The benefits of Cu K-beta radiation for the single crystal X-ray structure determination of crystalline sponges

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The Crystalline Sponge method enables the structural elucidation of scarce, small organic analytes and hard-to-crystallize compounds. By diffusion of solvent and analyte molecules into the cavities of a metal-organic framework (the crystalline 'sponge') and molecular orientation by the MOF's functional groups, an analyte becomes part of the crystal structure and thus observable through X-ray diffraction methods.[1]

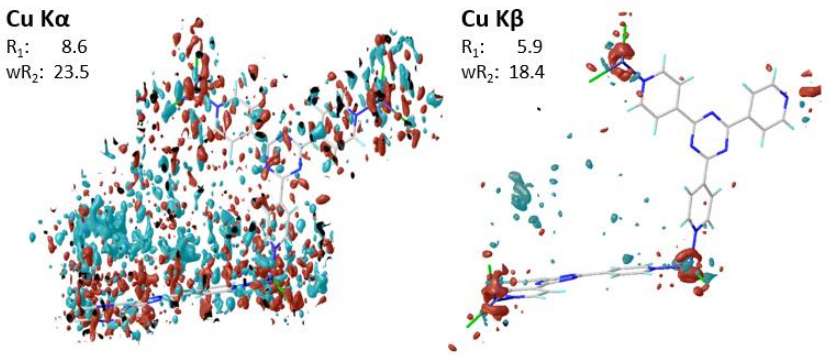

Figure 1: Comparison residual electron density maps with the different wavelengths (iso-level: 0.4 e·Å^{-3})

Unfortunately, many problems inherent to the structural elucidation of MOFs limit the possibilities of this method. These include weak host-guest interaction, incomplete diffusion, twinning, disorder of both analyte and solvent and sample decay. As much as the physical and chemical aspects of the method have recently been improved, the crystallographic aspects pose challenging problems onto the method. As we have recently adopted the use of the very rarely used Cu Kβ radiation in our X-ray department and found promising results in the analysis of our small molecule data, we also applied Cu Kβ radiation to the Crystal sponge method and compared it to the more commonly used wavelength Cu Kα in a total of six comparison experiments. Cu Kβ inherits a shorter wavelength than Cu Kα radiation (1.39222 Å compared to 1.54187 Å) and thus results in up to 38 % more unique reflections and up to 136 % total reflections. This is mainly due to the maximum resolution of 0.72 Å is accessible for Cu Kβ radiation, compared to 0.80 Å for Cu Kα radiation. Less absorption by consistently 25 % in absorption coefficient for Cu Kβ leads to less background and absorption damage.[2]

This results in better crystallographic models for the Cu Kβ data sets: Significantly lower quality parameters were obtained in every Cu Kβ experiment. Bond precision was mainly better and the compared residual electron density maps (Fig. 1) look much cleaner. Additionally, more solvent positions could be modelled in the Cu Kβ data sets. In total, way fewer restraints and no constraints had to be used in the models collected using Cu Kβ radiation. Our findings suggest a routine use of Cu Kβ radiation – not only for the crystalline sponge method. The same advantages are to be expected in general for the structural elucidations of metal-organic frameworks but also standard small molecule crystallography.

[1] Hoshino, M., Khutia, A., Xing, H., Inokuma, Y. & Fujita, M. (2016). *IUCrJ*. **3**, 139–151
[2] Florian Meurer, Carolina von Essen, Clemens Kühn, Horst Puschmann, Michael Bodensteiner, **2022**, in preparation