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Evaluation of Electron Microscopy Techniques for the Purpose of Classification of Nanomaterials.

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One current and much-debated topic in the characterization of nanomaterials (NM) is the implementation of the recently introduced recommendation on a definition of a nanomaterial by the European Commission [1]. According to this definition [1], a material is a NM when for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm. The European *NanoDefine* project [2] was set up to develop and validate a robust, readily implementable and cost-effective measurement approach to obtain a quantitative particle size distribution and to distinguish between NMs and non-NMs according to the definition [1].

All currently available sizing techniques able to address nanoparticles were systematically evaluated. It was demonstrated that particle sizing techniques like: analytical centrifugation, particle tracking analysis, single-particle inductively coupled plasma mass-spectrometry, differential electrical mobility analysis, dynamic light scattering, small angle X-ray scattering, ultrasonic attenuation spectrometry, but also gas adsorption analysis based on the BET-method can be applied for a screening classification. However, the quality of the results depends on the individual material to be classified. For well-dispersed, nearly spherical (nano)particles most of the sizing techniques can be applied in a quick and reliable way. In contrast, the classification of most real-world materials is a challenging task, mainly due to non-spherical particle shape, large polydispersity or strong agglomeration/aggregation of the particles. In the present study it was shown that these issues can be resolved in most cases by electron microscopy as a confirmatory classification technique [3-6].

Electron microscopy techniques such as TEM, STEM, SEM or TSEM (transmission in SEM) are capable of assessing the size of individual nanoparticles accurately (see Figures 1 and 2). Nevertheless the challenging aspect is sample preparation from powder or liquid form on the substrate, so that a homogeneous distribution of well-separated (deagglomerated) particles is attained. The systematic study in this work shows examples where the extraction of the critical, smallest particle dimension - as the decisive particle parameter for the classification as a NM - is possible by analysing the sample after its simple, dry preparation. The consequences of additional typical issues like loss of information due to screening of smaller particles by larger ones or the (in)ability to access the constituent particles in aggregates [5] are discussed.

By means of practical examples the inherent statistical evaluation of the particle size is highlighted together with all its pitfalls such as setting of a suitable threshold for delimitation of the particle

boundaries in the electron micrograph or consideration of systematic (bias) deviations from the true particle size because of evaluation *via* surface sensitive secondary electron detectors, e.g. *In-Lens*.

[1] European Commission, Commission Recommendation of 18 October 2011 on the definition of nanomaterial (2011/696/EU). Official J. Europ. Union **54** (2011) p. 38.
[2] www.NanoDefine.eu
[3] F Babick *et al*, submitted.
[4] K Yamamoto, Microsc. Microanal. **21** (Suppl 3) (2015) p. 2399.
[5] P-J de Temmerman *et al*, Powder Technol. **261** (2014) p. 191.
[6] P Müller *et al*, Microsc. Microanal. **21** (Suppl 3) (2015), p. 2403.
[7] The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 604347-2. (www.nanodefine.eu).

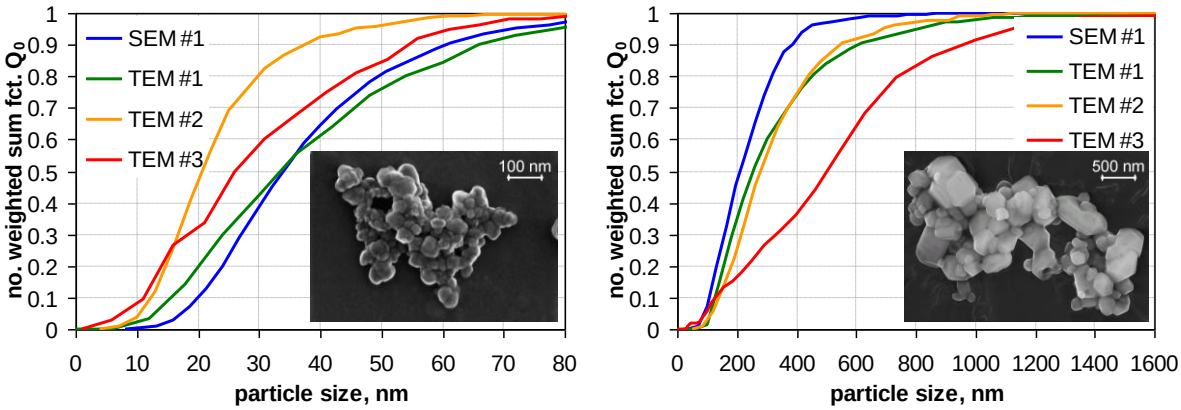

Figure 1. Cumulative number-weighted size distribution functions of barium sulfate in ultra-fine (left) and fine (right) grades evaluated by SEM (1 lab) and TEM (3 labs) together with the corresponding SEM *In-Lens* micrographs.

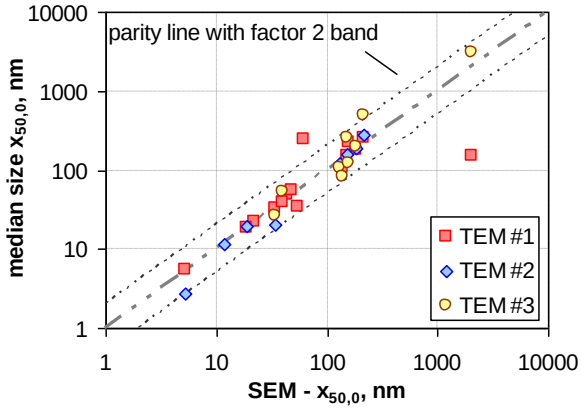

Figure 2. Parity plot of the median size, as determined for 18 materials by 3 TEM labs in correlation with the corresponding values obtained by an SEM.

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