EMERGING GUIDANCE ON METHODS AND DECISION TREE FOR THE IDENTIFICATION OF NANOMATERIALS

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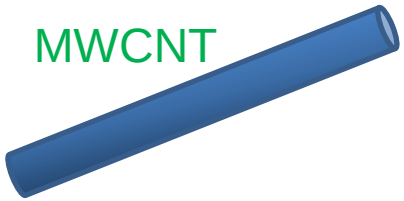
Objective of Nanodefine (2014-2017)

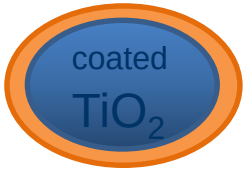
Provide ***Industries*** and ***regulatory agencies*** with the tools that support the implementation of **the definition** in all relevant regulatory contexts.

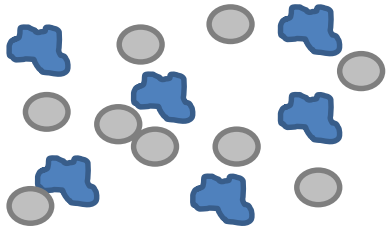
The NanoDefine foreseen solution will be:

- **Easy to implement**: as it integrates the current practice/facilities/expertise present at end-users with new developments
- **Cost efficient**: as it offers a tiered approach for the selection of the most adequate analytical route to get to a classification according to the definition with the least possible effort
- **Flexible**: as it defines criteria for the inclusion of novel technologies and can be adopted easily to changing regulatory requirements
- **Sustainable**: as the developed approach will be implemented in structures that persist beyond the duration of the project

