Accessory publication

Humidity driven nanoscale chemical separation in complex organic matter

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Fig. A1 shows ratios of absorption maps measured at 310 eV divided by the absorption map measured at 550 eV. Yellow coloured regions show the carbon-rich region whereas in violet are shown the oxygen-rich regions.
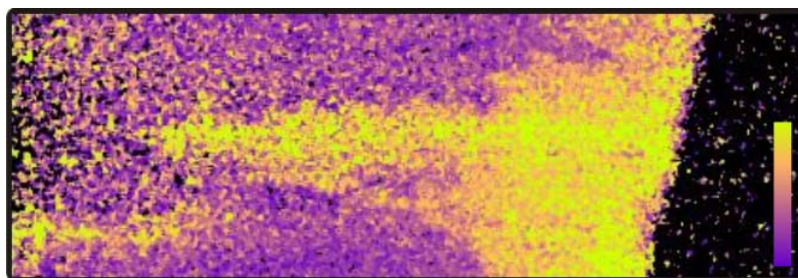

Fig. A1.   Ratios of the absorption map measured at 310 eV divided by the absorption map at 550 eV. The colour bar range from 1.1 (violet) to 2.9 (yellow).

Fig. A2 shows the PCA-CA analysis of the wet bulk SRFA using axis2000.[1] Principle component analysis (PCA) was used to orthogonalise and noise filter the recorded spectromicroscopic data. The cluster analysis (CA) was further used to classify the single pixels according to spectral similarity. This analysis was done along the lines used previously by others.[2,3] Two main regions can be identified, a carboxylic/aromatic-C rich region coloured in yellow, and a phenol-C rich region coloured in red. Note that the PCA-CA analysis as obtained here did not reveal any further structural features. We did not attempt to run a lower level analysis to eventually see the apparent substructures. We do not believe that the parameter space covered

by this limited dataset is large enough to constrain such an analysis well enough. We therefore remain with the qualitative analysis as presented in the main text. Also, the interpretation of the region with overabsorption at 288.5 eV, see Fig. 13, needs to be done carefully.
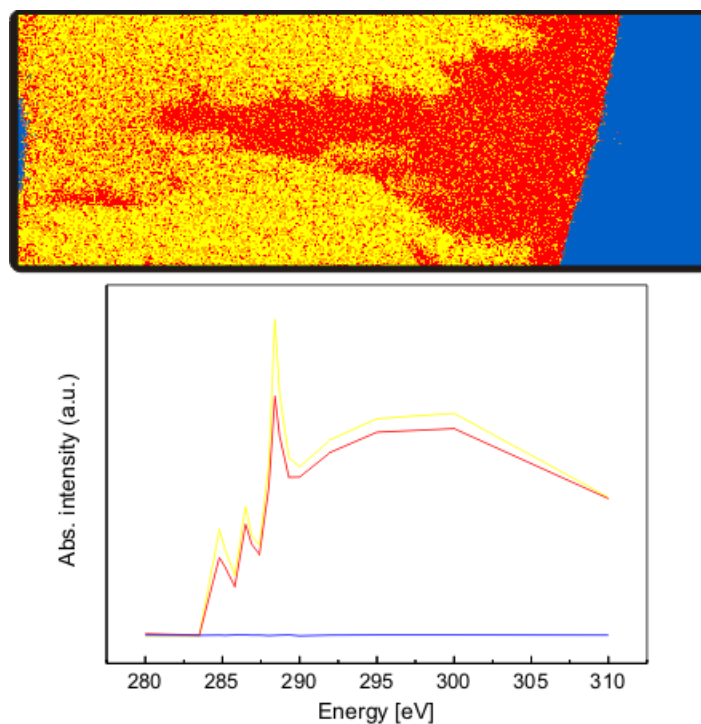

Fig. A2. PCA-Cluster analysis, which revealed two regions.

Fig. A3 shows ratios of chemical maps measured at different energies. Upper panel shows ratios of aromatic-C and phenol-C, middle panel shows ratios of aromatic-C and carboxyl-C, and lower panel shows the ratios of phenol-C and carboxyl-C.
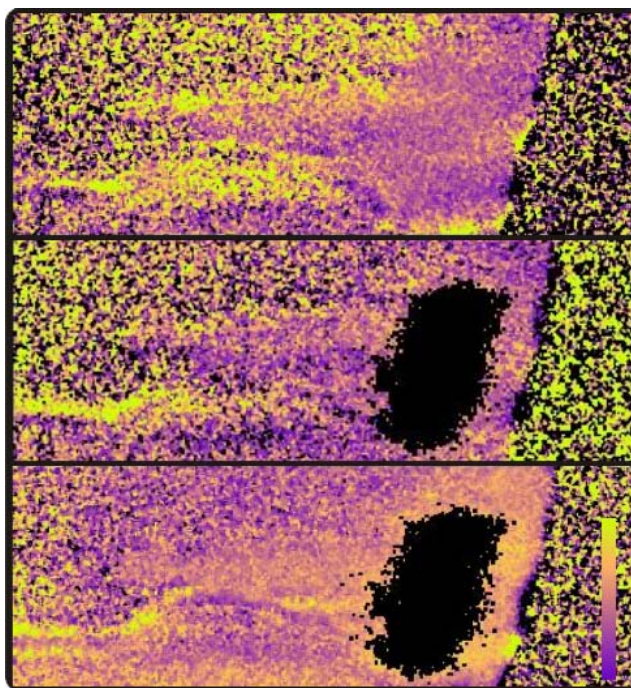
Fig. A3.   Upper panel: ratios of chemical maps measured at 285 and 286 eV, OD varies from 0.4 to 1.2; middle panel: ratios from chemical maps measured at 285 and 288 eV OD varies from 0.2 to 0.5; lower panel shows ratios of 286 to 288 eV whereby OD varies from 0.1 to 0.7.

