Exposure estimation of airborne particle release from nanostructured materials by propagation modelling

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6. Sustainable Nanotechnology Organization Conference 2017, Los Angeles
3A Fate & Exposure I

Release – Exposure

Release from moving powders

sanding composites

spraying suspensions

Propagation of the released particles

TUD release studies on nanostructured materials

- ❑ powder handling (🗐 Göhler & Stintz 2015)
- ❑ spray can/gun application of liquid coatings (🗐 Göhler & Stintz 2014)
- ❑ weak abrasion of solid composites (🗐 Vorbau et al. 2009)
- ❑ sanding of solid composites; also aged ones (🗐 Göhler et al. 2010, 2013)
- ⇨ release data: particle size distributions & fractional particle release numbers

Risk assessment requires data on exposure !

- ❑ release (≠) exposure
- ❑ release = state of dispersion (particle size and concentration) at source
- ❑ exposure = state of dispersion at entrance to subject of protection
- ❑ exposure = f(release, transport & transformation)
- ⇨ exposure data: release data in combination with propagation modeling

Exposure *(incl. background)*

↑

Transport/Transformation = *f(environm. scenario)*

↑

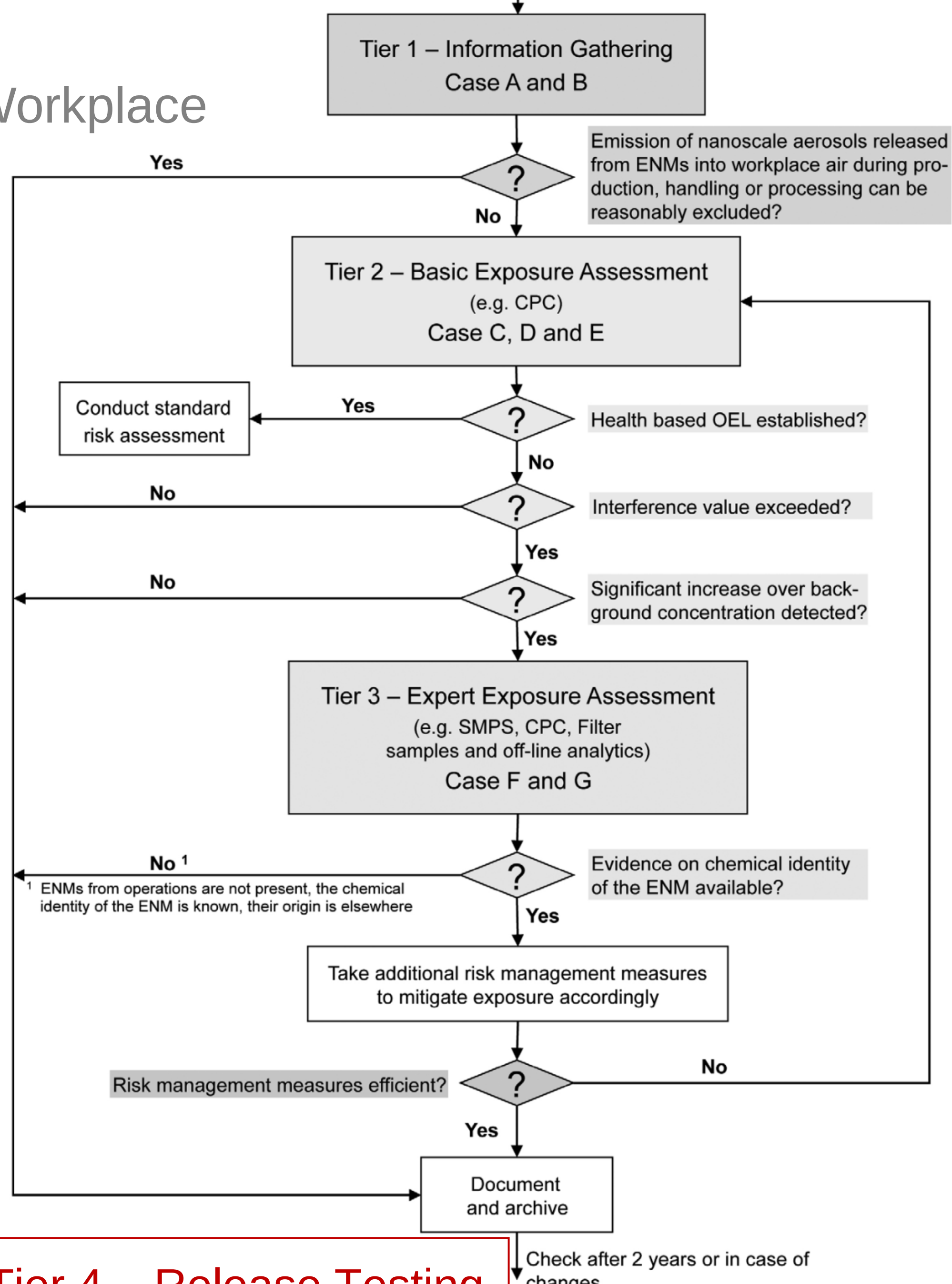
Nanoparticle release = *f(Material, Process)*

(ISO-Nanotechnology – Nano-object release)

Release at Workplace

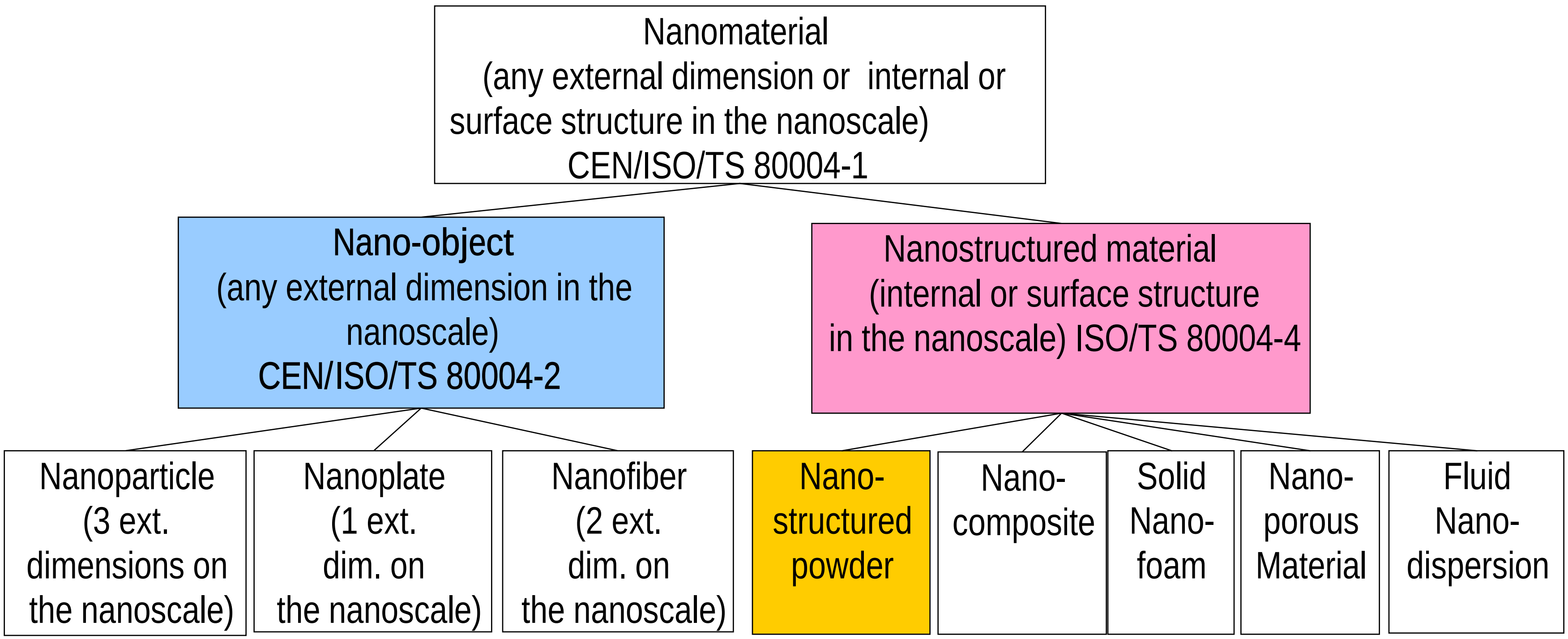
Tiered Approach to an Exposure Measurement and Assessment of Nanoscale Aerosols, Released from Engineered Nanomaterials in Workplace Operations

https://www.vci.de/vci-online/services/leitfaeden/2012-02-28-expositionsermittlung-und-bewertung-nanoskaliger-aerosole-vci.jsp



Tier 4 – Release Testing

Nanoobjects in Nanomaterial Terminology



Assemblies of nanoparticles or nano-objects, which extend the nanoscale, are covered by ISO/TS 80004-4 Nanotechnologies -Terminology and definitions for nanostructured materials

Besides: **NOAA** (Description from WG3, summarization of 2 definitions):
Nano-objects and their larger **A**gglomerates and **A**ggregates (Nanostructured material)

European Commission definition (decision) draft: count median $x_{50,0} < 100$ nm

Many Publications on nano-object release into air:

- inconsistent terminology,
- no standardized metrological procedures,
- arbitrary kind of data evaluation.