Nanodefine sample overview:
Clariant, Solvay, L'Oreal, BASF, …

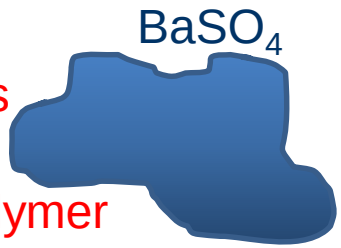




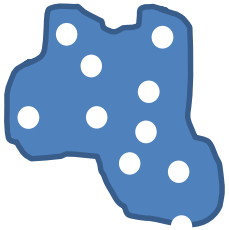


food with SiO_2

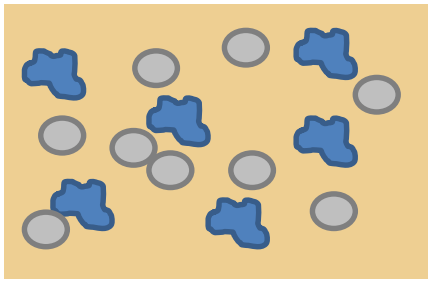
pigments



polymer particles

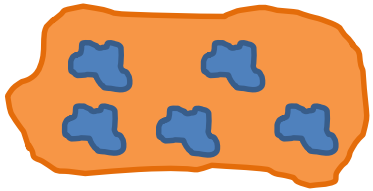


products



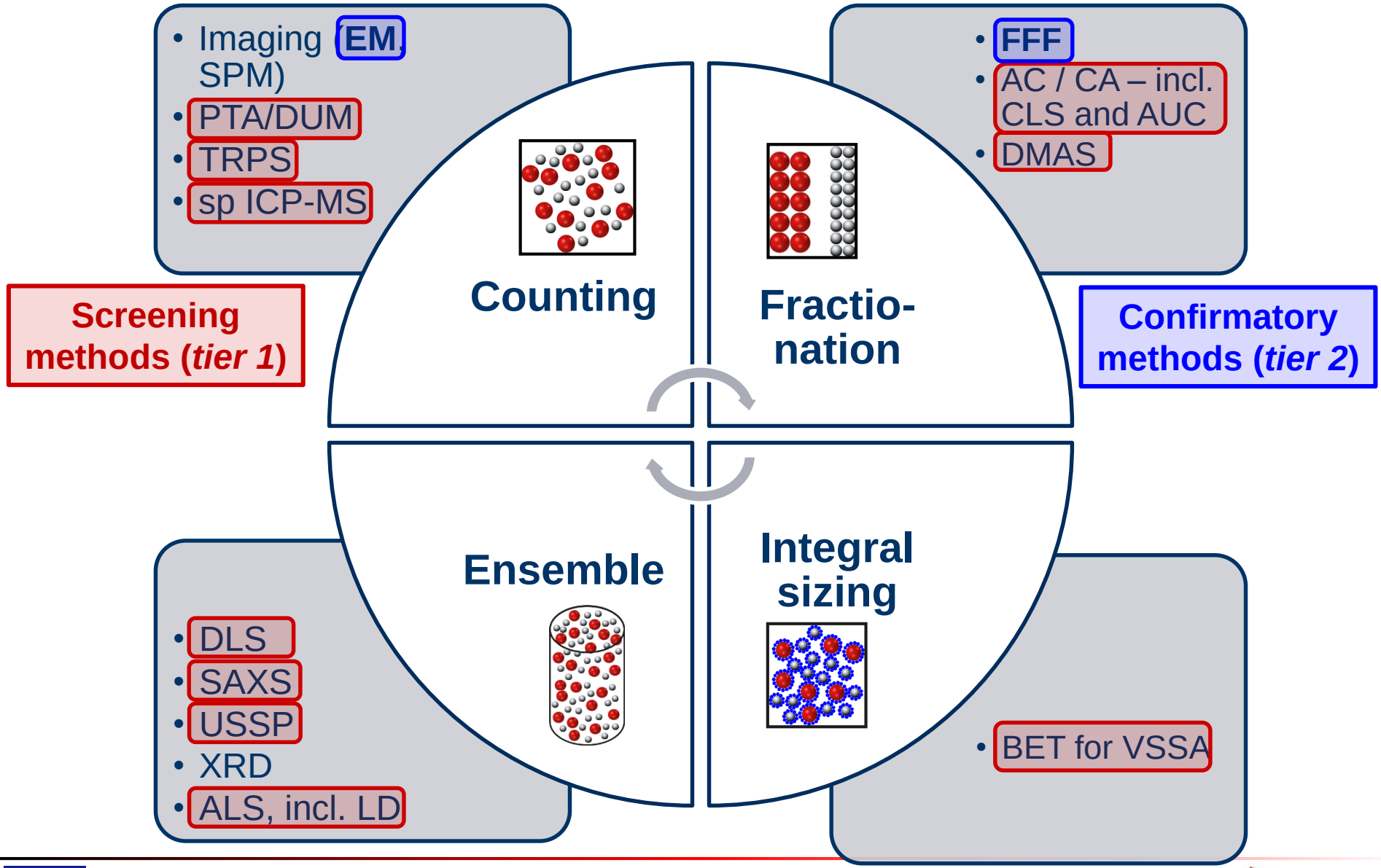
Sunscreen with TiO_2
Toothpaste

substances



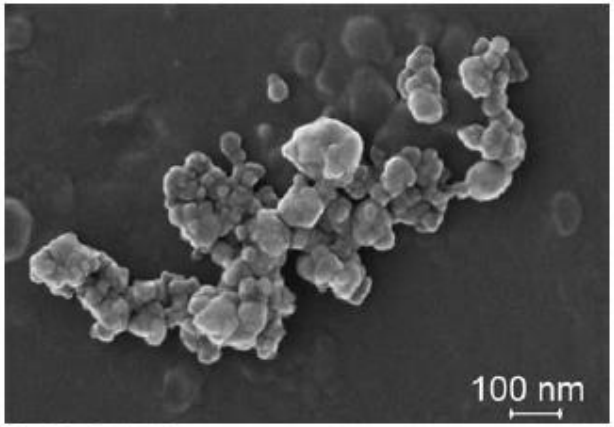
Fe_2O_3 in PE

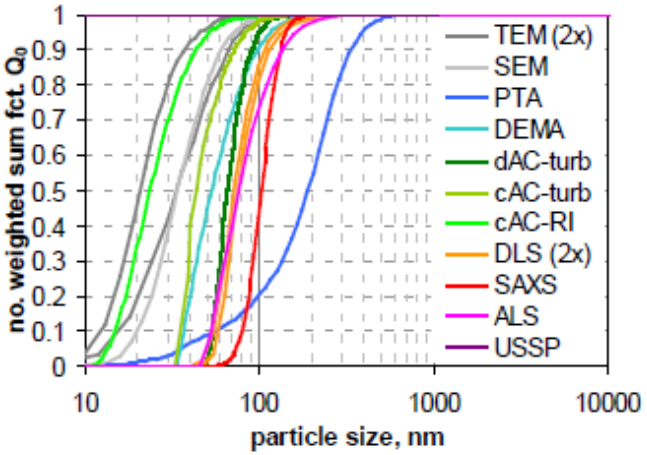
Measurement techniques able to probe the size of (nano)particles

