

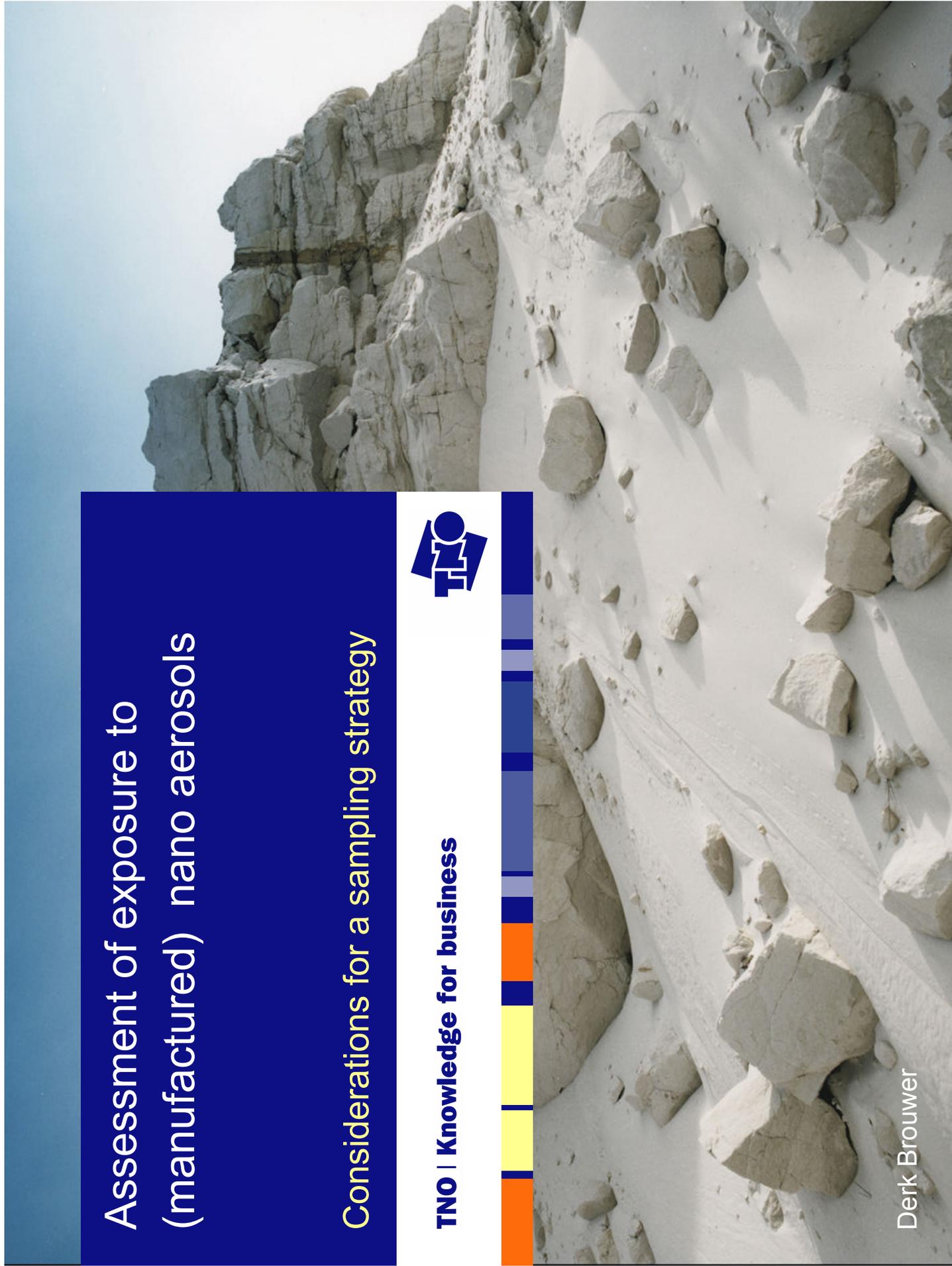
Assessment of exposure to (manufactured) nano aerosols

Considerations for a sampling strategy



TNO | Knowledge for business

Derk Brouwer



Content

- Needs and relevance nano particles exposure measurements
- Measurement and sampling methods
- Observations in workplace practice relevant for measurement
- Interpretation for exposure estimates
 - Role of measurement strategy
- Conclusions