No quantitative comparison, if necessary parameters are missing.

ISO/TC 229/JWG 2/PG 10 has developed the technical specification ISO/TS 12025 (now rev.2017), which is a general framework for determining airborne release of nano-objects from **nanostructured powders** by means of aerosol analysis.

Information on the methodology for nano-object release quantification covers
- necessary measurands, - process parameters - presentation of measurement results by specific release numbers.

Support for standardization of nano-object release testing of **nanocomposites**, e.g. by abrasion procedures.

ISO/TS 12025:2012, Nanotechnologies — Quantification of nano-object release from powders by generation of aerosols

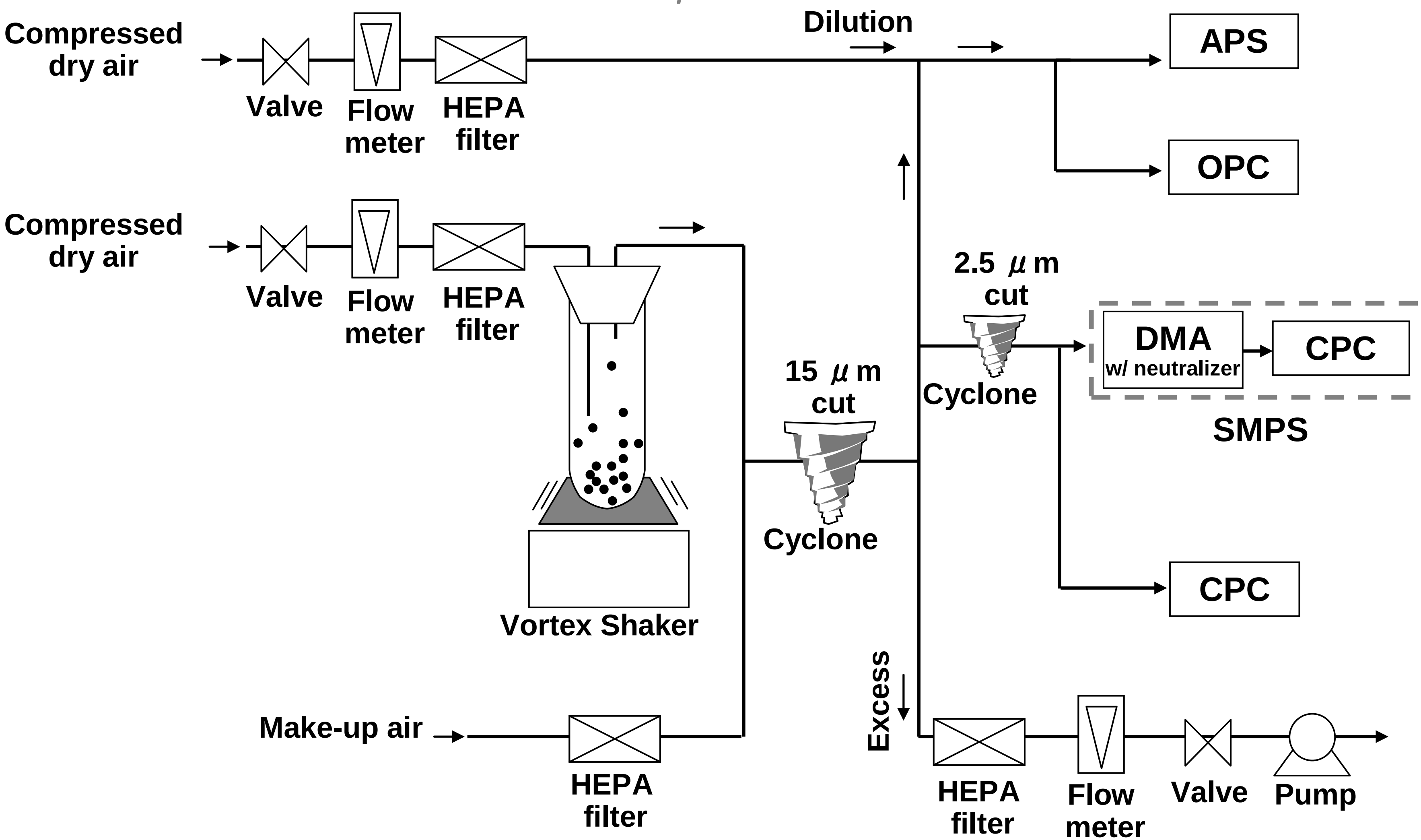
Symbol	Quantity	SI Unit
n	nano-object number release	dimensionless
n_t	nano-object release rate	s^{-1}
c_n	nano-object aerosol number concentration	m^{-3}
n_m	mass specific nano-object number release	kg^{-1}
V_t	aerosol volume flow rate	$m^3 s^{-1}$

nano-object number release
total number of nano-objects, released from a sample as a consequence of a disturbance

nano-object release rate
total number of nano-objects, released per second as a consequence of a disturbance

mass specific nano-object number release
Nano-object number release, divided by the mass of the sample before the disturbance

Informative Example Vortex Shaker method



Experimental details - Experimental apparatus

sanding process

particle free environment
sampling of all emissions
sampling at particle source

process parameters

- 2010: industrial sanding process
- project A: comparability with 2010
- project B – AC[B]: sanding only within weathered region of the samples (< 5 µm)
- project B – PP[B]: avoidance of thermal particle generation

parameter		2010	A	B	
		SC	SC	AC[B]	PP[B]
sanding area	[cm²]	13.0	10.4	10.4	10.4
sample speed	[mm/min]	5.0	5.0	5.0	5.0
sanding time	[s]	16.0	16.0	16.0	16.0
face velocity	[m/s]	3.9	4.8	4.9	4.9
normal force	[N]	0.5	0.5	0.5	0.5
paper graining	[-]	P600	P600	P1200	P240
rotational velocity	[m/s]	1.83	1.83	1.83	0.73
cutting velocity ratio	[-]	366	366	366	146
cutting power	[W]	1.3	1.3	1.3	0.5

Göhler et al. (2010) *Ann. Occup. Hyg.*; 54(6): 615-624.

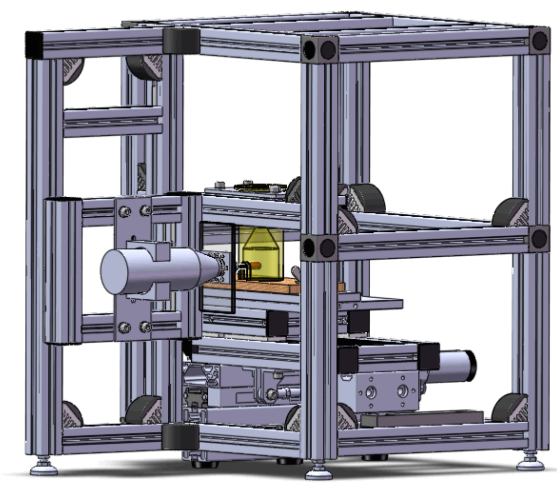
Results - Data evaluation

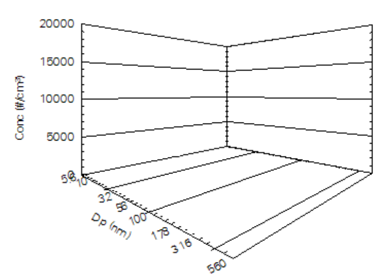
aerosol measurement data

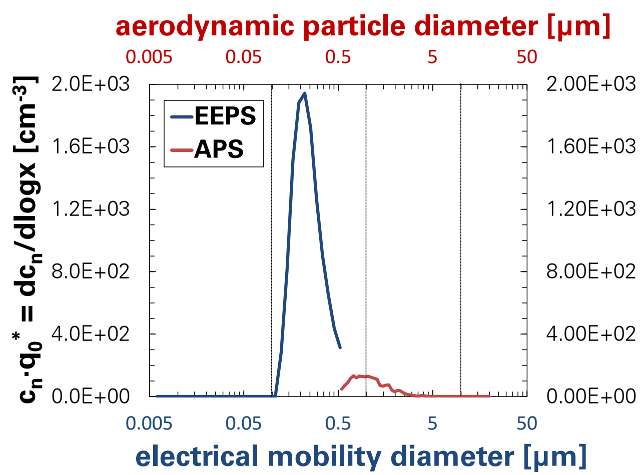
- ❑ particle number concentration
- ⇨ without additional information not suitable as release parameter
- ❑ number-weighted particle size distributions

independent release parameter

- ❑ fractional particle release numbers n_A (e.g. x ≤ 100 nm, x< 10 µm, x ≥ 1 µm)
- ❑ relation to stressed area ⇨ area specific release numbers [#/cm²]







ISO/TC 256 NWIP: Pigments and extenders — Determination of experimentally simulated nano-object release from paints, varnishes and pigmented plastics

Scope

This standard specifies a method for experimental determination of the release of nanoscale pigments and extenders into the environment following an abrasive stress of paints, varnishes and pigmented plastics.