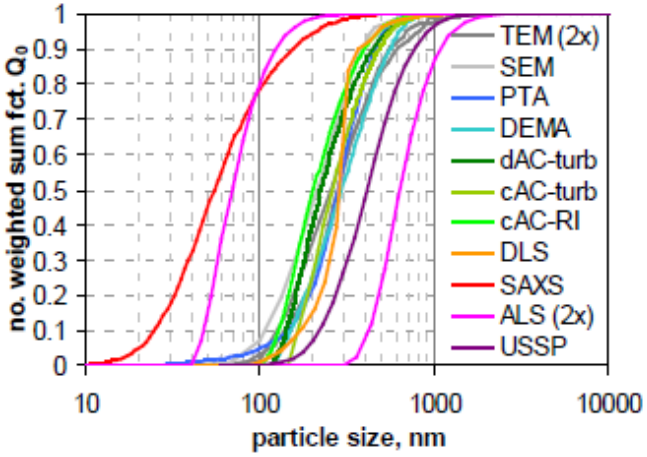


Can techniques differentiate nano vs non-nano grades?

EC nanodefinition (number metrics size distribution) determined for „ultrafine“ $BaSO_4$ & „fine“ $BaSO_4$







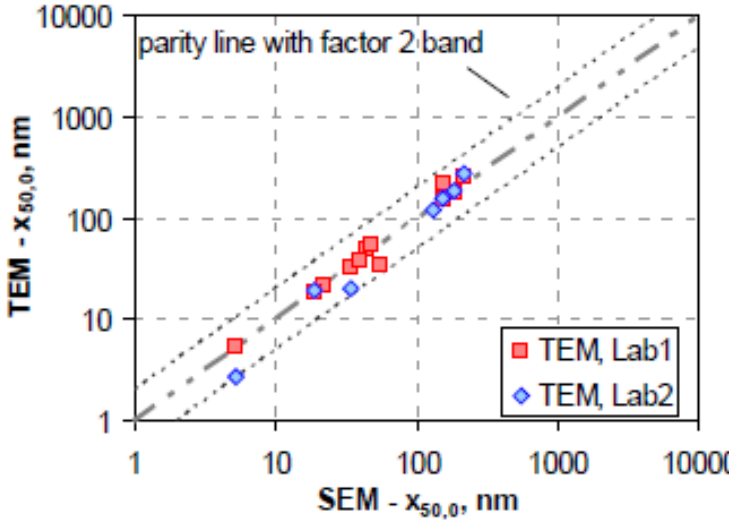
How reliably can a material be classified as a nanomaterial? Available particle-sizing techniques at work

Frank Babick · Johannes Mielke · Wendel Wohlleben · Stefan Weigel · Vasile-Dan Hodoroaba

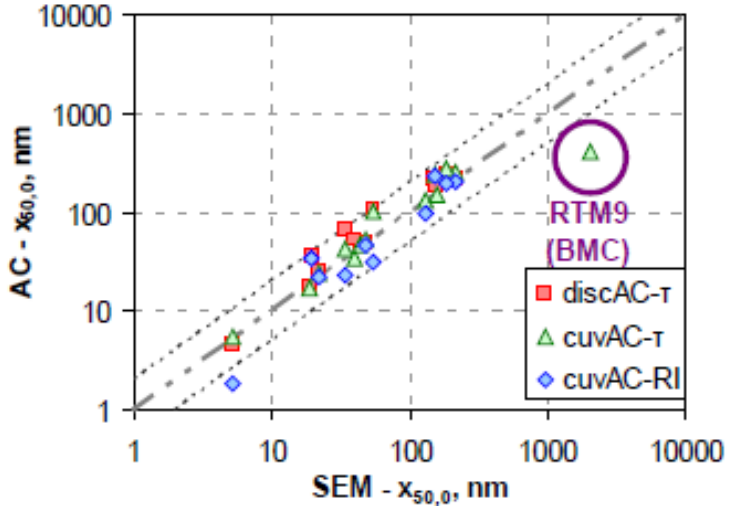
J Nanopart Res (2016) 18:158
DOI 10.1007/s11051-016-3461-7

