ESRF	**Experiment title:** Characterization of road traffic non-exhaust emission sources by XAS techniques: the relevance of Zn and Cu as specific tracers	**Experiment number**: 08-01-981
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Report:

Abstract: in this experiment we investigated road dust samples collected along the bridge that connects Venice (Italy) to the mainland. The samples are composed of particles originating from natural sources as well as other non-exhaust source such as tire, brake and asphalt wear, and, along with other elements, such as Fe, they contain significant amount of Cu, Zn, and Sb. The aim of the experiment was to unravel the speciation of Cu, Zn, and Sb in the samples by the means of x-ray absorption spectroscopy (XAS).

Experiment: the Cu and Zn K-edge, and the Sb L_3-edge were measured using 311 monochromator crystals to obtain absorption spectra with good resolution. The samples were measured in vacuum at 80K to avoid possible beam-induced modifications in their redox state and to enhance the quality of the extended part of the spectra (EXAFS). Due to the high dilution of the elements under analysis, fluorescence acquisition were performed using a solid state multi-element detector. Several standards were measured in transmission mode for comparison with the samples' spectra, namely: Sb_2O_3, Sb_2O_4, Sb_2O_5, Sb_2S_3 at the Sb edge, $(ZnCO_3)_2$-$(Zn(OH)_2)_3$, $Zn(NO_3)_2$-xH_2O, $ZnSO_4$-$7H_2O$, ZnS, ZnO at the Zn edge, and $CuCO_3$-$Cu(OH)_2$, $CuSO_4$, $Cu(NO_3)_2$-$3H_2O$, CuO, Cu_2O, CuS at the Cu edge. Cu, Zn, and Sb metallic foils were used for precise energy calibration at the corresponding absorption edges.

Preliminary results: Due to the high dilution of the elements under analysis the extended part of most of the spectra resulted very noisy, and information from EXAFS analysis can be obtained on a limited number of samples. Therefore, preliminary analysis focused on the XANES part of the spectra, and, in particular, on its

comparison with the XANES spectra of the standard compound acquired. This procedure was carried out both by fingerprint analysis and by performing linear combinations of the standard compounds to reproduce the experimental spectra. The latter procedure was carried out using the IFEFFIT software package [1].

Some of the best linear combination fit (LCF) obtained at the Cu, Zn, and Sb edges are shown in **Figure 1** and the corresponding speciation is reported in **Table 1**.

Probably due to the lack of one or more relevant standards, at the Zn edge it was possible to retrieve the speciation of only few samples. The spectra acquired at the Sb edge, on the other hand, suffer of the limited resolution, which makes difficult determining the speciation by LCF.

Preliminary results are compatible with the results of XPS analyses performed on the same samples and reported by our group in a recently published paper [2].

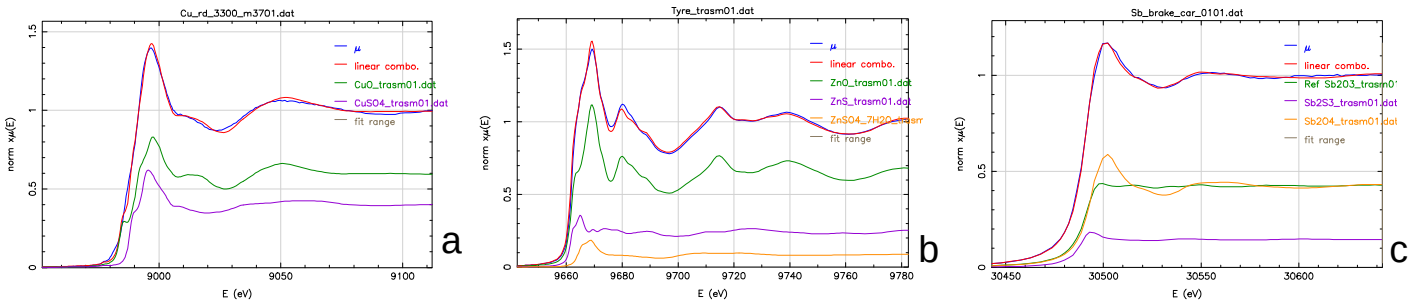

Figure 1. Linear Combination Fits (LCF) of the XANES spectra of selected samples at the Cu (a), Zn (b), and Sb (c) edges. The corresoponding relative proportion of the standards used to reproduce the experimental spectra are reported in **Table 1**.

Table 1. Relative fractions (in wt%) of the standard compounds in some selectect samples (road dust, car tyre, car brake) as calculated from linear combination fitting. The corresponding plots are reported in panels a, b, and c in Figure 1 respectively for samples road dust, car tyre, and car brake. The error on the reported values was estimated to be about 10%, therefore species occurring in amount < 5% were neglected.

Edge	Road dust	Car tyre	Car brake
Cu	60 CuO		
	40 $CuSO_4$		
Zn		67 ZnO	
		24 ZnS	
		9 $ZnSO_4$	
Sb			31 Sb(0)
			31 Sb_2S_3
			38 Sb_2O_5

References

(1) Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* **2005**, *12* (Pt 4), 537–541 DOI: 10.1107/S0909049505012719.

(2) Valotto, G.; Rampazzo, G.; Visina, F.; Gonella, F.; Cattaruzza, E.; Glisenti, A.; Formenton, G.; Tieppo P. Environmental and traffic-related parameters affecting road dust composition: a multi-technique approach applied to Venice area (Italy). On press on *Athmospheric Environment*.