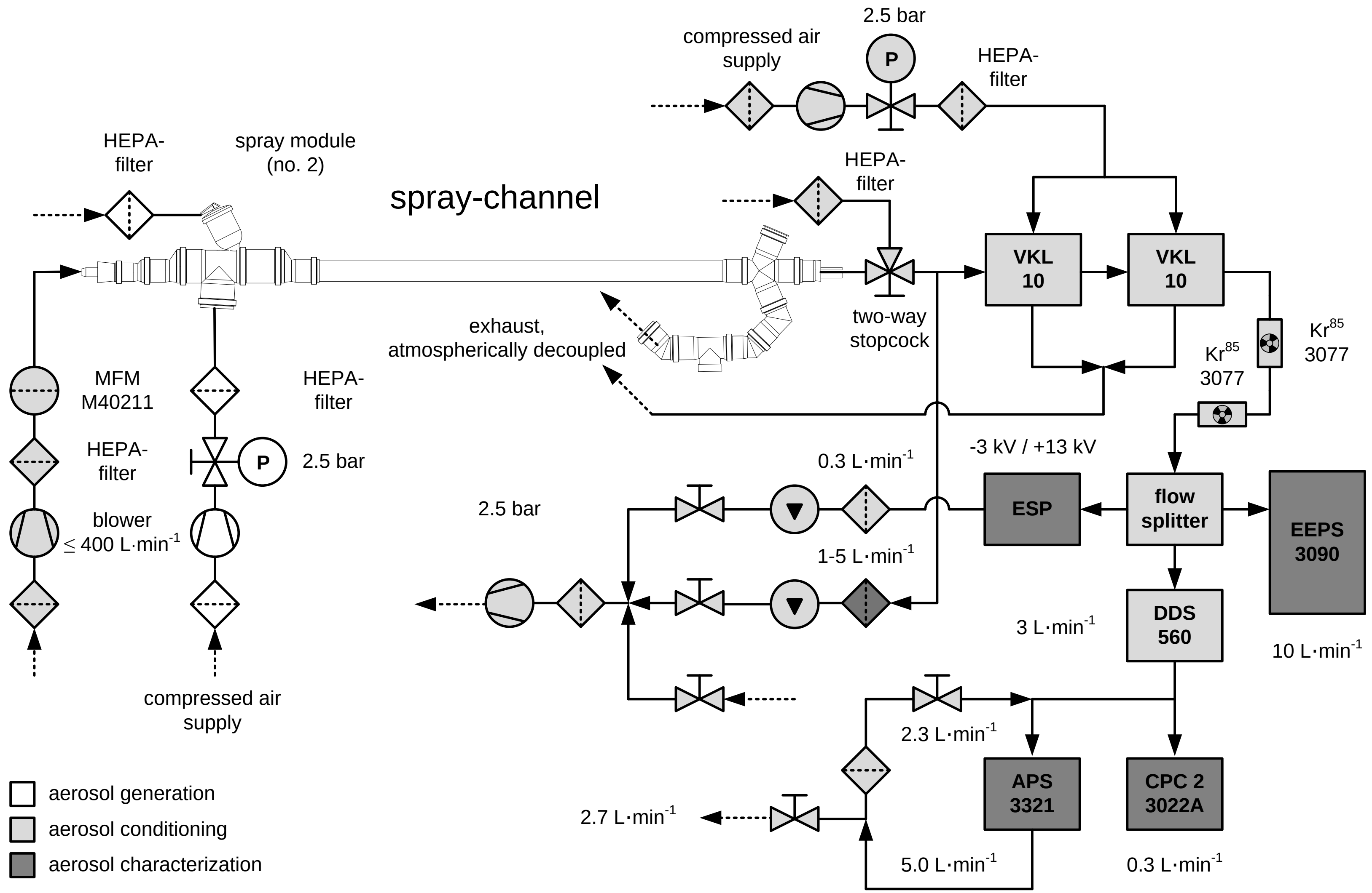
The method is used to evaluate if and how many particles of defined size and distribution under stress (type and height of applied energy) are released from surfaces and emitted into the environment.

The samples may be aged, weathered or otherwise conditioned to simulate the whole lifecycle.

Nanoparticle Release Test - Spraying

Göhler, Stintz: Granulometric characterization of airborne particulate release during spray application of nanoparticle-doped coatings. J Nanopart Res (2014) 16:2520

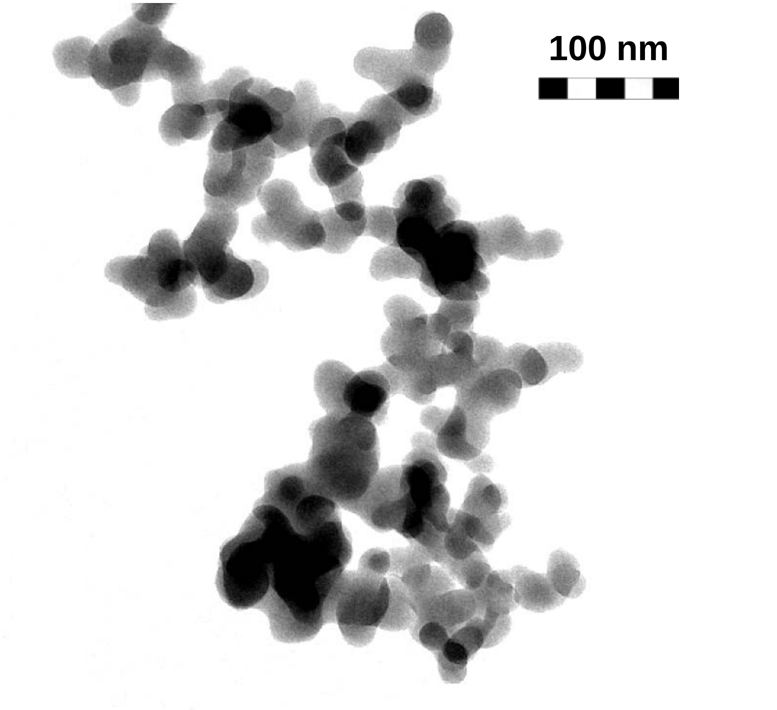
Nanoparticle Release Test - Spraying

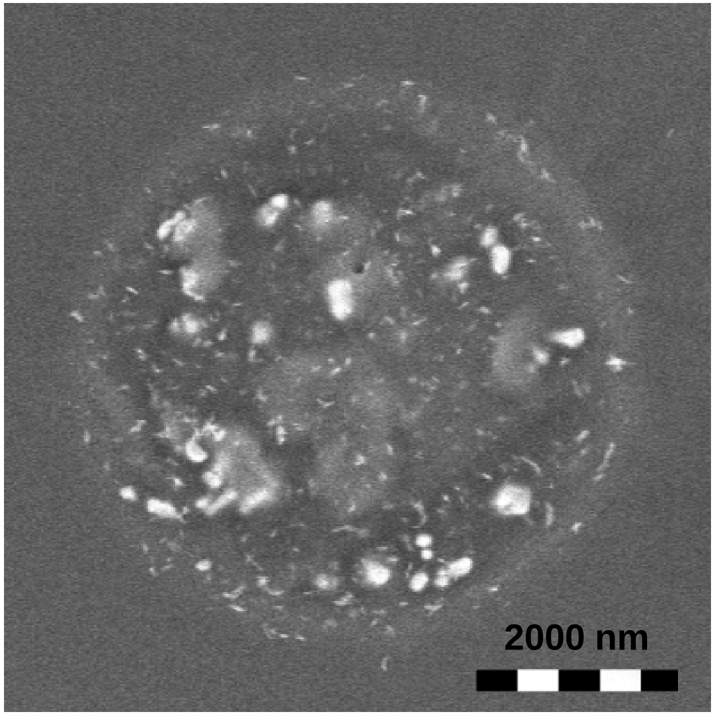


Whole setup scheme for spray application, aerosol conditioning and characterization

Sprayed Nanostructured Particles

which fulfil the EC recommendation on the definition of nanomaterials.



