)Mn(CO)₃). The PM_{2.5} particulate matter of geological origin is represented by Ca–K, Ca–K–Sr and Ca–Sr–K–Rb microparticles (Fig. 2). What is common in all types of particulate matter studied by means of Synchrotron radiation concerns the isolated microparticles of Pb and As which are not related to other heavy metals (Table 1). Lead, originating to both fuel

combustion (tetra-ethyl lead/TEL, (CH₃CH₂)₄Pb which is a common antiknock additive in gasoline) and the industry, and arsenic, originating also to fuels (particularly in fine particles) and the industry, are extremely hazardous chemical elements. Lead in the recorded isolated microparticles most likely appears in the form of the divalent oxide (PbO) while arsenic may also occur as oxide. In order to elucidate the speciation of As, and conclude if As(III) or As(V) compounds are formed, direct solid-state information was obtained using μ -XANES spectroscopy. The As K-edge XANES spectrum of the sample shows a main peak at about 11.874 keV and a shoulder slightly above 11.870 keV (Fig. 3). Comparison with reference spectra showed that the main peak at higher energies matches with the position of the whiteline of the As(V) reference spectrum. The whiteline of the As(III) reference is located at somewhat lower energies than the shoulder meaning that the As(III) reference compound chosen here does not sufficiently represent the sample As(III) which complicates the determination of the As(V)/As(III) ratio by linear combination of the reference spectra here. Because several fluorescence mappings have been performed prior to the XANES measurements redox reactions due to beam irradiation cannot be completely excluded. But in a series of about 20 XANES scans the shape of the XANES spectra remains constant within the noise level of a single scans. According to the above data, isolated As-containing microparticles in the Athens PM_{2.5} (respirable) fraction correspond mainly to As(V)-oxides such as As₂O₅ or even to peculiar arsenate (containing AsO₄³⁻) compounds. According to Sánchez-Rodas et al. [24], who used indirect chemical extraction methods, PM₁₀ samples from the city of Huelva (S.W. Spain) contain both As(V) and As(III) due to local industrial activity (e.g. copper smelter) coupled the atmospheric circulations. It is notable that the above authors emphasized the importance of As speciation in PM in contrast to current EU air quality Directive 2004/107/CE (related to Greek Φ EK920B/2007) which strangely considers only the bulk As content despite great toxicity difference between As(III) and As(V). On the other hand, Huggins et al. [25,26], using direct Synchrotron-based techniques (XANES), concluded that NIST Diesel PM SRM and coal-derived PM contain more than 97% As(V). However, NIST Urban SRM, showing a small shoulder on the low-energy side of the main peak in the As K-edge XANES spectrum (like in the present study) may contain about 10% of As(III). Thus, the small presence of the much more toxic As(III) in Athens PM_{2.5} cannot be entirely excluded. The main sources of As may be traffic (mostly diesel exhaust particles/DEP from local vehicles), exhausts of residential central heating and to a smaller extent industrial activity (maybe coal-burning power plants). The present

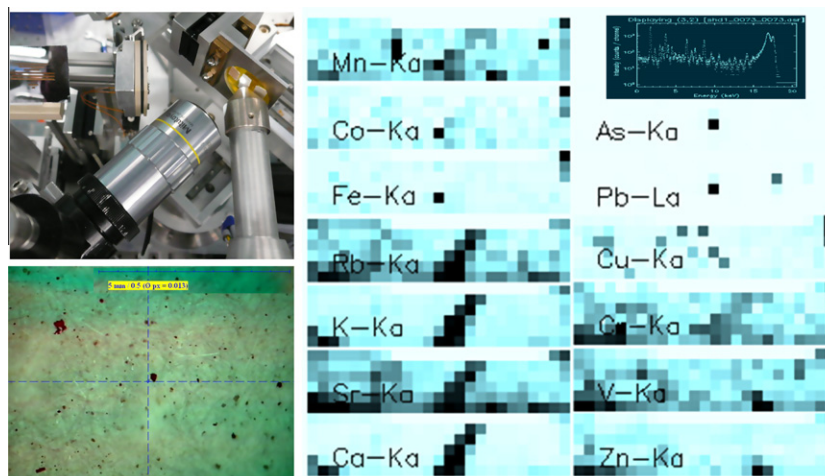


Fig. 2. Representative data from Synchrotron μ -XRF investigation (FLUO beamline) of the respirable fraction (PM_{2.5}) of Athens urban particulate matter. Elemental maps correspond to an area of 80 × 80 microns and resolution of 3.2 × 13.3 microns.

