Role of the VSSA in the NanoDefine decision flow scheme

Dan Hodoroba (BAM) & Hubert Rauscher (JRC)

- VSSA concept
- VSSA as measured by BET
- Results of the NanoDefine evaluation, selected examples on real-world materials
- Recommendations for application of the EC definition of nanomaterial
Measurement techniques (MT) able to probe the size of nanoparticles

- Imaging (EM, SPM)
- PTA/DUM
- TRPS
- sp ICP-MS

- FFF
- AC / CA – incl. CLS and AUC
- DMAS

Screening methods (tier 1)

- DLS
- SAXS
- USSP
- XRD
- ALS, incl. LD

Confirmatory methods (tier 2)

- BET for VSSA
**VSSA**

- **Volume specific surface area**, \( S/V \) [m\(^2\)/cm\(^3\)]

- Minimum dimension can be extracted: \( d_{\text{min}}^{VSSA} = \frac{2D}{VSSA} \)

- \( D = \) nr. of small dimensions: from descriptive SEM

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**BET**

- Brunauer-Emmett-Teller theory for physical adsorption of gas molecules on solid surface
- widely used, cost-effective
- no sample preparation
- standardized (ISO 9277:2010)
- traceable
- result: **Specific Surface Area** [m\(^2\)/g]
- \( \text{SSA} \times \rho = VSSA \)
Experimental MT evaluation (incl. BET)
Example #1: pigment Y83, transparent

BET equiv. min. size

![Image of pigment Y83](image_url)

particle size, nm

no. weighted sum fct. $Q_0$

- TEM
- SEM
- PTA
- dAC-turb
- cAC-turb
- DLS (2x)
- SAXS
- ALS
Experimental MT evaluation (incl. BET)

Example #2: pigment Y83, opaque

BET equiv. min. size

no. weighted sum fct. $Q_0$

particle size, nm

TEM
SEM
PTA
dAC-turb
cAC-turb
DLS (2x)
ALS (2x)
Experimental MT evaluation (incl. BET)

Example #3: BaSO₄ f
Experimental MT evaluation (incl. BET)

Example #4: BaSO₄ uf
Experimental MT evaluation (incl. BET)

Example #5: Kaolin

BET equiv. min. size

No access of EM to the min. dimension of platelets!!

Particle size, nm

No. weighted sum fct. Q₀

TEM, SEM, PTA, DEMA, cAC-turb, cAC-RI, DLS, SAXS, ALS (2x)
What can EM offer? Example #5 (Kaolin) revisited

Access of EM to the min. dimension of platelets: possible!
Experimental MT evaluation (incl. BET)

Example #6: coated TiO$_2$

![Coated TiO$_2$](image)

**EDX**

- Porous coating

**BET equiv. min. size**
VSSA Evaluation as a *Tier 1* method - VSSA Correlation to EM

- 26 real-world materials (*NanoDefine* + more):
  - Various compositions
  - Strong agglomeration
  - Broad size range: 10 nm – 4 µm
  - 50% polydispersity

- **VSSA-derived smallest dim.**:
  \[ d_{\text{min}}^{_{\text{VSSA}}} = \frac{2D}{VSSA} \]

- e-Microscopy: *via* Feret

NanoDefine Final Outreach Event, Brussels, 19-20 September 2017
Reliable nanomaterial classification of powders using the volume-specific surface area method

Wendel Wohlleben · Johannes Mielke · Alvise Bianchin · Antoine Ghanem · Harald Freiberger · Hubert Rauscher · Marion Gemeinert · Vasile-Dan Hodoroba

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Abstract The volume-specific surface area (VSSA) of a particulate material is one of two apparently very different metrics recommended by the European Commission for a definition of “nanomaterial” for regulatory purposes: specifically, the VSSA metric may classify nanomaterials and non-nanomaterials differently than the median size in number metrics, depending on the