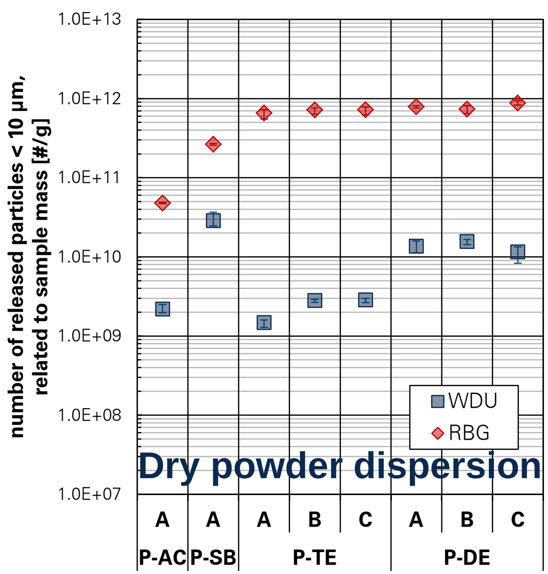


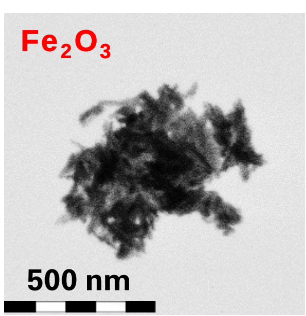
TEM-image of a synthetic and fractal SiO_2-aggregat (≈ 500 nm) containing sintered nanoscale primary particles (≈ 18 nm)

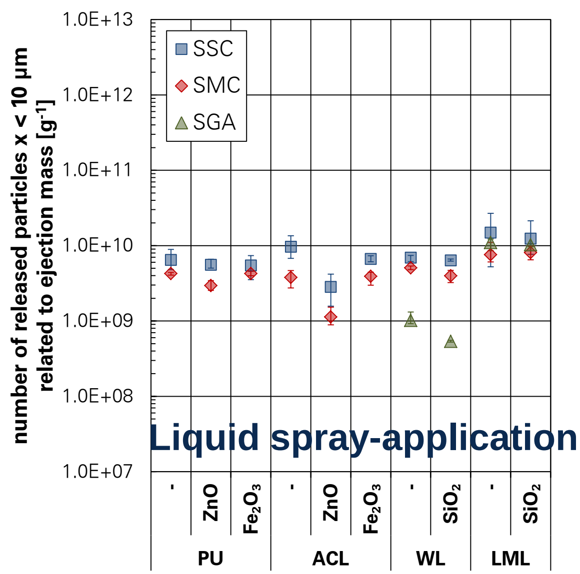
SEM-image of a dried spray droplet (≈ 5µm) made of acrylate topcoat with embedded TiO_2 pigment particles (≈ 200 nm) and embedded iron oxide nanoparticles (< 100 nm)

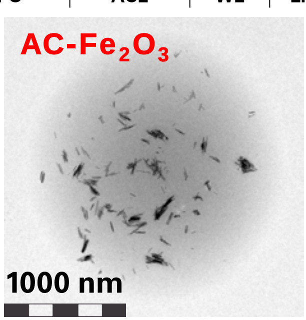
Release Comparison of 3 Processes

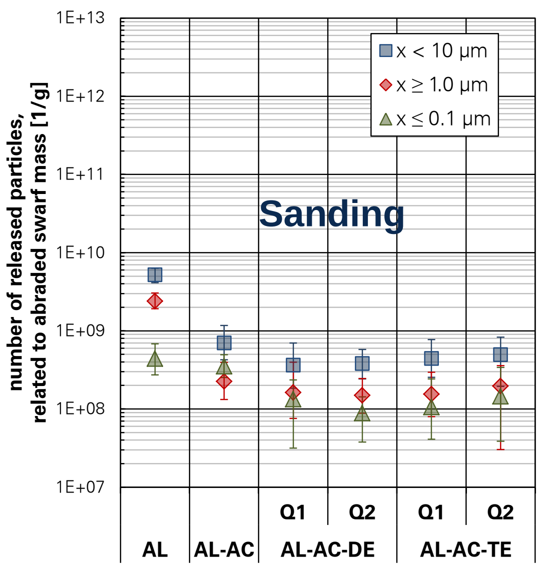
Göhler et al. (2015, 2014, 2013)

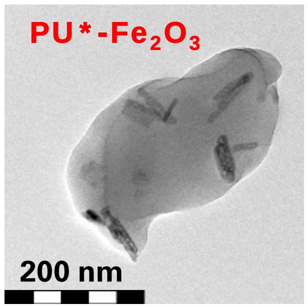












Release – Exposure

Release from moving powders

sanding composites

spraying suspensions

Propagation of the released particles

Modeling details

Computational tools and simplifications

IET Institut für Energietechnik

propagation modeling (FEM)

- ❑ computational fluid dynamics (ParallelNS, e.g. 🗐 Knopp et al. 2005)
- ❑ thermal building simulation (TRNSYS-TUD)
- ⇨ module combination in parallel virtual machine (e.g. 🗐 Gritzki et al. 2003)

main appointed simplifications regarding release

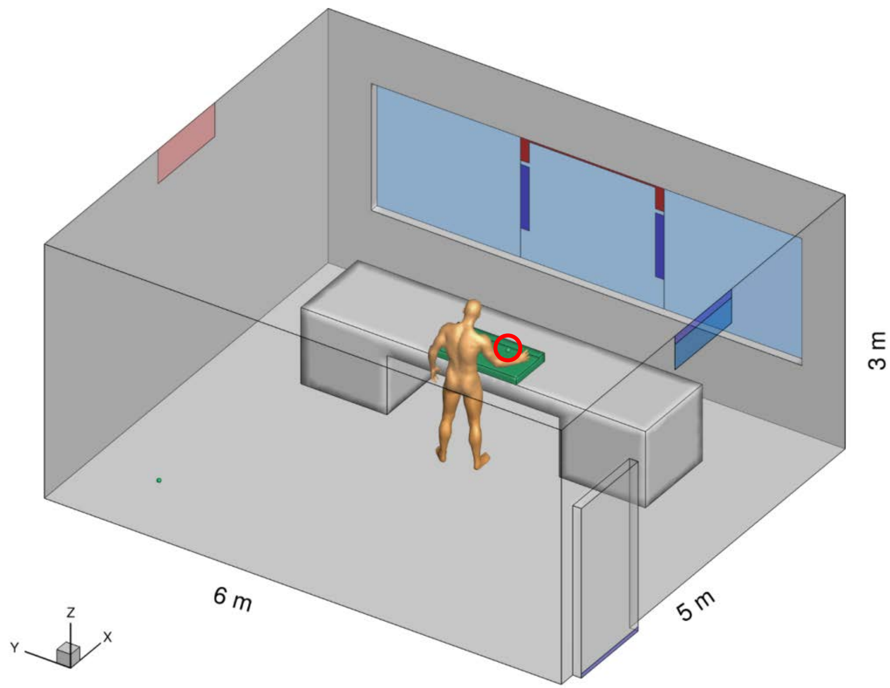
- ❑ release processes do not interact with the environment
- ⇨ no flow displacement (i.e. interference-free particle supply)
- ⇨ no directional momentum
- ⇨ …
- ❑ gas-like behavior of released airborne particles
- ⇨ no particle-particle interaction (e.g. reagglomeration)
- ⇨ no particle-wall interactions (e.g. particle losses)
- ⇨ …

Modeling details

Selected specifications

model room (e.g. workshop)

- ❑ room envelope
- ⇨ 5 m x 6 m x 3 m = 90 m³
- ⇨ triple-part window ($\vartheta_{outdoor} \stackrel{def}{=} 5$ °C)
- ⇨ floor heating ($\vartheta_{room} \stackrel{def}{=} 20$°C)
- ❑ room interior
- ⇨ workbench
- ⇨ person (1.8 m, $\vartheta_{clothes} \stackrel{def}{=} 26$°C)



3 ventilation scenarios (blue = inlet air; red = exit air)