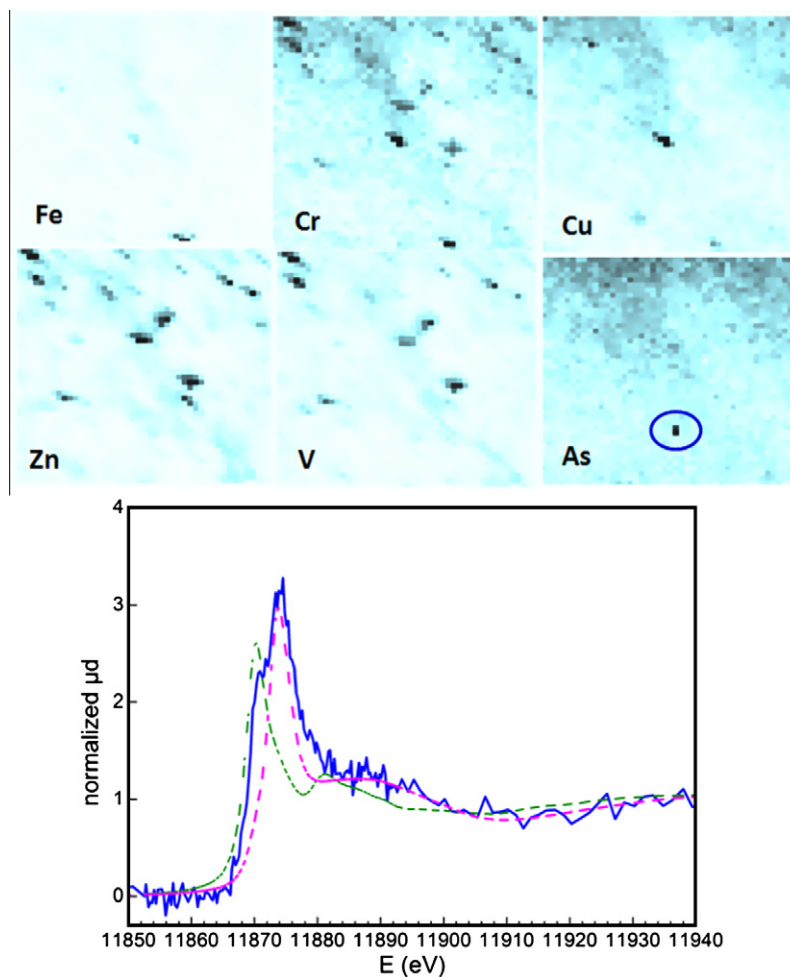


Fig. 3. Synchrotron μ -XRF maps (1.5×1.5 mm, resolution 33×33 microns) and As K-edge micro-XANES spectra (SUL-X beamline) of the As hot spot detected in Athens urban particulate matter (PM_{2.5}). The dash-dotted line is the spectrum of an As(III) reference compound (As₂O₃), the dashed line represents an As(V) reference compound (As₂O₅). Energy has been calibrated to the first derivative of the Au-*L*_{III} edge (11.919 keV).

Table 1
Summary of the results obtained for Athens particulate matter.

Particle size/ method	SEM-EDS	SR μ -XRF and μ -XANES
PM ₁₀ -PM _{2.5} (coarse fraction)	Ca, Ca-Mg-S-Cl, Na-P, C, Fe, Fe-Cr, Fe-Cu, Fe-Cr-Cu-Mn-Ca, Cu-Zn, Sn	Ca, K, Ca-Ti, Fe-Co, Fe-Cu-Co-V, Fe-Cu-Co-V-Ni, Fe-Co-Cu-Ni-Cr-Zn, Zn, Pb, As
PM _{2.5} (respirable fraction)	Fe, Fe-Mn	Ca-K, Ca-K-Sr, Ca-Sr-K-Rb, Fe-Co, Fe-Co-Cu, Zn-V, Zn-V-Ti, Cu-Cr-Fe, Fe-Mn, Fe-Co-Mn, Mn, Ni, Pb, As(V)

first non-bulk approach to the partitioning and solid-state speciation of As in urban microparticles, can be the basis for further research by governmental and academic groups to fully clarify the behavior of this chemical element in the atmosphere of greater Athens area.