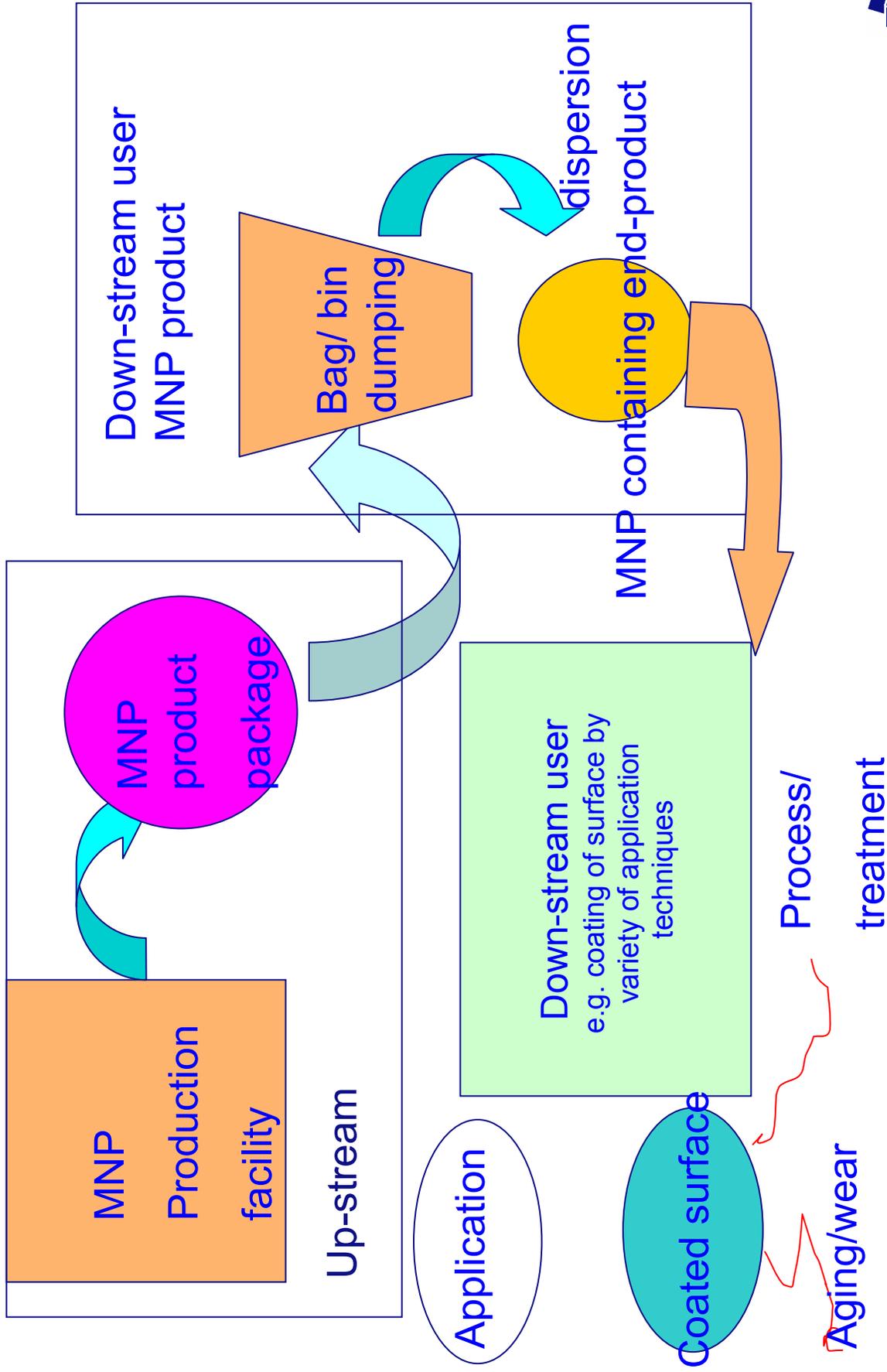
Terminology BSI PAS 71:2005/ PAS 138:2007

1. Nano-material discrete piece of material with **one or more** dimensions in nano-scale (<100nm)
 2. Nanofibre nano material with **2** dimensions in nano-scale and aspect ratio > 3:1
 3. Nanoparticles (discrete) particles/ spheres with all **three** dimensions in nanoscale
 - ▶ Incidental (formed) nanoparticles (by-product of man-made or natural processes)
 - ▶ Intentionally manufactured ('engineered') particles
- Nanoaerosols** 1 + 2+ 3 with Dae< 100 nm
- Agglomerates group of particles held together by relatively weak forces, e.g. van der Waals- electrostatic forces, surface tension
 - Aggregates NOTE resulting external surface area= sum of individual components
 - Aggregates NOTE resulting external surface area<sum of individual components

Current developments relevant for exposure sampling

- Research
 - NIOSH
 - NANOSAFE II (FP6)
 - NANOSH (FP6)
- Report
 - ISO/TC 146/SC 2 (2006) Technical report 27628 “ *Workplace Atmospheres- Ultrafine, nanoparticle and nano-structured aerosols- Exposure characterization and assessment*”
- Publications
 - 2004-2008

Potential for exposure to MNP in different exposure scenarios;
Coating products as an example



WHY Exposure measurements?