- ❑ natural ventilation by door slit infiltration (NVD) 0.5 h^{-1}
- ❑ natural ventilation by pivot-hung window (NVW) 1.5 h^{-1}
- ❑ “improved” technical ventilation system (TVS) 8.0 h^{-1}

Selected specifications

3 release scenarios

- ❑ wiping (WIP)
- ⇨ procedure: dry wiping of a coated item with a surface area of 0.5 m² for 10 s
- ⇨ conditions: Vorbau et al. 2009 (UV-ZnO)
  area specific particle release number < 10 µm = $5.0 \cdot 10^{05}$ #/m²
  very low release -> particle size distribution (PSD) could not measured
- ❑ sanding (SAN)
- ⇨ procedure: sanding of a coated item with a surface area of 0.5 m² for 60 s
- ⇨ conditions: Göhler & Stintz 2010, 2013, 2014 (UV*-ZnO)
  area specific particle release number < 10 µm = $1.0 \cdot 10^{11}$ #/m²
  lognormal PSD ($x_{50,0}$ = 240 nm; GSD = 1.4); density “1000” kg/m³
- ❑ spraying (SPR)
- ⇨ procedure: standard spray can application for 60 s
- ⇨ conditions: Göhler & Stintz 2014 (PU-ZnO)
  particle release rate x < 10 µm = $7.5 \cdot 10^{09}$ #/s
  lognormal PSD ($x_{50,0}$ = 120 nm; GSD = 2.0); density 1000 kg/m³

Göhler D, Gritzki R, Stintz M, Rösler M, Felsmann C. Propagation modelling based on airborne particle release data from nanostructured materials for exposure estimation and prediction. J. Phys.: Conf. Ser., 2017, accepted.

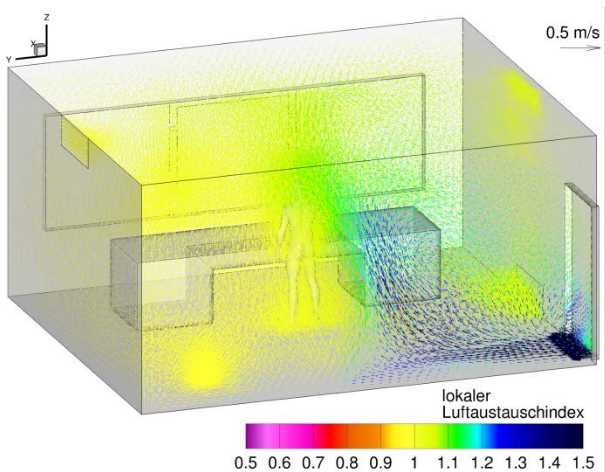
Results - Ventilation scenarios, steady state

Velocity field and local air exchange quality

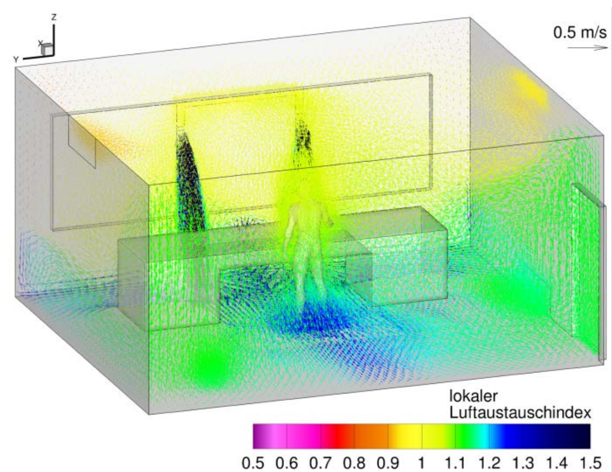
steady state conditions reached after 30 min

- ⇨ purple/orange regions: local air exchange is less than mean air exchange rate
- ⇨ yellow regions: local air exchange corresponds to mean air exchange rate
- ⇨ green/blue regions: local air exchange is better than mean air exchange rate

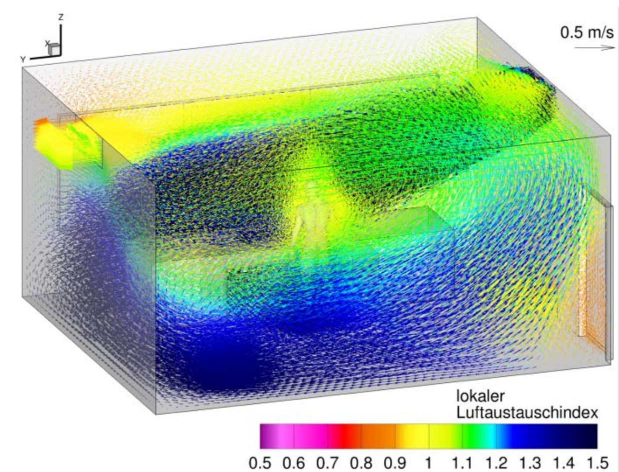
NVD (0.5 h^{-1})
natural ventilation by door slit



NVW (1.5 h^{-1})
… by window



TVS V3 (8.0 h^{-1})
technical vent. system

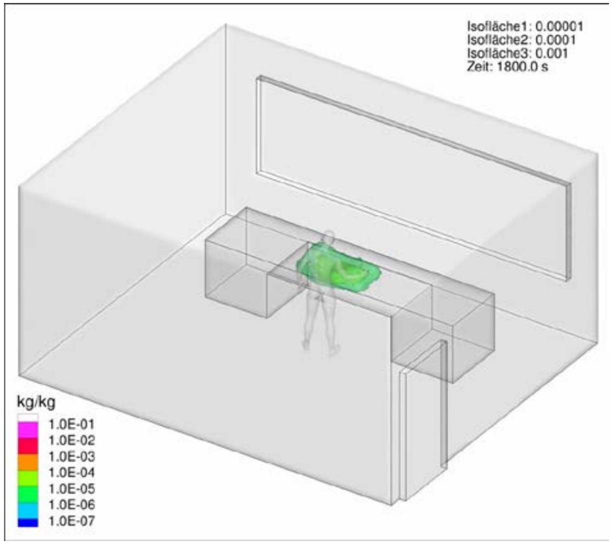


Results - Exposure Scenarios

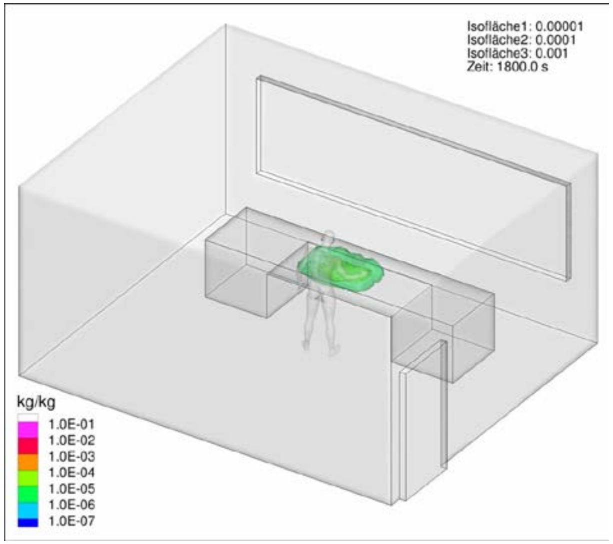
Aerosol propagation: **Wiping**

- 3 iso-surfaces of relative gas exchange (~ particle concentration)
- release process (duration 10 s) starts at 1800 s, videos run until 1900 s
- tenfold playback speed

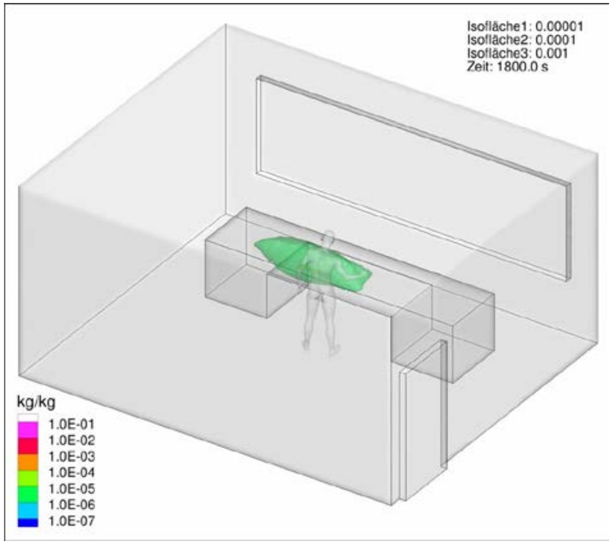
NVD (0.5 h^{-1})



