PARTICLE SIZE MEASUREMENT – LESSONS LEARNED FROM EU NANOMATERIAL DEFINITION

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Abstract

Particle size measurement method which can completely fulfill EU nanomaterial definition is technically impossible due to fundamental problems in this definition. There are two main sources of problems – understanding nature of primary particles and emphasis on number based distribution. There is no particle size measuring method which can distinguish between primary particles and agglomerates without ambiguity. Common are ensemble methods which usually measure aggregates as single particles and cannot provide directly number size distribution. Particle counting method also count aggregates as single particles. Even with electron microscopy it can be difficult to clearly distinguish between aggregates and primary particles. Possible improvements of this definition are to use number size definition only after screening with well established ensemble methods and consider aggregates which cannot be dispersed to its constituent parts under reasonably severe conditions (intractable aggregates) as primary particles.

Keywords: Particle, measurement, variation, nanodefinition

1.   NANOMATERIAL DEFINITION

In 2011 European commission adopted well known nanomaterial definition [1]:

A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm to 100 nm.

'Particle' means a minute piece of matter with defined physical boundaries; EC in one paragraph also states that: *There is no unequivocal scientific basis to suggest a specific value for the size distribution below which materials containing particles in the size range 1 nm- 100 nm are not expected to exhibit properties specific to nanomaterials.*

Let us look to the practical issues regarding this definition.
a.) Primary particle
b.) Number size distribution

2.   DEFINITION AND MEASUREMENT ISSUES

2.2   Primary particles

Concept of primary particles can be viewed from various sides, depending on background of person. If you ask crystallographer what is primary particle he will say that it is crystallite – the smallest amount of matter which has defined structure and scatters Xray electromagnetic radiation. For colloid chemist it is tiny amount of material which behaves like one entity regardless of its internal structure and which can form aggregates or agglomerates. And for people in aerosol technology it is a particle which manifests itself as a single particle in measurement techniques, again without considering its internal structure.

Measuring size and size distributions in nanomaterials is challenging in many cases and different measurement methods may not provide comparable results. This was mentioned in preamble to EU nanomaterial definition and this statement still has not changed. For particles below 1 µm there are many

methods claiming to provide correct, precise and simple measurement. It is usually demonstrated on model particles (latex, metal) which are usually monomodal with sphere or rounded shape and without substantial aggregation. Some methods are better than others regarding resolving mixtures of these particles some are not sensitive enough to reach bottom range of definition some are sensitive to oversized big particles.

In is quite difficult to measure and express particle size unambiguously. Some shapes can be described exactly with only one number from which spheres are probably most often used and their mass, volume or surface can be exactly computed from it. For most crystal shapes there is necessary some additional information. Therefore it is not surprising that in many measurements methods the results are recalculated to spherical approximation. In microscopic evaluation one can express result as a sphere of the same minimum or maximum length or projected area, in sedimentation technique the result is sphere having the same sedimentation time, in laser scattering the result is expressed as spheres of the same scattering power.

The problem does not end with this recalculation, though. When we measure some kind of distribution one usually wants to evaluate some average particle size. This can be accomplished e.g. by summing all diameters divided by number of particles measured.

$$\frac{\Sigma d}{n}$$

where d is particle diameter and n is number of particles.

However we can sum not diameters but surface area, volume or mass, which can give quite different results.

$$\sqrt{\frac{\Sigma d^2}{n}}, \sqrt[3]{\frac{\Sigma d^3}{n}}$$

Those averages can be expressed as D[1,0], D[2,0], D[3,0] as there are no diameter terms in denominator.

Another possibility is to get rid of particle counting and express the average particle size as a Sauter mean (sphere which has the same volume to surface area ratio as the measured particles) D[3,2] or so called Volume moment mean, which is usually expressed as D[4,3].

$$\frac{\Sigma d^3}{\Sigma d^2}, \frac{\Sigma d^4}{\Sigma d^3}$$

It is easy to show that all this can result in quite different results from measurement even with the instruments of the same physical principle but different way of evaluation. There is no single standard method which can be applied for all situations and is considered as so called "golden standard" in particle size measurement.