- In general
 - Exposure analysis
 - Evaluation of control measures
 - Risk assessment
 - Epi studies (association exposure-effect)
 - Compliance
- (Manufactured) Nano particles
 - Explorative
 - Range-finding
 - Benchmarking



(Inhalation) Exposure measurements for risk assessment

- RA should 'give guidance' to select
 - Relevant exposure metric, e.g.,
 - **mass concentration ($\mu\text{g}/\text{m}^3$)**
 - **number concentration (p/cm^3)**
 - **total particles surface area concentration ($\mu\text{m}^2/\text{cm}^3$)**
 - Relevant exposure measure e.g.,
 - **average concentration**
 - **peak concentration**
 - **cumulative concentration (average*time)**

However,.....

Needs & Possibilities Measurements

- On-line detection/ real-time monitoring
 - Mass concentration
 - Number concentration
 - Surface area concentration
- Sampling and off-line characterisation e.g SEM/ TEM and variety of analysis techniques
 - Size
 - Shape/ morphology
 - Agglomeration state
 - (chemical) composition
 - Crystallinity
 - Solubility



Metric	Devices	Remarks
Mass	Size selective personal sampler	No current devices offer a cut point of 100 nm.
	Size selective static sampler	The only devices offering a cut point around 100 nm are cascade impactors.
	TEOM®	Sensitive real-time monitors such as the Tapered Element Oscillating Microbalance (TEOM®) with a suitable size selective inlet.
	SMPS	Only if particle shape and density are known or assumed.
	ELPI	Data may be interpreted in terms of mass concentration if particle charge and density are assumed or known.
	CPC	No suitable pre-separators are currently available
Number	SMPS	Real time size-selective (mobility diameter) detection of number concentration.
	ELPI	Real time size-selective (aerodynamic diameter) detection of active surface-area concentration.
	Electron Microscopy	Off-line analysis of electron microscope samples can provide information on size-specific aerosol number concentration.
	SMPS	Data may be interpreted in terms of aerosol surface-area under certain circumstances. For instance, the mobility diameter of open agglomerates has been shown to correlate well with projected surface area. ³
Surface -area	ELPI	Active surface-area does not scale directly with geometric surface-area above 100 nm. Size-selected samples may be further analyzed off-line.
	SMPS and ELPI used in parallel	Differences in measured aerodynamic and mobility can be used to infer particle fractal dimension, which can be further used to estimate surface-area.
	Diffusion Charger	Real-time measurement of aerosol active surface-area. Diffusion chargers are only specific to nanoparticles if used with an appropriate inlet pre-separator.
	Electron Microscopy	Off-line analysis of electron microscope samples can provide information on particle surface-area with respect to size.



Measurement

3.8 pounds. A built-in carry-handle provides added convenience.



Number concentration

- Total number conc.:
- CPC

Size distribution:

- Mobility particle sizers: SMPS
- electron microscopy
- Thermal precipitator (qualitatively)
- ELPI (indirect)