NVW (1.5 h^{-1})



TVS V3 (8.0 h^{-1})

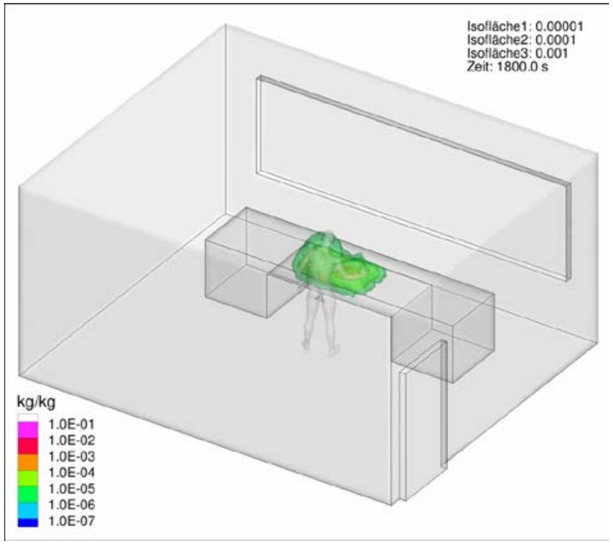


Results - Exposure Scenarios

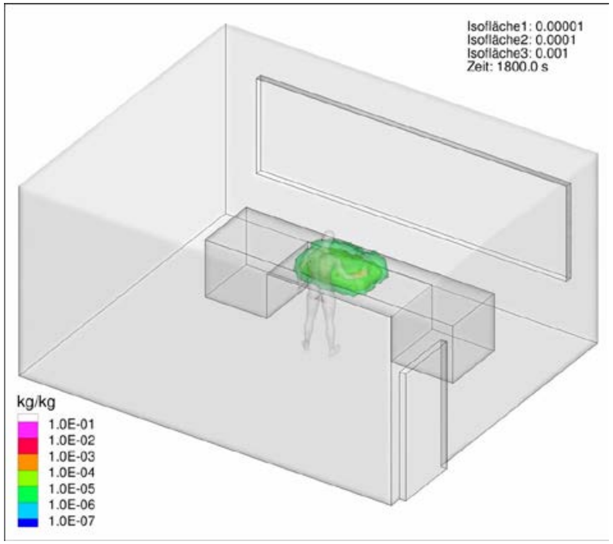
Aerosol propagation: **Sanding**

- 3 iso-surfaces of relative gas exchange (~ particle concentration)
- release process (duration 60 s) starts at 1800 s, videos run until 1900 s
- tenfold playback speed

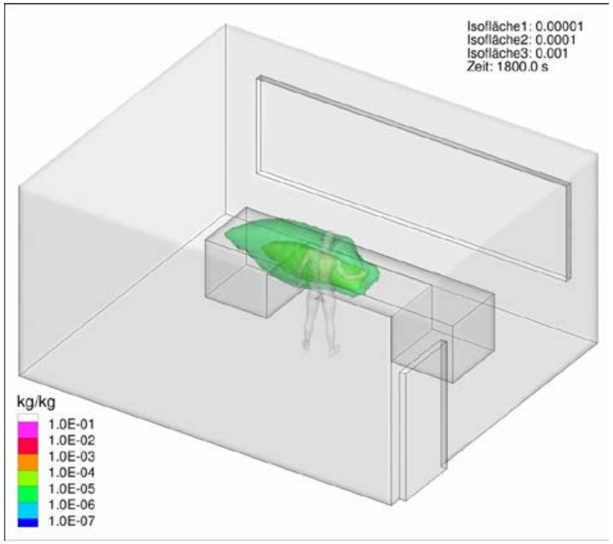
NVD (0.5 h^{-1})



NVW (1.5 h^{-1})



TVS V3 (8.0 h^{-1})

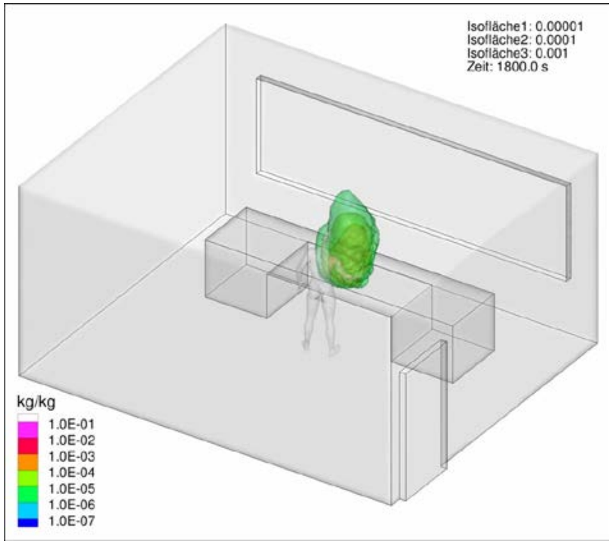


Results - Exposure Scenarios

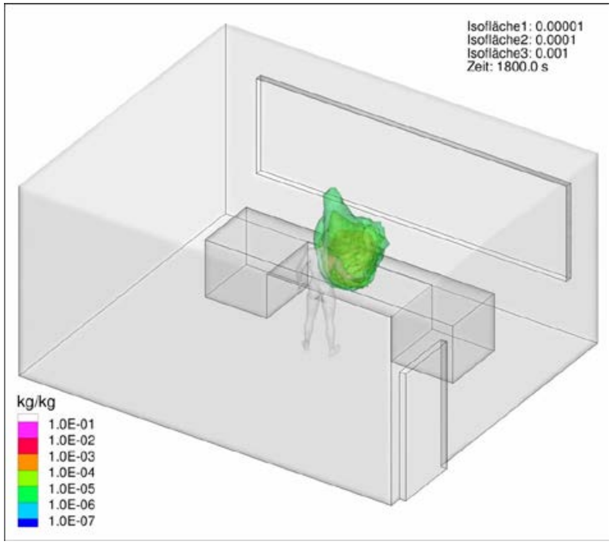
Aerosol propagation: **Spraying**

- 3 iso-surfaces of relative gas exchange (~ particle concentration)
- release process (duration 60 s) starts at 1800 s, videos run until 1900 s
- tenfold playback speed

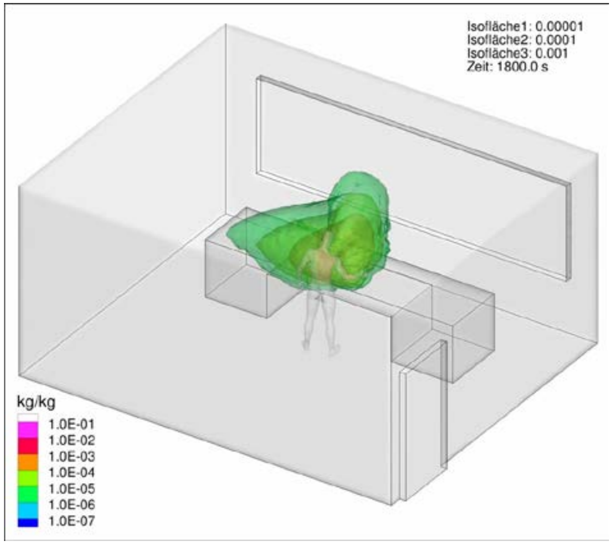
NVD (0.5 h^{-1})



NVW (1.5 h^{-1})



TVS V3 (8.0 h^{-1})



