Physicochemical characterisation of nanomaterial

Possible stress factors for substances during sample preparation and analysis

• Stress factors for both BET and EM are (i) temperature, (ii) vacuum, (iii) holding time or duration of measurement, (iv) unsuitable solvents
• Additional stress factor for EM is the voltage of the electron beam (e.g. normal vs. gentle beam)
• So far, a lot of data was compiled on how to properly assess inorganic molecules, such as SiO$_2$ or TiO$_2$
• Overall, organic substances tend to be less stable during sample preparation and analysis compared to inorganic molecules whilst there is less experience on proper nano assessment
Physicochemical characterisation of nanomaterial

So which sample preparation and analysis conditions should be used in case of organic materials?

• Sample preparation and analysis needs to assure that organic molecules are not (partially) destroyed which would lead to artefacts and thus, false analytical results
• Additionally, organic material often exists in hydrate forms which are integral part of the crystal lattice
• Crystal water is likely to be released during sample preparation and analysis by BET/EM due to too harsh treatment (vacuum, temperature, solvents, electron beam)
• This may destroy the crystal lattice and thus lead to artefacts, i.e. too high surface area in BET analysis or de-novo nano structures in EM assessment

➢ No clear defined conditions available yet which take special material properties into account
➢ Varying results from different external laboratories
Physicochemical characterisation of nanomaterial

VSSA screening together with shape definition according to Wohlleben et al (2017);

VSSA cutoff \[ = 60 \frac{m^2}{cm^3} \times \frac{D}{3} \]

• In an ideal world, a defined substance can be properly categorized by EM into one category and thus, VSSA cut-off scheme can be applied
• But how to use VSSA cut-off if the dimension of the material cannot be clearly defined (e.g. complex mixture of 1 and 3 dimensional particles)?
Physicochemical characterisation of nanomaterial

Current issues with EM for routine analysis
• Limited knowledge of how EU nano assessment can be applied
• Limited (TEM) or no (EM) automated assessment of particle size, particularly for one-dimensional particles
• Manual assessment of 100-1000 particles takes several hours and is thus very expensive (1000-5000€ per sample)
• Sample size (few µg) not representative for products which are produced in mt scale
• Thus, EM measurement is currently neither an objective, validated nor robust analytical assessment of nano status

Some questions
• Are there automated EM measurements available for nano classification of 1, 2 and 3-dimensional particles and mixtures thereof?
• How many particles have to be counted for a statistical correct evaluation, e.g. in case of a non-homogenous particle size distribution and polymorph materials?