Here we evaluate the extent of agreement between classification by electron microscopy (EM) and classification by VSSA on a large set of diverse particulate substances that represent all the anticipated challenges except mixtures of different substances. EM and VSSA are determined in multiple labs to assess also the level of reproducibility. Based on the results obtained on highly
### Comparison VSSA by BET to EM

\[ \text{\(d_{\text{min}_{\text{VSSA}}}\) vs. \(\text{\(Feret}_{\text{min}}\)} \]

\[ \text{BET} \rightarrow (M)\text{SSA} \quad \left[ \frac{m^2}{g} \right] \]

\[ \text{SSA} \times \rho = \frac{S}{V} = \text{VSSA} \quad \left[ \frac{m^2}{m^3} \right] \]

\[ \text{\(d_{\text{min}_{\text{VSSA}}} = \linebreak \frac{2D}{\text{VSSA}} \)} \]

<table>
<thead>
<tr>
<th>Material</th>
<th>(D)</th>
<th>(d_{\text{min}_{\text{VSSA}}})</th>
<th>(\text{STD})</th>
<th>(d_{\text{min}_{\text{EM}}})</th>
<th>(\text{STD})</th>
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**NonNM** | **NM**
---

**EU**

**BAM**
Comparison of VSSA by BET to EM

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<th>Material</th>
<th>$D$</th>
<th>VSSA (BET)</th>
<th>$d_{\text{min}}^{\text{VSSA}}$</th>
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</tbody>
</table>
NanoDefine decision scheme for powders applied on a training set of industrial materials

VSSA \((d_{\text{min}}_{\text{VSSA}})\) vs. EM \((\text{Feret}_{\text{min}})\)

- **VSSA** (VSSA) 100nm cutoff = \(60 \text{ m}^2 \text{ cm}^{-3}\)
- **EM** (Feret)  

### Graph

- **true \(D\)**
- **\(t\)-plot**

### Legend
- **Perfect correlation**
- **Factor 2.5 mismatch**
- **Factor 10 mismatch**
- **NanoDefine**
- **Eurocolour/JRC**

### Equations
- \(d_{\text{min}}_{\text{VSSA}} = \frac{D}{3} \cdot \frac{1}{VSSA} \cdot 100\text{nm}\)

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NanoDefine Final Outreach Event, Brussels, 19-20 September 2017
**NanoDefine decision scheme for powders**

1. **Measurement as powder**
   - BET-Measurement + skeletal density

2. **VSSA**
   - Yes: Non-Nanomaterial by EC definition
   - No: Determination of shape (descriptive EM)

3. **Determination of shape (descriptive EM)**
   - Yes: accept homogeneous
   - No: Non-Nanomaterial by EC definition

4. **Shape**
   - d_{min,VSSA} < 250 nm
   - d_{min,VSSA} < 100 nm

5. **Borderline:**
   - 100 nm < d_{min,VSSA} < 250 nm
   - Spherical shape (aspect ratio <3:1) and 24 < VSSA < 60 m²/cm³ or Rod (aspect ratio >3:1:1) D=2 and 16 < VSSA < 40 m²/cm³ or Platelet (aspect ratio >3:3:1) D=1 and 8 < VSSA < 20 m²/cm³

6. **Nanomaterial by EC Definition**
   - x_{50} ≤ 100
   - Tier 2 E-Microscopy
   - x_{50} > 100

For irregular/mixture of shapes apply most conservative cut-off value.

\[ d_{min,VSSA}(D) = \frac{2D}{VSSA} \]
NanoDefine decision scheme for powders applied on a test set of industrial materials

VSSA (+ descriptive/quick SEM) for screening

VSSA screening, first step (assuming D=3)

VSSA screening, second step (best estimate for D)
Conclusions

• VSSA<sub>BET</sub> is a simple and reliable method
• As integrated in the decision flow scheme it can help to classify a material (powder) as **nano or non-nano**

• Conditions for use as proxy in the decision flow scheme:
  • Non-norderline materials (d<sub>min, VSSA</sub> < 100 nm or d<sub>min, VSSA</sub> > 250 nm)
  • Porous and coated materials: to be treated with care, *i.e.* combined with EM analysis or more advanced BET analysis (e.g. *t*-plot)
  • Monomodal size distribution
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- Dr. Marion Gemeinert (BAM, Berlin)

www.NanoDefine.eu

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