Results - Exposure Scenarios (spraying)

from exposure via inhalation to deposition

exposure

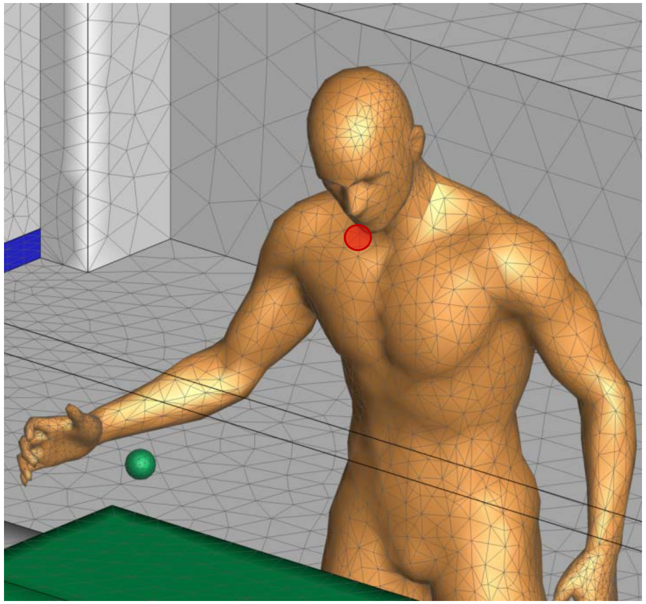
- ❑ sensor at person in breathing zone
- ⇨ particle number concentration over time
- ⇨ particle mass concentration over time

inhalation

- ❑ gender averaged breathing rate 383cm³/s
- ⇨ cumulative number of inhaled particles
- ⇨ cumulative mass of inhaled particles

deposition in human airways

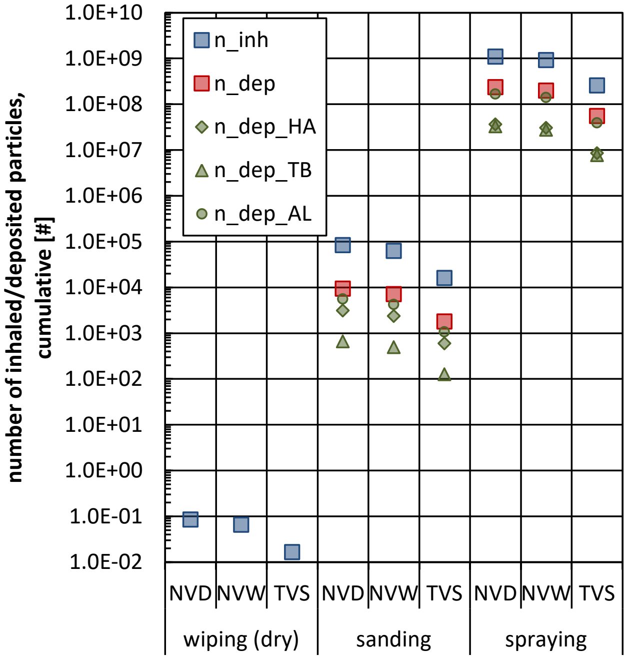
- ❑ modified IRCP 66 Modell (Hinds 1999); gender/activity averaged
- ⇨ deposition fraction based on PSDs
- ⇨ combination with inhalation

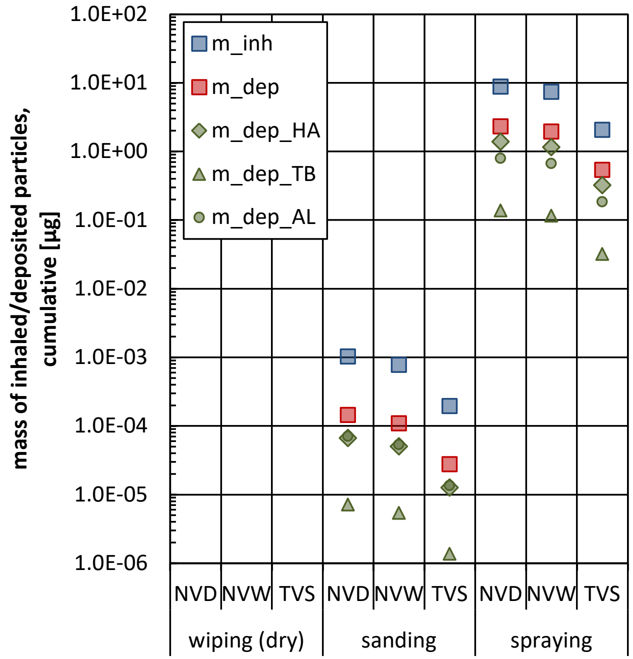


Results - Inhalation & Deposition

number/mass of inhaled/deposited particles

- negligible exposure levels by wiping, highest exposure levels by spraying
- $n_{released}/n_{inhaled}$ depends on exposure scenario and varied from 4E2 … 3E8





$n_{released}/n_{inhaled}$

	NVD	NVW	TVS
SPR	4E2	5E2	2E3
SAN	3E5	4E5	2E6
WIP	6E7	8E7	3E8

From **characterisation of nanomaterial release:**

- Particle size distribution and concentration alone are not sufficient
- Sample amount related quantities (e.g. numbers) and also larger particle size ranges for plausibility balancing are necessary

- Sample treatment processes can be more important than sample material
- Matrix and nanoparticle embedding properties are important
- Nanoparticle release from non-nanomaterials like polymer matrices must be tested for comparison.

General Conclusions

For **characterisation of nanomaterial release** and transport:

- Methods are now available and subject of international standardization.
- World wide community has test methods adopted and validation and ILC started.
- Estimation of potential release (Precaution) on basis of TEM-images of prepared nano-object structures should be replaced by measurement.

For **characterisation of exposure**:

- Condition of ventilation defines fundamentally the level of exposure
- Convective flows due to personal heat can move particle in breathing z.
- Highest exposure levels arise immediately during material processing
- Measured release data are more resistant than exposure ones, because they are less affected from conditions of the surrounding scenario.

Thank you!

References

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Organization	TC / SC	Main Responsibilities
ISO	TC 24 / SC 4	**Particle characterization**
	TC 142	Cleaning equipment for air and other gases
	TC 146 / SC 2	Air Quality – Workplace Atmospheres
	TC 194	Biological evaluation of medical devices
	TC 201	Surface chemical analysis
	TC 202	Microbeam analysis
	TC 229	**Nanotechnologies**
	TC 256	**Pigments, dyestuffs and extenders**
IEC	TC 113	Nanotechnology standardization for electrical and electronic products and systems
CEN	TC 137	Assessment of workplace exposure to chemical and biological agents
	TC 138	Non-destructive testing
	TC 162	Protective clothing including hand and arm protection and lifejackets
	TC 195	Air filters for general air cleaning
	TC 230	Water analysis
	TC 248	Textiles and textile products
	TC 352	**Nanotechnologies**

ISO/TC 24/SC 4 „Particle Characterization”

WG1 Results representation, WG2-17 Measurement methods

“vertically”, measurement methodology oriented

TC 256 “Pigments, dyestuffs and extenders”

WG2 Nanotechnological properties of pigments and extenders

ISO/TC 229 „Nanotechnologies“

WG1 Terminology, WG2 Measurement, WG3 HSE-Aspects, WG4 Material spec.

“horizontally”, interdisciplinary, application oriented

CEN/TC 352 „Nanotechnologies“

WG1 Measurement, WG2 Commercial Aspects, WG3 HSE-Aspects

ISO-catalogue http://www.iso.org/iso/home/store/catalogue_ics.htm

searching for a **standard** with a key word or

ICS (International Classification for Standards) - "ICS 19.120: Particle size analysis. Sieving" or

TC (technical committees) - "TC 24/SC 4 Particle characterization".

Accessible are: table of content, introduction and scope.

ISO 26824:2013 ISO-Vocabulary with more than 263 **definitions** on

ISO Online Browsing Platform (https://www.iso.org/obp) at "Terms and Definitions".

ISO/TC 24/SC 4 Particle Characterization

(16 P-Members, 12 O-Members, Liaison to ISO TC 229 and CEN TC 352)

WG 1 "Representation of analysis data"
WG 2 "Sedimentation, Classification"
WG 3 "Pore Size distribution, porosity"
WG 5 "Electrical sensing zone methods"
WG 6 "Laser diffraction methods"
WG 7 "Dynamic light scattering"
WG 8 "Image Analysis methods"
WG 9 "Single Particle light interaction methods"
WG 10 "Small angle X-ray scattering"
WG 11 "Sample preparation"
WG 12 "Electrical mobility and number concentration analysis for aerosol particles"
WG 14 "Acoustic methods"
WG 15 "Focused scanning beam techniques"
WG 16 “Characterisation of particle dispersion in liquids”
WG 17 "Methods for zeta potential determination"

Standardization in nanoparticle characterization is performed in 15 Working Groups within ISO/TC 24/SC 4. Additionally to imaging methods for morphology inspection of single particles, aerosol measurement devices have some benefits for exposure analysis compared with particle measurement techniques for liquid dispersions (i.e. emulsions, suspensions or combinations of them), for instance the ability of providing absolute count numbers or the independency from specific material properties (e.g. from the index of refraction).

