

Copper speciation in size-fractionated aerosol samples using TXRF-XANES

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The health effects of aerosol depend on the size distribution and the chemical composition of the particles. Heavy metals of anthropogenic origin are connected to the fine aerosol fraction (PM_{2.5}). The composition and speciation of aerosols can be variable in time, due to the time-dependence of anthropogenic sources as well as meteorological conditions. Synchrotron-radiation total-reflection X-ray fluorescence (SR-TXRF) provides very high sensitivity for aerosol characterization [1]. X-ray absorption near-edge structure (XANES) spectrometry in conjunction with TXRF detection can deliver speciation information on heavy metals in aerosol particles collected directly on the reflector surface. The suitability of TXRF-XANES for zinc speciation in size-fractionated aerosols from a short sampling period was previously tested. Information on Zn speciation could be obtained from air concentration of Zn as low as 100 pg/m³ for a 20-min sampling time in the 0.5-1 μm aerosol fraction [2]. The measurements were extended to speciation of copper, another environmentally important element.

Aerosol samples were collected on silicon wafers at different urban and background locations in Hungary using a 7 stage May cascade impactor [3], with aerodynamic cut-off diameters of 2, 1, 0.5 and 0.25 μm at stages 4, 5, 6 and 7, respectively. The collected particles are deposited on the silicon reflectors as a thin strip with approximate dimensions of 20 mm × 0.3 mm. In addition, soil samples collected from the neighbourhood of the aerosol sampling sites were resuspended and deposited on silicon wafers with May-impactor.

The measurements were performed at HASYLAB Beamline L using the TXRF vacuum chamber [4]. The white beam of a bending magnet was monochromatized by a Si(111) double monochromator. The vertical dimension of the beam was set to 0.5 mm. The absorption spectra were recorded in TXRF mode, tuning the excitation energy near the K absorption edge of Cu by stepping the Si(111) monochromator, while recording the Cu-Kα fluorescent yield using an energy-dispersive Radiant silicon drift detector. The used energy step size varied between 0.5 (edge region) to 2 eV (more than 50 eV above edge). CuSO₄ containing particles deposited to Si wafers using the May-impactor as well as Cu(NO₃)₂ and CuSO₄ prepared using a nanoliter injector were used as standards. The measuring time for each energy point varied from 5 s to 30 s depending on the concentration of the element of interest. Cr standards having a known mass in dimensions identical to the deposited aerosol particles could be used for calculating the copper concentration in the samples.

As an example, Figure 1 shows (TXRF-)XANES spectra of Cu standards, as well as an aerosol sample set and a soil sample originating from the airport of Budapest (Hungary). The fine aerosol fractions (< 2 μm) contained Cu mostly as sulfates. By comparison, Zn was present as a mixture of sulfates and nitrates in this aerosol fraction [2]. Although the Cu concentration near the runway was six times higher than at the terminal on the same day (59 and 10 ng/m³, respectively) [1], the speciation of Cu in the fine fraction was found to be the same at the two sites. The TXRF-XANES spectrum of the neighbouring soil (< 4 μm fraction) reveals that Cu is present as a mixture of Cu(II) compounds, mostly CuCO₃ and CuO. Coarse (2–4 μm) aerosol particles collected near the runway showed a Cu K-edge absorption spectrum very different from that of the fine fractions. Significant amount of Cu is present as Cu(I) in this fraction. It should be noted that the self absorption effect

can be neglected because of the low Cu content in the samples (<3 ng). In contrary to Zn [2], the Cu K-edge TXRF-XANES results indicate that soil resuspension is only a minor source of Cu in the coarse aerosol fraction at the airport, aircraft brake pad erosion seems to be a more probable source of Cu.

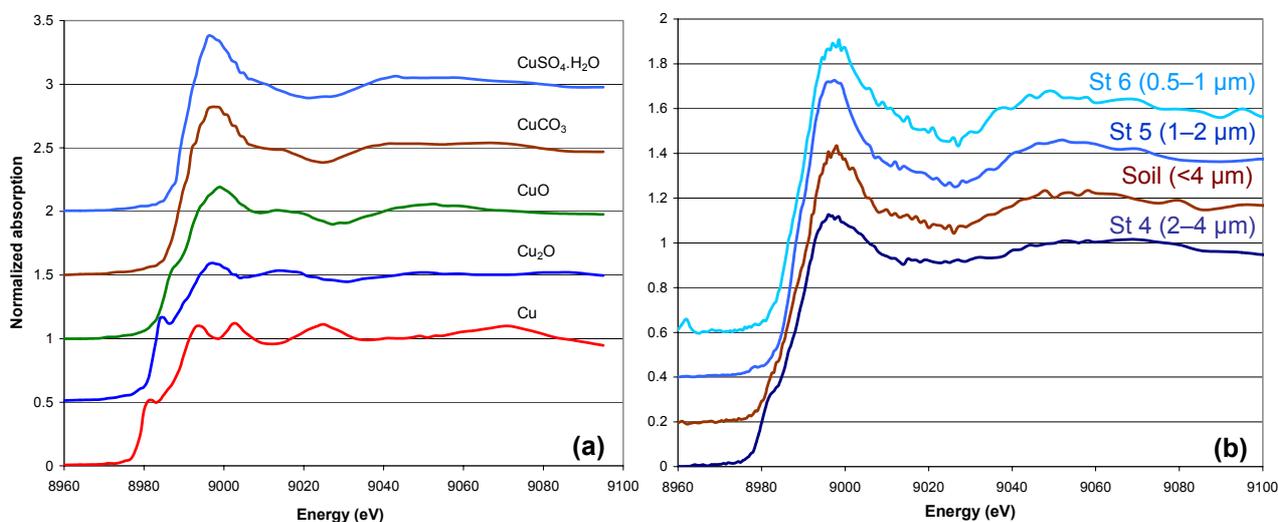


Figure 1: (TXRF-)XANES spectra of copper standards (a), as well as aerosol and soil samples collected at Budapest (airport) at impactor stages 6, 5 and 4 (b).

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