Table 1 – Brief overview of some measurement methods

Priciple	Features
XRD broadening	Indirect method, cannot measure particle size distribution. It estimates average dimension in crystals along direction appropriate to Bragg angle. Only for crystalline particles.
Microscopy	In optical microscopy resolution is limited to about 200-500 nm. Electron microscopy (TEM, SEM) can go down to about 10 nm and in special HRTEM down to atomic dimension. Particles can be evaluated by hand counting or by automatic counters. Automatic counters or automatic picture evaluation can be used only in special case, where particles do not overlap.
Light scattering	Particles can be measured in air or in liquid. Two theories are usually used for particle size evaluation – Fraunhofer and Mie. Sample has to be substantially diluted. Intensity of scattered light is evaluated and based on scattering patterns the particle size distribution of sample is calculated. Indirect method with complicated computation behind it. In DLS method hydrodynamic diameter is computed from diffusion coefficient calculated from fluctuations of light scattering. Those fluctuations are proportional to particle movement and hence their size.
Sedimentation	Uses Stokes law and expects laminar sedimentation, calculates hydrodynamic diameter
SMPS	Measures only aerosol particles, directly computes number based distribution.

From mentioned methods light scattering and centrifugation are most widely used in industrial praxis. The problem is, that there is no method which can easily distinguish between primary particles and aggregates. Actually, most methods measure aggregates or agglomerates and not primary particles. The issue of primary particles is also rather cloudy. From crystallographic point of view primary particle is single crystal (crystallite). In colloid chemistry primary particle is any particle which is behaving like single entity in suspension although its structure can be quite complicated and it can consist from aggregate or agglomerate of smaller particles.

Some may conclude that electron microscopy can be used for such evaluation, but actually it is hardly true as can be seen from **Fig.1**.
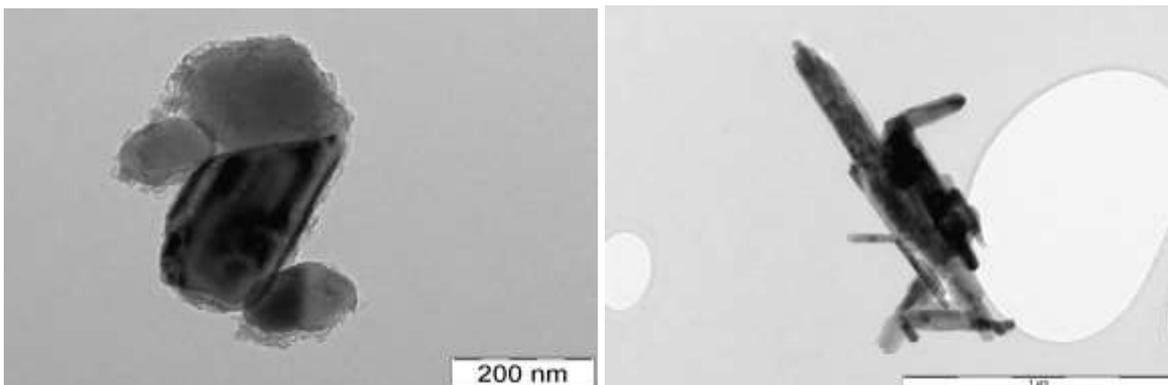

Fig. 1 Real TiO2 and FeOOH particles

2.3 Number size distribution

Most methods for particle size measurement are ensemble methods, they measure collection of particles. These include centrifugation, lased diffraction and dynamic light scattering. Methods also require specific sample preparation which can strongly affect results. We measured sample by several ensemble methods and in different laboratories and the results were not satisfactory. The differences between laboratories and principles (Fig.2.) and recalculation principles are compelling and indicate that it is difficult and maybe impossible to get consistent results without distinct dispersion protocol and uniting measurement principle.

Number size distribution measurement is quite common among aerosol scientists. They have sophisticated instrumentation eg. Scaning mobility particle sizer (SMPS) or Aerodynamic particle sizer (APS). Although these

Fig. 2. One sample of TiO2 measured by various methods in 8 different laboratories

methods can be used for measurement particles already in air, at present time it is technically impossible to

