

Supplementary Information

The Influence of Physical State on Shikimic Acid Ozonolysis: A Case for in situ Microspectroscopy

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Carbon contamination and spectral distortion

Carbon contamination of the optical elements and windows of the beamline are a problem for measurements at the carbon edge since it preferentially absorbs X-rays in the carbon K-edge - the spectral region of interest. This directly leads to a significant dip in the spectrum of the X-ray flux arriving at the detector and hence a reduction of count statistics and thereby increases noise. However, it also increases the relative contribution of higher order light since the X-rays passed by the monochromator at 2 and 3 times the principally selected photon energy (due to higher diffraction orders of the grating) is absorbed by the contamination far less strongly. Commonly utilised X-ray detectors do not separate X-ray photons of different energies and all counted X-rays are assumed to be of the principal photon energy, despite the fact that they interact with the sample very differently (usually much more penetrating). This tends to make the sample appear more transparent than it actually is, leading to a distortion of the spectrum. The amount of distortion can vary rapidly with photon energy across the carbon K-edge, largely because the principal spectrum is strongly affected by the beamline contamination, while the higher order contribution is fairly constant. As a general rule, one can expect the spectral distortions to be greatest where the detected signal is closest to zero. An example of this can be seen in figure (S1): the grey spectrum shows a strong distortion between 287 eV and 304 eV, in the energy region where the incident X-ray flux (blue, dashed line) is lowest and thus the relative contribution of higher order light is largest. The black spectrum was measured without the microreactor and after cleaning some of the optical elements, thereby reducing the influence of higher order light. This spectrum therefore shows much stronger absorption at 287 eV to 304 eV. This comparison also demonstrates that other energy regions (e.g. below 287 eV) are not significantly affected by the problem. Since we are only interested in spectral features outside the affected region for data analysis, distorted spectra can be included in our dataset without problems. Figure (S2) presents the spectrum of shikimic acid measured with optimised measurement parameters in order to show the more subtle features. For a more detailed discussion of the problems encountered in carbon K-edge spectroscopy and approaches in solving these issues see (Watts et al., 2006).

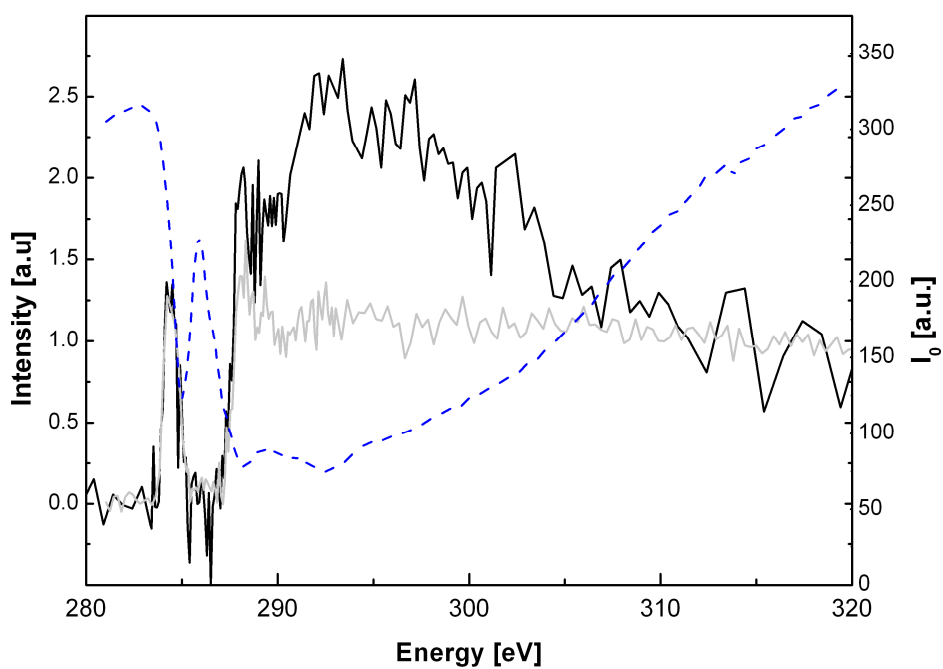


Fig. S1. Spectrum of shikimic acid extracted from stack measurements at high levels of carbon contamination and low I_0 (solid grey line), defocused line spectrum of shikimic acid at low contamination and high I_0 (solid black line) and a typical I_0 spectrum with strong carbon contamination (dashed blue line).

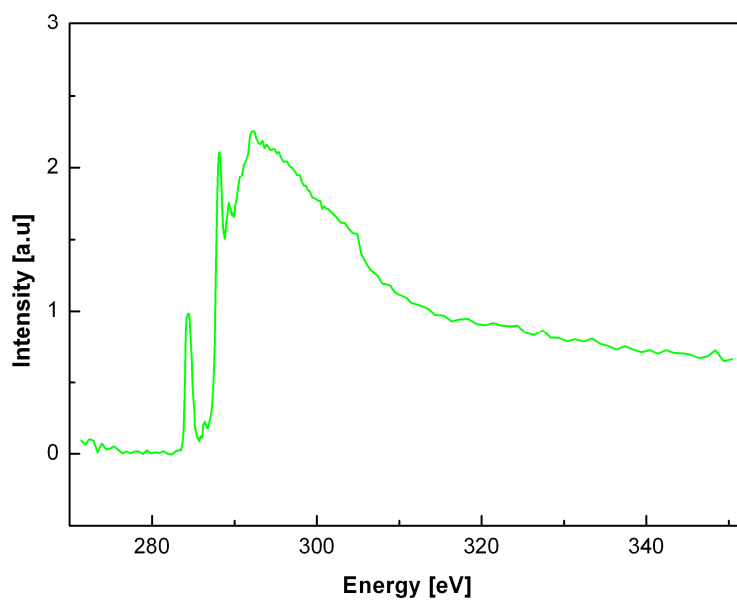


Fig. S2. Optimized spectrum of shikimic acid

Chemical mapping

Chemical maps can be used to identify chemical inhomogenities. To demonstrate the capability of chemical mapping to identify marked chemical gradients with our experimental setup, we show here an image of a particle with an accidental contamination (fig. S3).

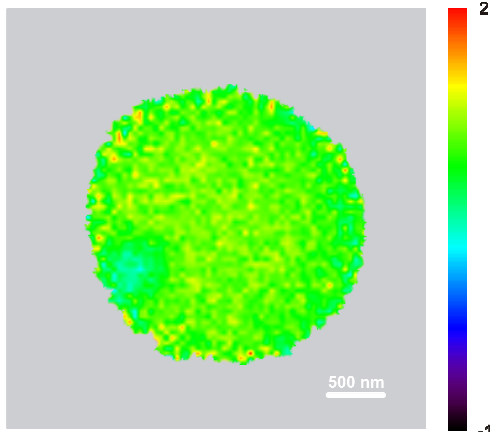


Fig. S3. Chemical map showing the distribution of the shikimic acid double bond in an unoxidized particle at 13% RH containing an inclusion of an accidental contamination.

References

Watts, B., Thomsen, L., and Dastoor, P. C.: Methods in carbon K-edge NEXAFS: Experiment and analysis, *Journal of Electron Spectroscopy and Related Phenomena*, 151, 105-120, 2006.