Established techniques applied to real-world particulate materials

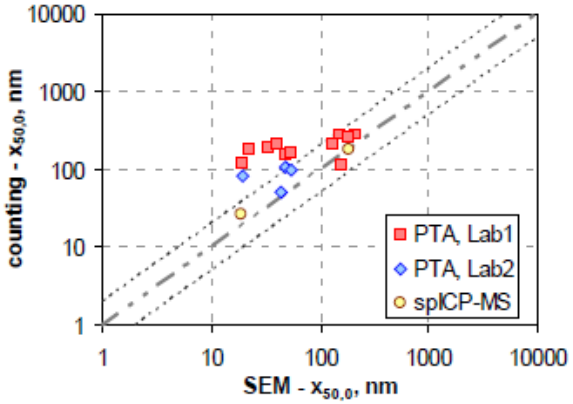
✓ Parity between TEM / SEM labs



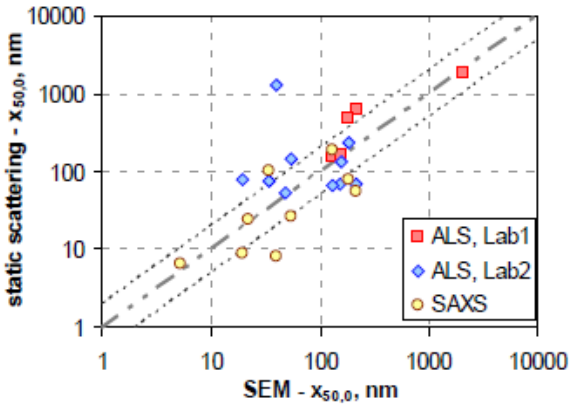
✓ Parity AUC – EM



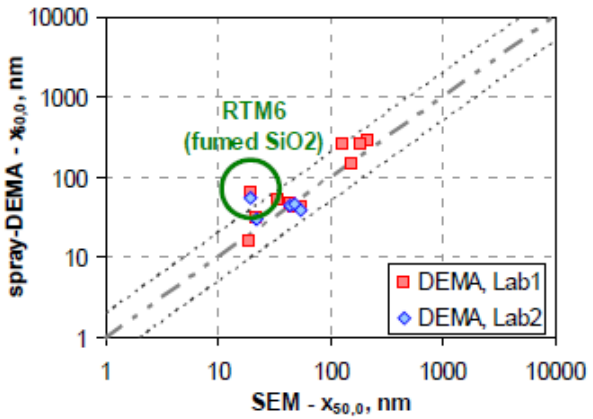
FAIL: PTA, spICPMS



FAIL: ALS, SAXS



✓ Promising: DEMA (SMPS)



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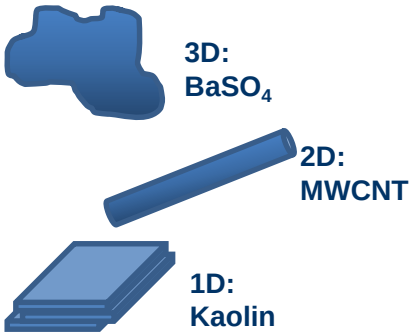
Quantitative relationship VSSA - EM

JRC report #2 introduces VSSA cutoffs adapted to shape.