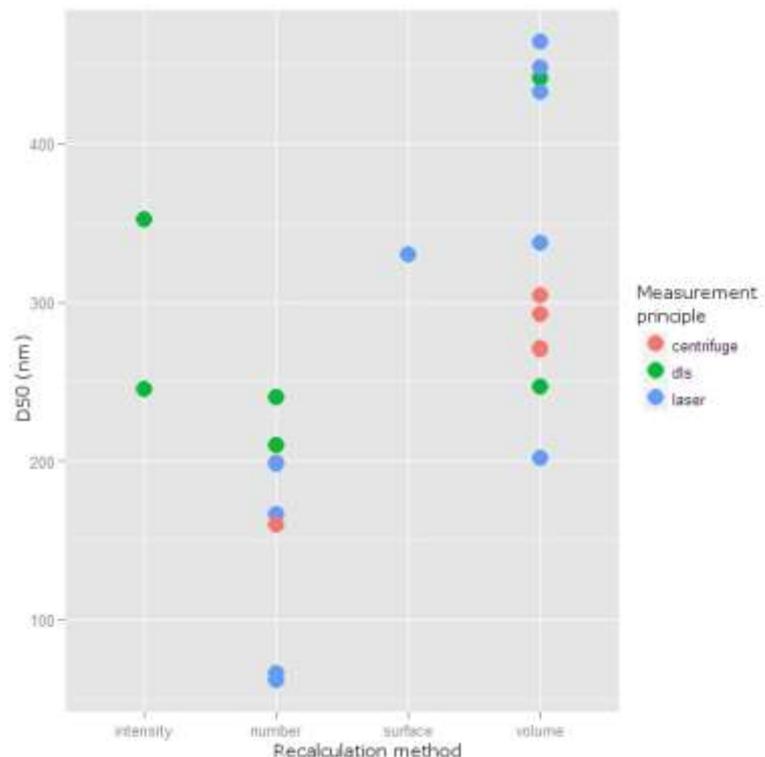measure particles which are in samples of real products and results from such attempts are not in agreement with particle sizes from other methods [2].

Obvious method could be electron microscopy. However it requires skilled personnel and experienced person for particle counting. There is also necessary to have some common agreement what is primary particle. For standards like gold it is possible to use automatic counting method as particles are usually round or isometric, without aggregates and easy to disperse (Fig 3).
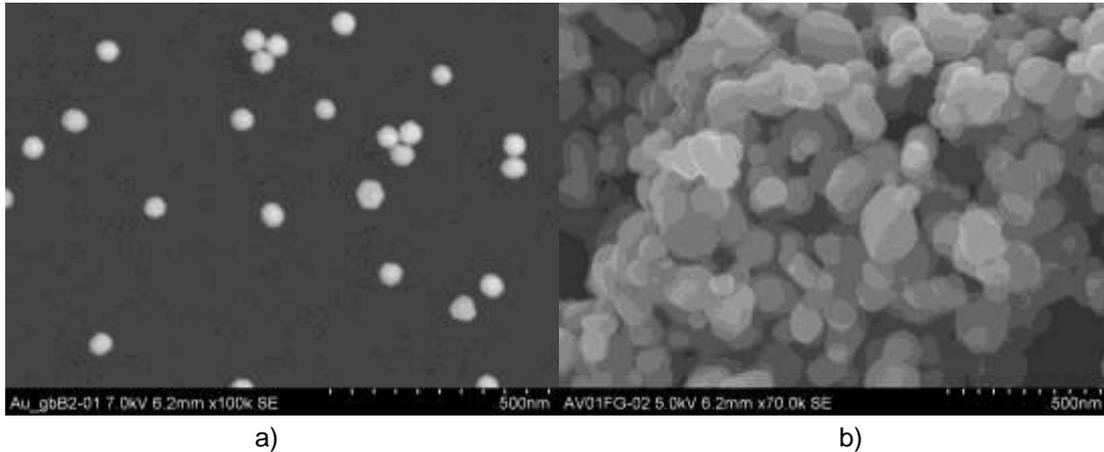