Experiments on beam damage

Because organic material is sensitive to beam damage,[4] several beam damage experiments were performed with SRFA. Mass loss and degradation of single function groups was investigated upon exposure to the X-ray beam. Fig. A4 illustrates the results of the beam damage experiment upon exposure of SRFA to the beam measured at 320 eV. The OD of the sample decreased by 15 % upon exposure for more than 300 ms. The error bars show the corresponding standard deviations.
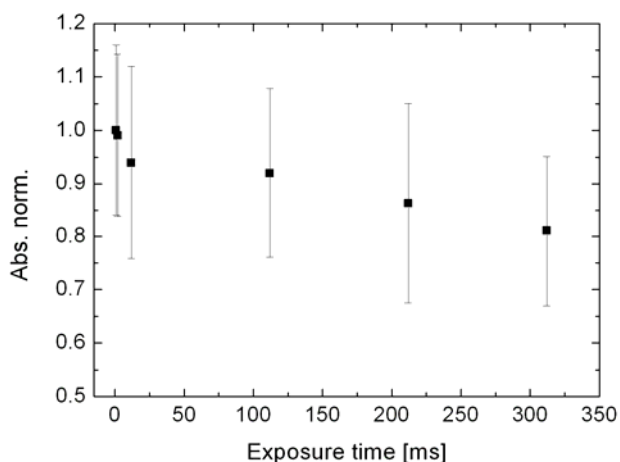
Fig. A4. Beam damage experiment with standard deviation, measured at 320 eV under dry conditions.

Single chemical functional groups show different sensitivity to radiation damage. Thus seven stacks with large energetic resolution were measured (0.5 eV steps until 292 eV and 1 eV steps until 320 eV) on one single SRFA deposited aerosol particle. These spectra were modelled using Gauss fits and an arctan function to model the ionisation point.[5] The maxima of the Gauss fits were fixed at the main absorption intensities of SRFA, 285, 286.6 and 288.5 eV and at 287.4, 289.5, 290.2 and 292.2 eV. From this chemical breakdown, the single contributions were plotted. Except for the carboxyl-C at 288.5 eV the fits showed no trends and remained the same within error. Fig. A5 shows the contribution of the carboxyl-C versus the exposure time to the X-ray beam. In this case a decrease in the absorption intensity is observed to ~83 % of its original value after 350 ms exposure time.

Usually, an exposure of ~150 ms is used to record a whole image stack. In this case the decrease in absorption intensity is only ~10 %, the loss in absorption intensity of the carboxylic group is even less than 10 %.
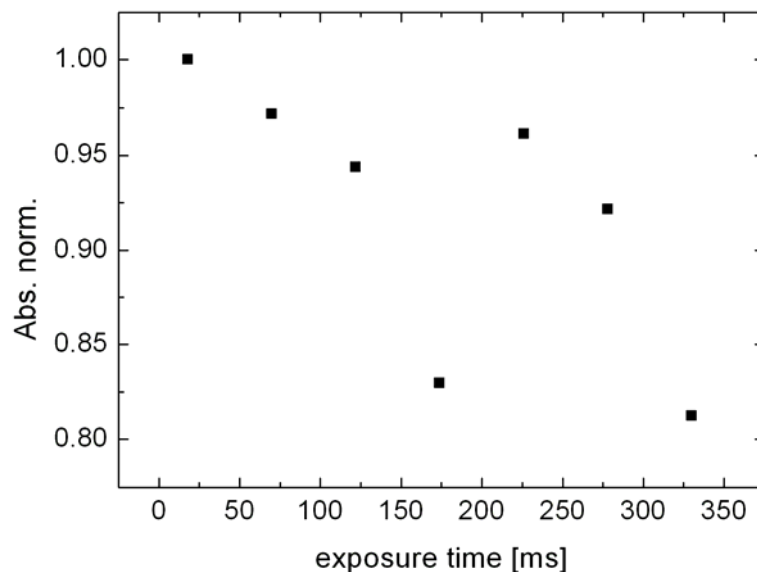
Fig. A5.   Gauss fits from the electron transition at 288.5 eV measured under dry conditions.

References

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