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References

- [1] D.P. Lalas, V.R. Veirs, G. Karras, G. Kallos, *Atm. Environ.* 16 (1982) 531.
- [2] G. Valaoras, J. Huntzicker, W. White, *Atm. Environ.* 22 (1988) 965.
- [3] P. Sceff, C. Valiozis, *Atm. Environ.* 24A (1990) 203.
- [4] A. Koliadima, A. Athanasopoulou, G. Karaiskakis, *Aerosol Sci. Technol.* 28 (1998) 292.
- [5] N. Thomaidis, E. Bakeas, P. Siskos, *Chemosphere* 52 (2003) 959.
- [6] G. Kaniias, L. Viras, A. Grimanis, *J. Rad. Nucl. Chem.* 256 (2003) 451.
- [7] G. Kaniias, L. Viras, A. Grimanis, *J. Rad. Nucl. Chem.* 260 (2004) 509.
- [8] N. Manalis, G. Grivas, V. Protonotarios, A. Moutsatsou, C. Samara, A. Chaloulakou, *Chemosphere* 60 (2005) 557.
- [9] A. Valavanidis, K. Fiotakis, Th. Vlachogianni, E. Bakeas, S. Triantafyllaki, V. Paraskevopoulou, M. Dassenakis, *Chemosphere* 65 (2006) 760.
- [10] A. Karanasiou, I. Sitaras, P. Siskos, K. Eleftheriadis, *Atm. Environ.* 41 (2007) 2368.
- [11] Ch. Vassilakos, D. Veros, J. Michopoulos, Th. Maggos, C.M. O'Connor, *J. Hazard. Mater.* 140 (2007) 389.
- [12] E. Karageorgos, S. Rapsomanikis, *Atmos. Chem. Phys.* 7 (2007) 3015.
- [13] M. Dall'Osto, R.M. Harrison, *Atm. Environ.* 40 (2006) 7614.
- [14] A. Valavanidis, A. Salika, A. Theodoropoulou, *Atm. Environ.* 34 (2000) 2379.
- [15] E. Boldo, S. Medina, A. LeTertre, F. Hurley, H.-G. Mücke, F. Ballester, I. Aguilera, D. Eilstein on behalf of APHEIS group, *Eur. J. Epidemiology* (2006), doi:10.1007/s10654-006-9014-0.
- [16] R. Simon, G. Buth, M. Hagelstein, *Nucl. Instrum. Methods B* 199 (2003) 554.
- [17] J. Göttlicher, R. Steininger, R. Simon, 12th European Conf. on X-Ray Spectrometry (EXRS 2006), Paris, F, June 19–23, 2006.
- [18] B. Ravel, M. Newville, *J. Synchrotron Radiat.* 12 (2005) 537.
- [19] McK.C.H. Lim, G.A. Ayoko, L. Morawska, *Atm. Environ.* 39 (2005) 463.
- [20] E.R. Sholkovitz, P.N. Sedwick, Th.M. Church, *Geochim. Cosmochim. Acta* 73 (2009) 3981.
- [21] G.M. Mastoi, M.Y. Khuhawar, R.B. Bozdar, *J. Quant. Spectr. Rad. Trans.* 102 (2006) 236.

- [22] Y. Chen, N. Shah, F. Huggins, G.P. Huffman, Environ. Sci. Technol. 38 (2004) 6553.
- [23] S.H. Cadle, P.A. Mulawa, E.C. Hunsager, K. Nelson, R.A. Ragazzi, R. Barrett, G.L. Gallagher, D.R. Lawson, K.T. Knapp, R. Snow, Environ. Sci. Technol. 33 (1999) 2328.
- [24] D. Sánchez-Rodas, A.M. Sánchez de la Campa, J.D. de la Rosa, V. Oliveira, J.L. Gómez-Ariza, X. Querol, A. Alastuey, Chemosphere 66 (2007) 1485.
- [25] F.E. Huggins, N. Shah, G. Huffman, J.D. Robertson, Fuel Proc.Technol. 65–66 (2000) 203.
- [26] F.E. Huggins, G.P. Huffman, W.P. Linak, C.A. Miller, Environ. Sci. Technol. 38 (2004) 1836.