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Supplement of

The influence of physical state on shikimic acid ozonolysis: a case for in situ microspectroscopy

S. S. Steimer et al.

Correspondence to: S. S. Steimer (sarah.steimer@psi.ch)

Carbon contamination and spectral distortion

Carbon contamination of the optical elements and windows of the beamline is 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 nominally set photon energy (due to higher diffraction orders of the grating) is absorbed by the contamination far less strongly. Commonly utilized 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), which shows the spectra of two particles from different samples, measured at beamtimes more than one year apart. The grey spectrum (particle 1) 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 (particle 2) 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 optimized 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).

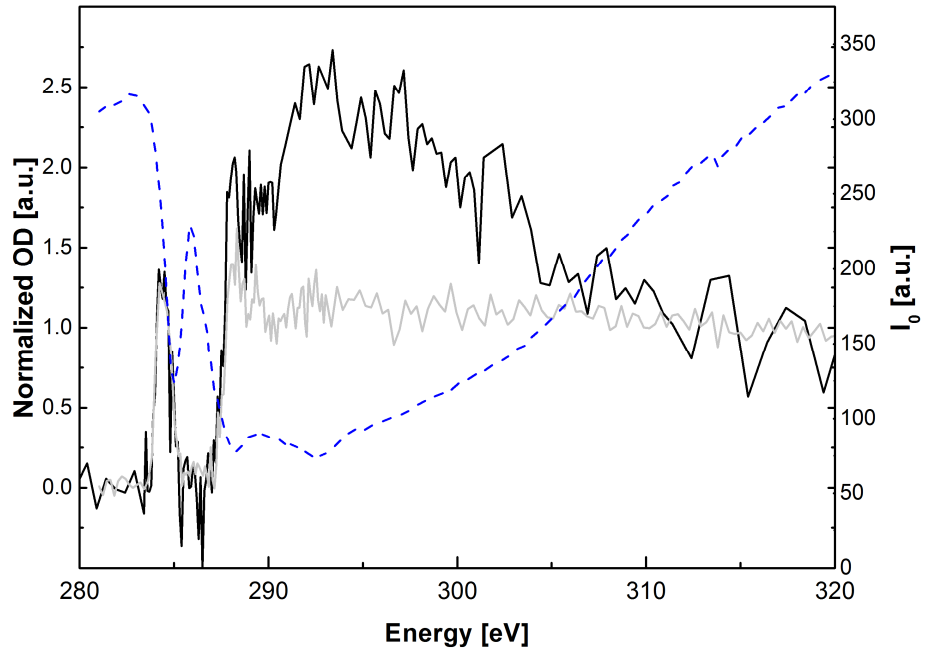


Fig. S1. Spectrum of shikimic acid extracted from stack measurements of a particle measured at high levels of carbon contamination and low I_0 (solid grey line), defocused line spectrum of a shikimic acid particle measured at low contamination and high I_0 (solid black line) and a typical I_0 spectrum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

