	Experiment title: Impact of solvent layer, size and ligand decoration on hydration shells around IONPs	**Experiment number**: CH-6070
Beamline: ID31	**Date of experiment**: from: 23rd November 2021 to: 26th November 2021	**Date of report**:
Shifts: 3 (6)	**Local contact(s)**: Marta Mirolo	*Received at ESRF:*

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Report:

With this proposal we wanted to investigate, how the interfacial signal exhibited by little residual amounts of polar organic solvents remaining in aqueous dispersions of iron oxide nanoparticles (IONPs) after purification of the particles, is differing from an expected hydration shell signal. Parameters under study were, adjacent to difference in preparation of the IONPs, freshly re-dispersed with residual amount of polar organic solvent vs. re-dispersed after freeze-drying of IONP powder, nanoparticle size (7 and15 nm in diameter), ligand decoration (covered with citrate, phosphocholine or diethlylene glycol) and particle concentration (5- 20 g/L).

Therefore, total scattering data of IONP dispersions with the just mentioned varying parameters, as well as corresponding IONP powders and “background samples” in capillaries was acquired. The “background samples” were namely water, ligand solutions with respective concentration as expected in IONP dispersions, as well as mixture of the organic solvents with water with low concentration of solvent. By subtracting both the solvent background as well as the contribution of the dry nanopowder double-differential pair distribution functions (dd-PDFs) are acquired. Those dd-PDFs are supposed to contain only interfacial signal, thus signal of restructured water/solvent around the IONPs. All IONP samples were prepared in the home laboratory beforehand and only IONP dispersions were freshly filled in capillaries on-site, since they otherwise evolve bubbles over time.

The proposed experiment was carried out using the 65 keV X-ray beam centered in the corner of the Pilatus 3 X CdTe 2M detector and a small (2 mm Pt) flying beamstop mounted close to the sample (sample-beamstop distance ca. 7 cm). With this set-up, the goal of acquiring total scattering data of IONP dispersions, which are of decent quality to retrieve dd-PDF signals with acquisition times of 6 seconds only in the EBS beam, was

achieved. It is noteworthy to mention, that this double-differential signal is only about 1% of the total scattering signal and therefore the measurement time of 6 s on a weakly scattering liquid sample is astonishingly. Since evaluation and interpreation of the retrieved signals is stilll on-going results should not be discussed here.

We want to mention a few technical aspects. From this beamtime we learned, that ghosting issues on the Pilatus 3X CdTe 2M detector with the new increased brilliance are a more severe problem than ever, also for weakly scattering samples and seem to be inavoidable. Accumulated charges create noise and for our dd-PDF studies using background measurements with different noise level than in the sample measurement worsen the subtraction a lot, resulting in noisy double-differences. Therefore, measurement times need to be minimized and background samples should be measured multiple times during the beamtime in order to have those data with the changing noise level. Further, the data quality for weakly scattering samples and small difference signals, even though already being good, could be improved, if a flat field correcton was provided.

While measuring our IONP dispersion in a mixture of ethanol and water with a low ethanol concentration of about 6 vol% for 1 minute with a loopscan, we noticed beam-induced changes, namely shifting Bragg peaks. Similar samples have already been investigated at ESRF before the EBS upgrade, where such changes were not observed, and are therefore associated with the highly increased brilliance. The origin of the changes was found to be radiolysis of the solvent mixture inducing a change in the redox chemistry of the IONP dispersions. Since we are convinced, that it is important to notify the scattering community, that with the new highly brilliant 4th generation synchtron sources also inorganic materials can be affected by beam-induced changes we just submitted a manuscript about this observation to Journal of Synchrotron Radiation.