- D = number of small dimensions (Roebben et al., 2014) :

$$\text{VSSA cutoff} = 60\,\frac{m^2}{cm^3} * \frac{D}{3}$$

- Concept assumes that the contribution to surface area is negligible from the surfaces that delimitate the large dimensions. Pagmatic approach to approximate dominating shape:
  - Particle (aspect ratio <3:1) D=3 → nano, if VSSA > 60 m²/cm³
  - Rod (aspect ratio >3:1:1) D=2 → nano, if VSSA > 40 m²/cm³
  - Platelet (aspect ratio >3:3:1) D=1 → nano, if VSSA > 20 m²/cm³

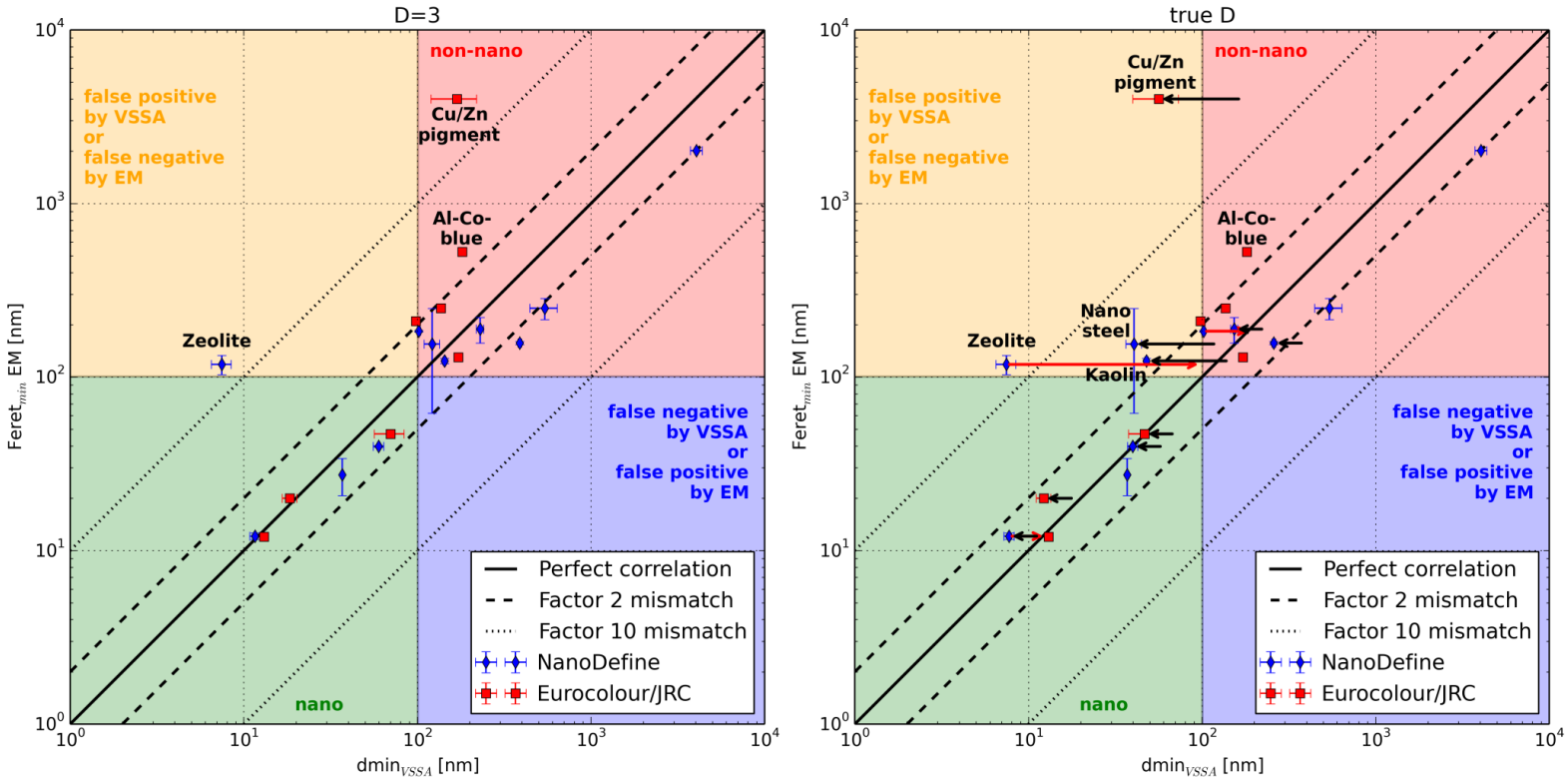


= Extract from a specific surface area measurement the diameter of the smallest dimension, and compare it to the 100 nm cutoff:

$$\text{VSSA \% of cutoff} = 60\,\frac{m^2}{cm^3} * \frac{D}{3} * \frac{1}{VSSA}$$