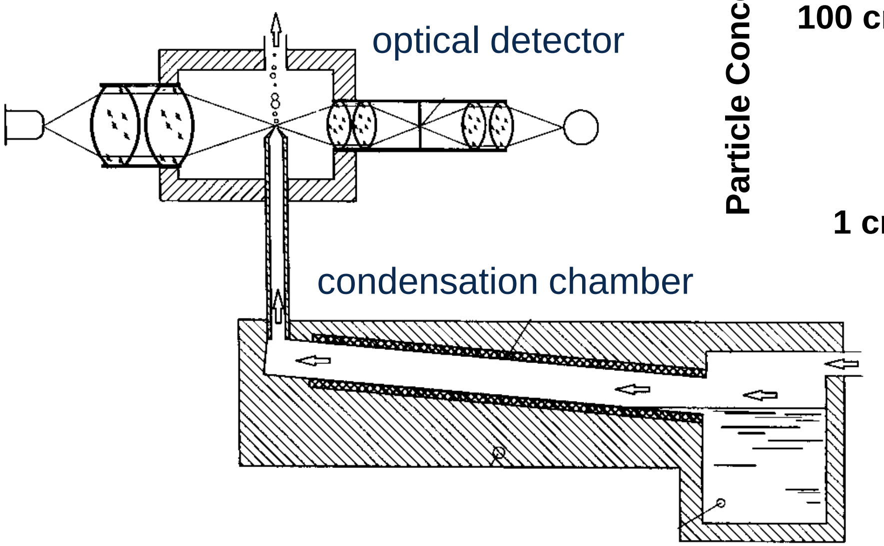
A fundamental aerosol measurement principle that allows the characterization of particles down to a view nanometre is the electrical mobility analysis as described within ISO 15900:2009 (now rev.). One problem from metrological view, which still exists for aerosol measurement technology, is the lack of a concentration reference material. An important step in this direction represents the international standard ISO 27891:2015 for the calibration of condensation counters.

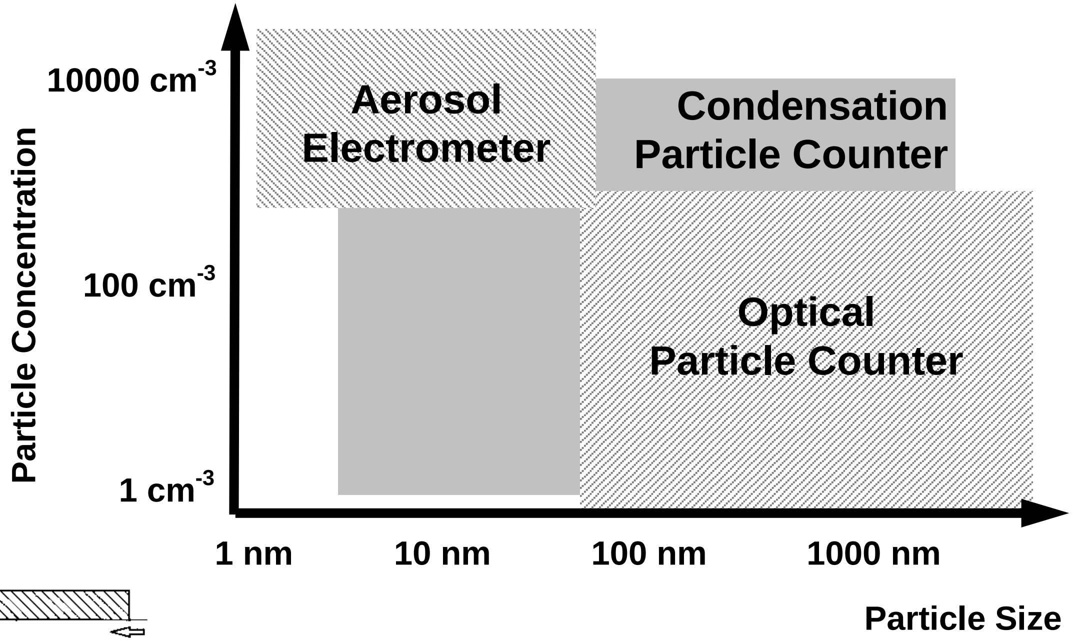
ISO 15900:2009

Determin. of particle size distribution — Differential electrical mobility analysis for aerosol particles

ISO 27891:2015

Aerosol particle number concentration — Calibration of condensation particle number counters





Concept of particle number concentration standard (detection efficiency determin.)

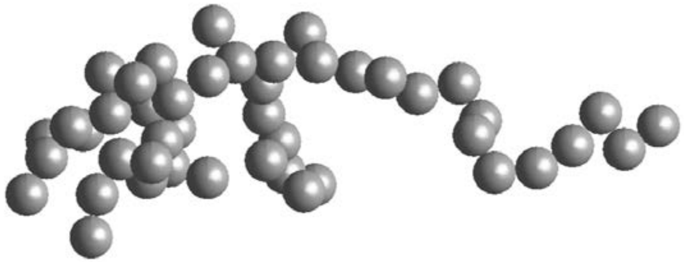
In the field of liquid dispersion characterization, a fundamental challenge is the characterization of the dispersion stability, i.e. "the absence of change in specified properties over a given timescale". Therefore, the technical report ISO/TR 13097:2013 was issued by WG 16, which describes two different approaches to determine relative property changes.

Especially in larger cluster research projects, dealing with fate, exposure and hazard of nanomaterials the sample preparation turned out to be the deciding step, e.g. for risk assessment of TiO2.

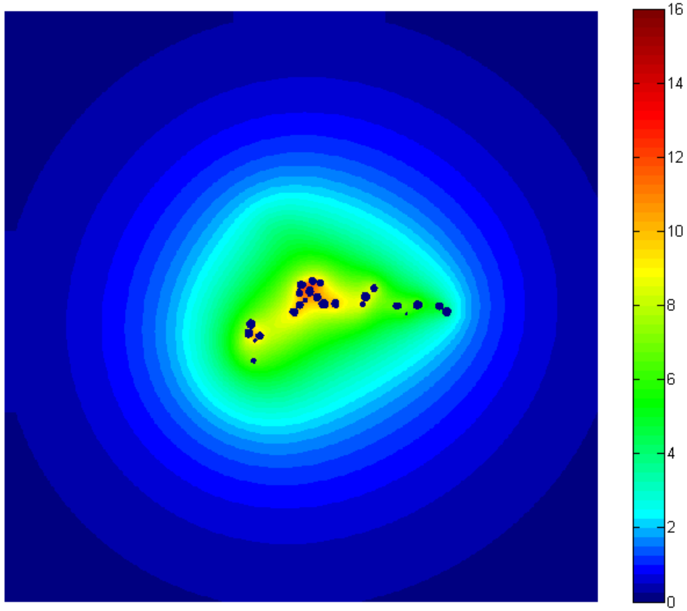
Zeta potential measurement proved to be a necessary tool for checking dilution and stabilization protocols. Therefore, WG 17 issued methods for zeta potential determination within ISO 13099, which consists currently of two standards and one final draft of an ISO standard (FDIS).

Respecting the preparation preconditions comparable and reproducible particle or agglomerate size measurement by centrifugal sedimentation or hydrodynamic mobility analysis (e.g. by dynamic light scattering - DLS) can be achieved.

WG 17 Zeta Potential Measurement

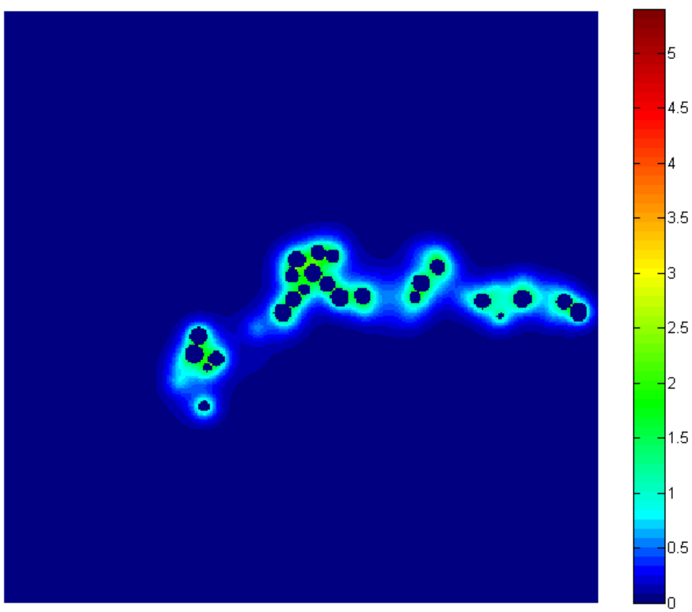


Nanoparticle Double Layer Interaction



$\kappa a = 0.1$

(e.g. x_p=6 nm, c_{Salt} 0.1 mM)



$\kappa a = 1$

(e.g. x_p=6 nm, c_{Salt}= 10 mM)

K. Schießl, F. Babick et al. Advanced Powder Technology 23 (2012) 139–147