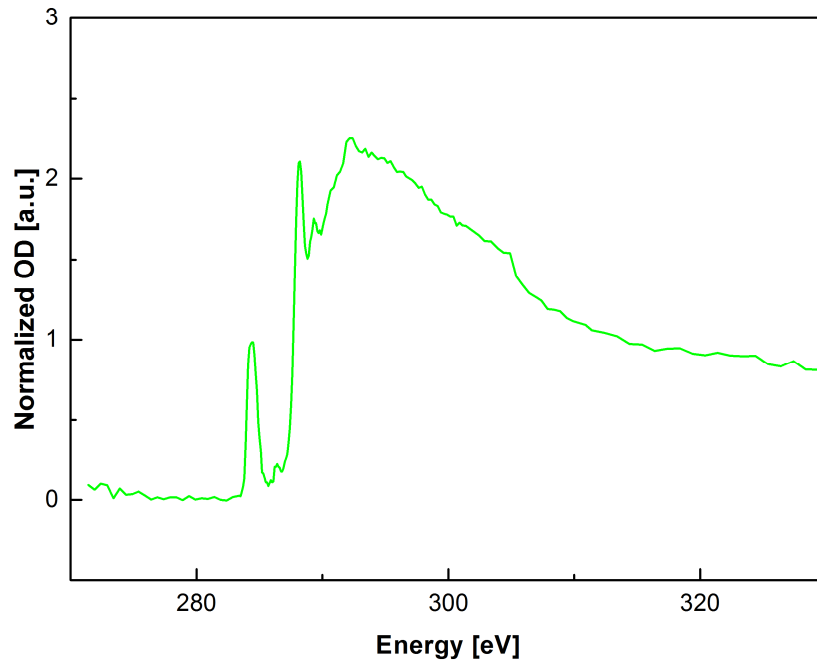


Fig. S2. Optimized spectrum of shikimic acid

Particle shape

To determine particle shape, we compared the OD cross sections of unoxidized particles to the projection of a circle and a semicircle. Figure S3 is showing such a comparison for two particles at different humidities (0% and 71%). It can be seen that the shape of the dry particle is between spherical and hemispherical while the particle at 71% RH is clearly flatter than hemispherical. Analysis of multiple OD cross sections shows this to be a general trend. However, no complete quantitative reconstruction is possible due to low contrast of the images.

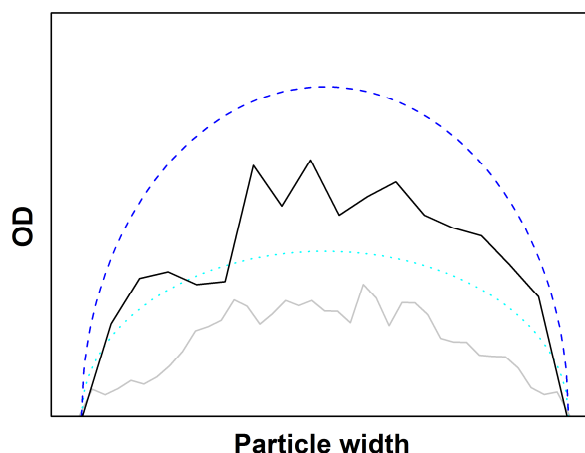


Fig. S3. Example of a dry particle (black line) and a wet particle (71%, grey line) cross section in comparison with the projection of a circle (dark blue, dashed line) and a semicircle (light blue, dotted line)

Chemical mapping

Chemical maps can be used to identify chemical inhomogeneities. STXM-NEXAFS has previously been demonstrated to reveal the presence of chemical heterogeneities on the order of 100 nm from spatial analysis of STXM images (Takahama et al. 2010). To demonstrate the capability of our experimental setup to identify small chemical heterogeneities, we show here an image of a particle with an accidental contamination (fig. S4). These carbonaceous impurities of an unknown nature were found only during measurement of the 12% RH sample in 3 out of 33 measured particles.

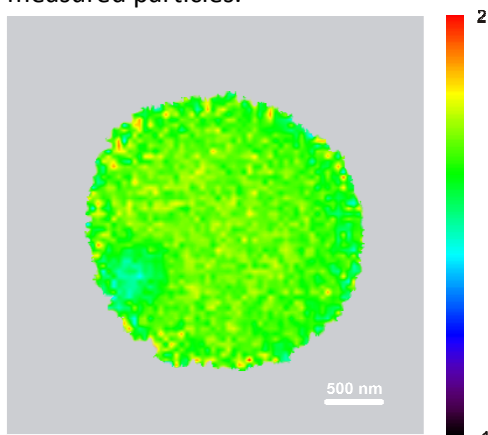


Fig. S4. Chemical map showing the distribution of the shikimic acid double bond in an unoxidized particle at 13% RH containing an inclusion of an accidental contamination.

References

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