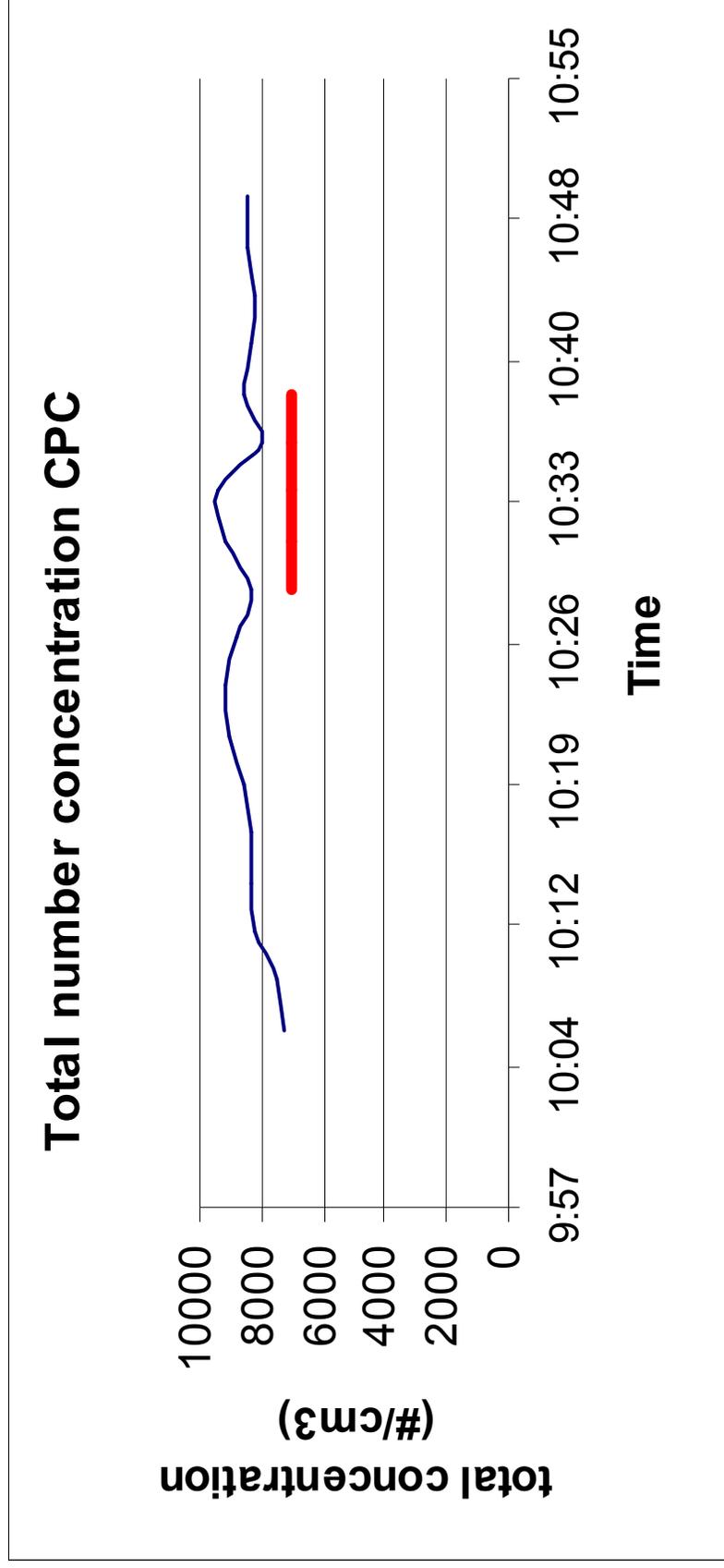
Condensation Particle Counter TSI 3007 CPC

