

Quantitative STXM-XANES at the C-K edge

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X-ray absorption near edge structure (XANES) at the carbon K-edge provides information on the speciation of carbon. Different functional groups are expressed at different energies, and aromatics, ketones, or aliphatics can thus be identified. So far, this technique has been mainly used: i) to attest of the presence/absence of a given function; ii) to compare, based on different absorption intensities, the relative abundance of a given functional group in different samples [1]. However, these comparisons remain qualitative because the absorption oscillator strengths (the probability for an X-ray to trigger an electronic transition) are unknown.

Here, we report an empirical, quantitative method that allows estimating absolute functional group concentrations from XANES data. The XANES spectra of ten reference polymers were measured and analyzed together with two additional datasets (~30 compounds) available online [1, 2]. Spectra are normalized to the total amount of carbon in a new fashion, using the integrated spectrum area between 280 and 291.5 eV (the carbon ionization energy). The N/C_{measured} vs. N/C_{standard} correlation is as good as the one classically obtained by fitting absorption cross sections. Spectra can then be fitted using ~ 20 gaussians set at given energies corresponding to published functional group assignments, with a fixed FWHM of 0.6 eV. We created a python software to automatically perform this data treatment procedure.

We obtained an excellent correlation ($R^2 = 0.96$) between the aromatic carbon concentration and the absorption between 284.7 and 285.4 eV. The same is true for the region of ketones, phenol and nitrile groups (between 286 and 287 eV). Although not as good, aliphatics provide an acceptable correlation ($R^2 = 0.75$). Altogether, we demonstrate that it is possible to determine the absolute aromatic concentration of an unknown molecule (with a ~ 15% accuracy), at the spatial resolution offered by STXM (25 nm), i.e. on very low amount of materials.

[1] Le Guillou et al., 2014, *Geochim. Cosmochim. Acta*, 131, 368 [2] Dhez et al., 2003, *J. Elec. Spectr. Rel. Phenomena* 128, 85 [3] Solomon et al., *Soil Science Society of America Journal*, 73(6), 1817.