NanoDefine VSSA decision scheme for powders applied on a training set of industrial materials

VSSA ($dmin_{VSSA}$) *vs.* **EM ($Feret_{min}$)**

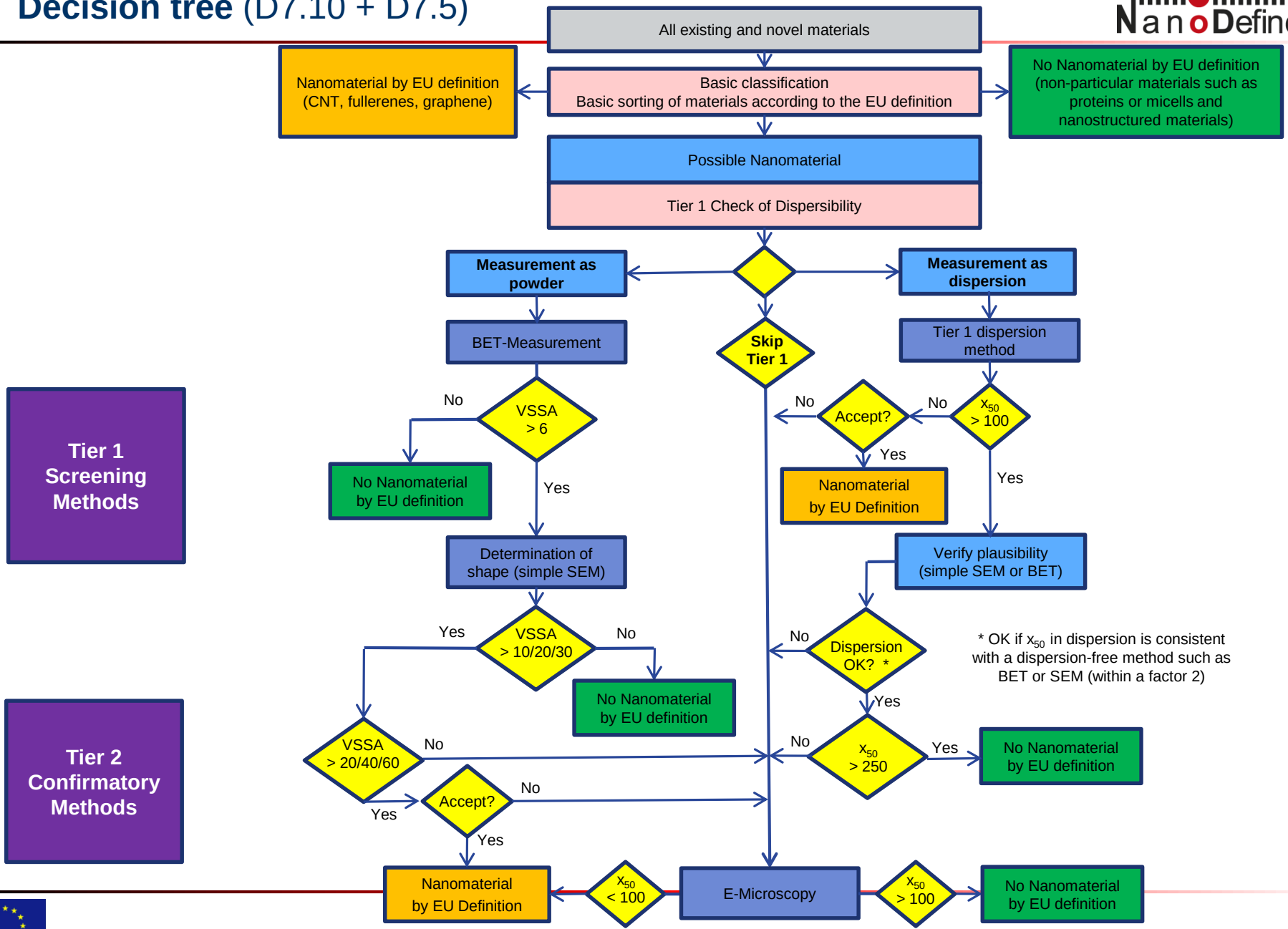


$VSSA\ 100nm\text{-}cutoff = 60\frac{m^2}{cm^3}$

$dmin_{VSSA} = 60\frac{m^2}{cm^3} * \frac{D}{3} * \frac{1}{VSSA} * 100nm$

W. Wohlleben, J. Mielke, A. Bianchin, A. Ghanem, H. Freiberger, H. Rauscher, M. Gemeinert and V.-D. Hodoroaba
BASF Ludwigshafen, BAM Berlin, MBN Vascon di Carbonera, Solvay Brussels, JRC Ispra, submitted (2016)

NanoDefine 2016 (consistent with VCI 2015)
Decision tree (D7.10 + D7.5)



Nanodefine Products

- **The NanoDefiner e-tool:** Standardised automated procedure for method selection and NM classification for the most economic implementation of the definition
- **The NanoDefine Method Manual:** Technical guidance on the use of available methodologies
- **Standard operation procedures (SOPs)** for analysis of materials and products
- **CEN/ISO work items** for key methods
- **Calibration standards and reference** materials
- **Instruments prototypes** tailored to the requirements of the definition
- **Technology transfer** of developed methods to end users

u 25 : catégories de substances produites et/ou importées en quantités supérieures à 100 t en 2014 (déclarations 2015)

Nom générique	Bande de tonnage
Carbon black	> 100 000 t
Silicon dioxide	> 100 000 t
Calcium carbonate	10 000 t à 100 000 t
Titanium dioxide	10 000 t à 100 000 t
Boehmite (Al(OH)O)	1000 t à 10 000 t
Copolymère de chlorure de vinylidène	1000 t à 10 000 t
Silicic acid, magnesium salt	1000 t à 10 000 t
Aluminium oxide	1000 t à 10 000 t
Polychlorure de vinyle	1000 t à 10 000 t
Mélange réactionnel de dioxyde de cérium et de dioxyde de zirconium	1000 t à 10 000 t
Calcium 4-[(5-chloro-4-methyl-2-sulphonatophenyl)azo]-3-hydroxy-2-naphthoate	1000 t à 10 000 t