Fig. 3. Gold NIST particles (a) and pigmentary anatase (b) SEM picture

With real particles the only reasonable way of measurement seems to be manual which means that number of particles measured is somewhat limited. In case of nearly spherical TiO2 particles the number of measured particles is not so important but the minimum is about 200-300 particles. Then there is question of measurement variability. With real TiO2 samples we proved that SEM gives usually more consistent results than TEM (Fig.4). The reason is that sample preparation for TEM measurement requires dispersion step which can influence aggregation/agglomeration. Moreover we found, that particles aspect ratio (Feret/minFeret) is strongly dependent on pixel size, which probably results in greater variation of minFerret estimation from TEM.
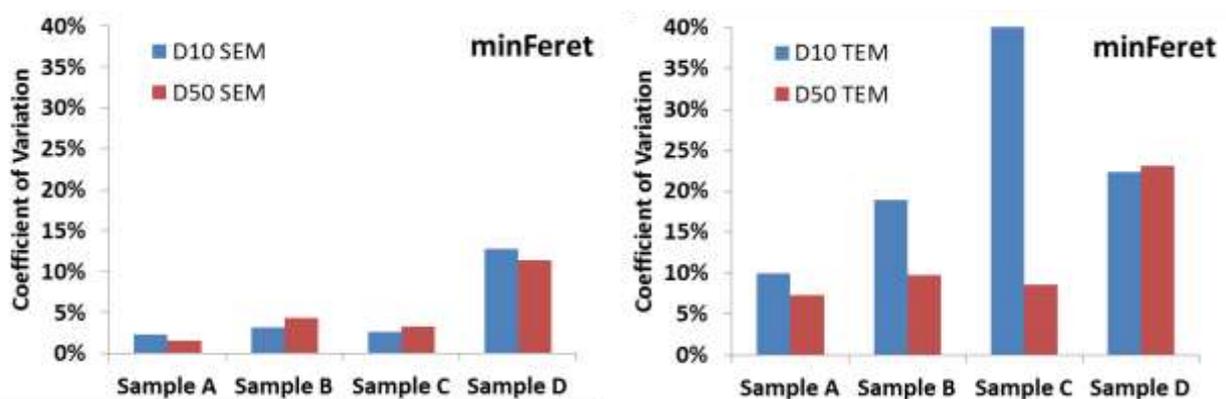

Fig. 4 Summary of Coefficients of Variation for the four pigmentary titanium dioxide materials for SEM (Right) and TEM (Left) separately.
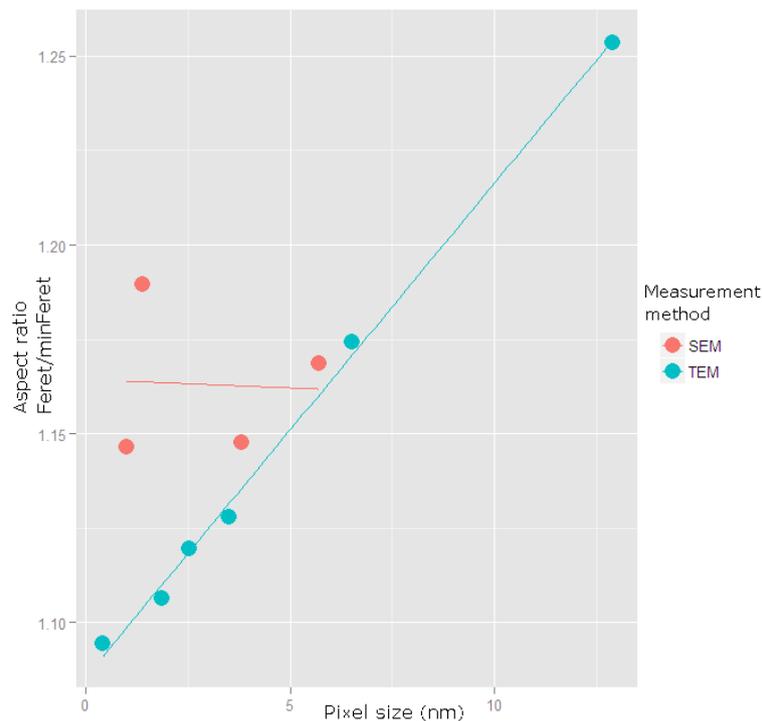
Fig. 5. Aspect ratio of gold NIST particles and its dependency on EM technique

Again electron microscopy, although powerful technique, is problematic for measuring particle size when there is no clear dispersion protocol, standardized procedure of evaluation and common understanding of distinction between primary particle and aggregate.

CONCLUSIONS

Based on fundamental difficulties connected with measurement method principles I can conclude there is time to introduce some changes to EU nanomaterial definition, which make it more applicable. Actually, as definition states, one of its main purposes is to enhance consumers and workers safety due to findings, that particle surface area is the better measurand for possible influence on health [3]. If we accept this metric, it is obvious, that the same number of bigger particles has greater surface area than smaller particles. Therefore some reliable ensemble method together with standardized dispersion protocol can screen out particles which are bigger than some newly defined threshold by easier way than problematic and tedious electron microscopy sizing. Considering aggregates, which are not dispersible to smaller particles with defined dispersion method, to be equivalent to primary particles within scope of definition is also advisable.

ACKNOWLEDGEMENTS

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[3]   NIOSH: Occupational exposure to TiO2, Current Intelligence bulletin 63, April 2011,