Kaolin	100 t à 1000 t
3,6-bis-biphenyl-4-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione	100 t à 1000 t
Iron hydroxide oxide yellow	100 t à 1000 t
Aluminium hydroxide	100 t à 1000 t
Diiron trioxide	100 t à 1000 t
Iron hydroxide oxide	100 t à 1000 t
3,6-diphenyl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione	100 t à 1000 t

French Inventory
Rapport publique 2015

2,2'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[N-(2,4-dimethylphenyl)-3-oxobutyramide]	100 t à 1000 t
3,6-bis(4-chlorophenyl)-1H,2H,4H,5H-pyrrolo[3,4-c]pyrrole-1,4-dione	100 t à 1000 t
3-hydroxy-N-(o-tolyl)-4-[(2,4,5-trichlorophenyl)azo]naphthalene-2-carboxamide	100 t à 1000 t
3,6-Bis(4-tert-butylphenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione	100 t à 1000 t
2-Propenoic acid, 2-methyl-methyl ester, polymer with 1,3-butadiene, butyl 2-propenoate and ethenylbenzene	100 t à 1000 t

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dione	100 t à 1000 t

In hindsight, NanoDefine chose the relevant materials

French Inventory
Rapport publique 2015

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3,6-bis(4-chlorophenyl)-1H,2H,4H,5H-pyrrolo[3,4-	
2-Propenoic acid, 2-methyl-methyl ester, polymer with 1,3-butadiene, butyl 2-propenoate and ethenylbenzene	100 t à 1000 t

DG ENV, *Draft Impact Assessment on Transparency Measures on Nanomaterials on the Market*, 5 October 2016; Doc. CA/63/2016

Experience from the French notification system […] concerns innovative nanomaterials only to a small extent. Rather, [it] relates to materials which have been on the market for a long time, and which companies were forced to assess against the nanomaterial definition for the first time.

NanoDefine Consortium

29 Partners form a consortium of European RTD performers, metrology institutes and nanomaterials and instrument manufacturers.