Nanoparticles are grown
In supersaturated vapor
Detected by light scattering

- Mobile
- Total number conc.
- up to 100 000 cm⁻³
- 10 nm - 1 µm



Example of CPC output





Principle of Scanning Mobility Particle Sizer -SMPS

Electrical mobility

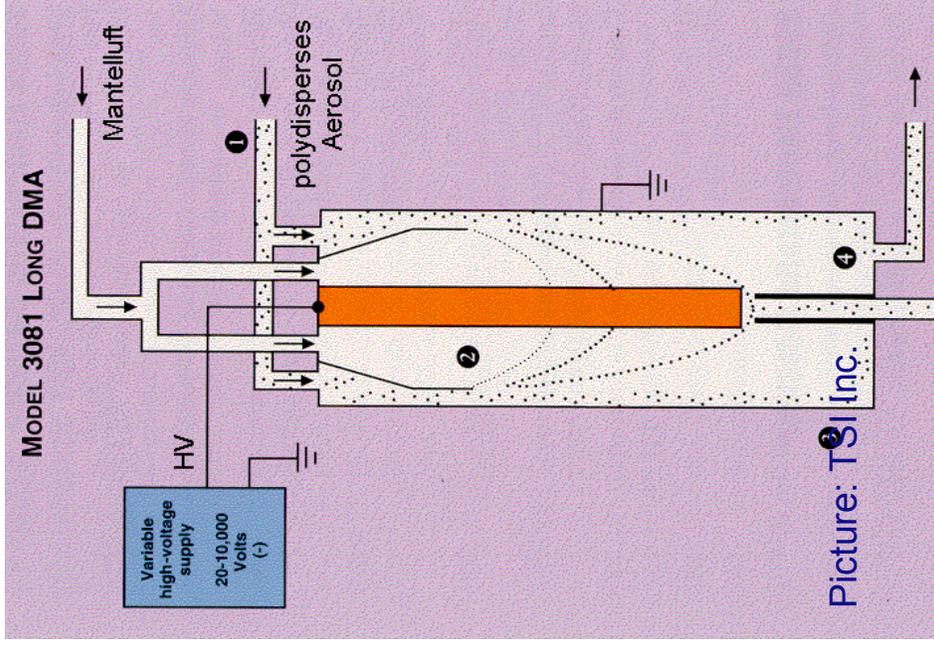
$$Z_p = n e C / 3 \pi \mu D_p$$

- C: Cunningham correction
- μ : Gas viscosity

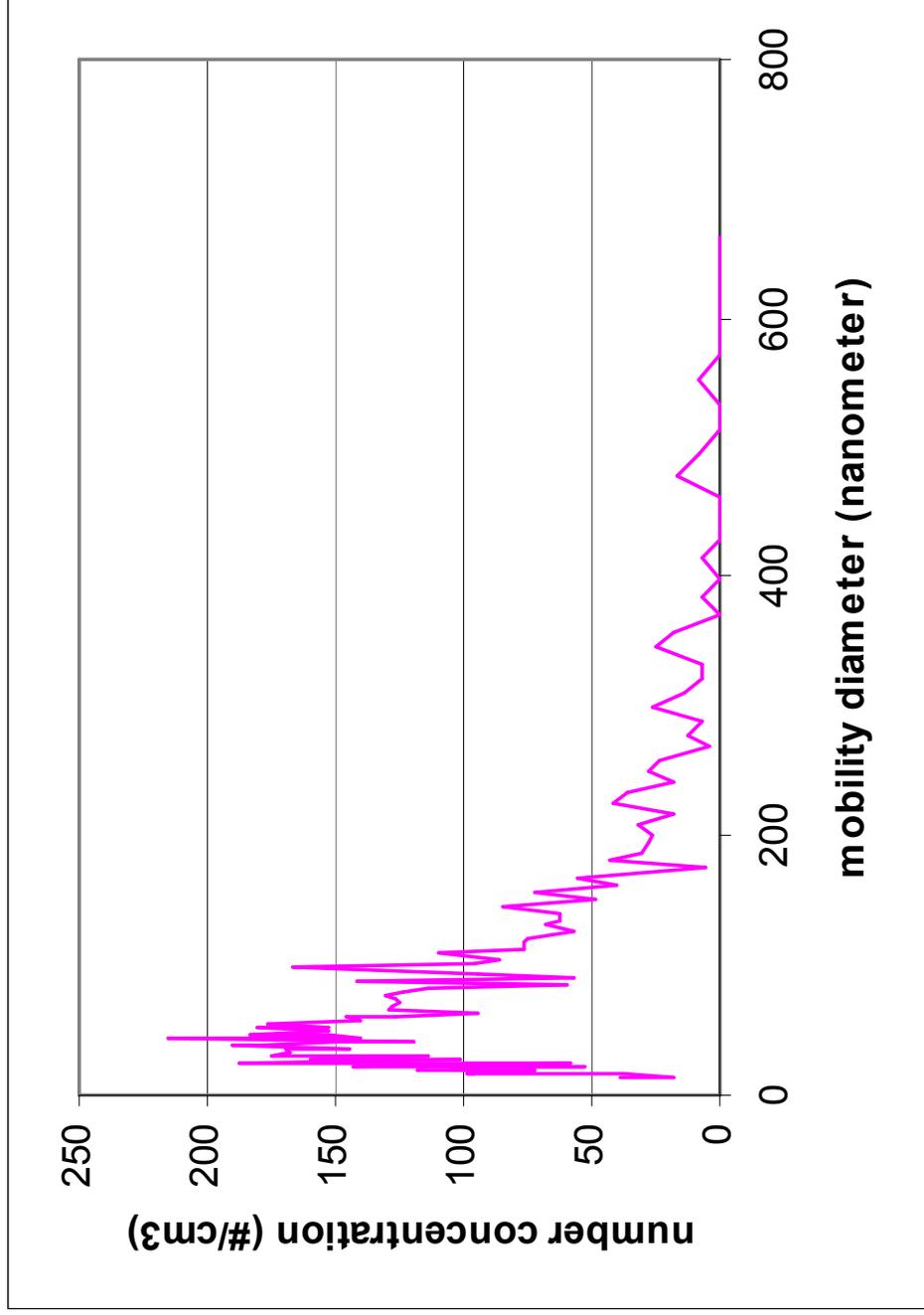
$$Z_p = q \ln(r_2/r_1) / 2 \pi V L$$

- q: Air flow sheath air
- V: Electrode voltage
- L: Length DMA

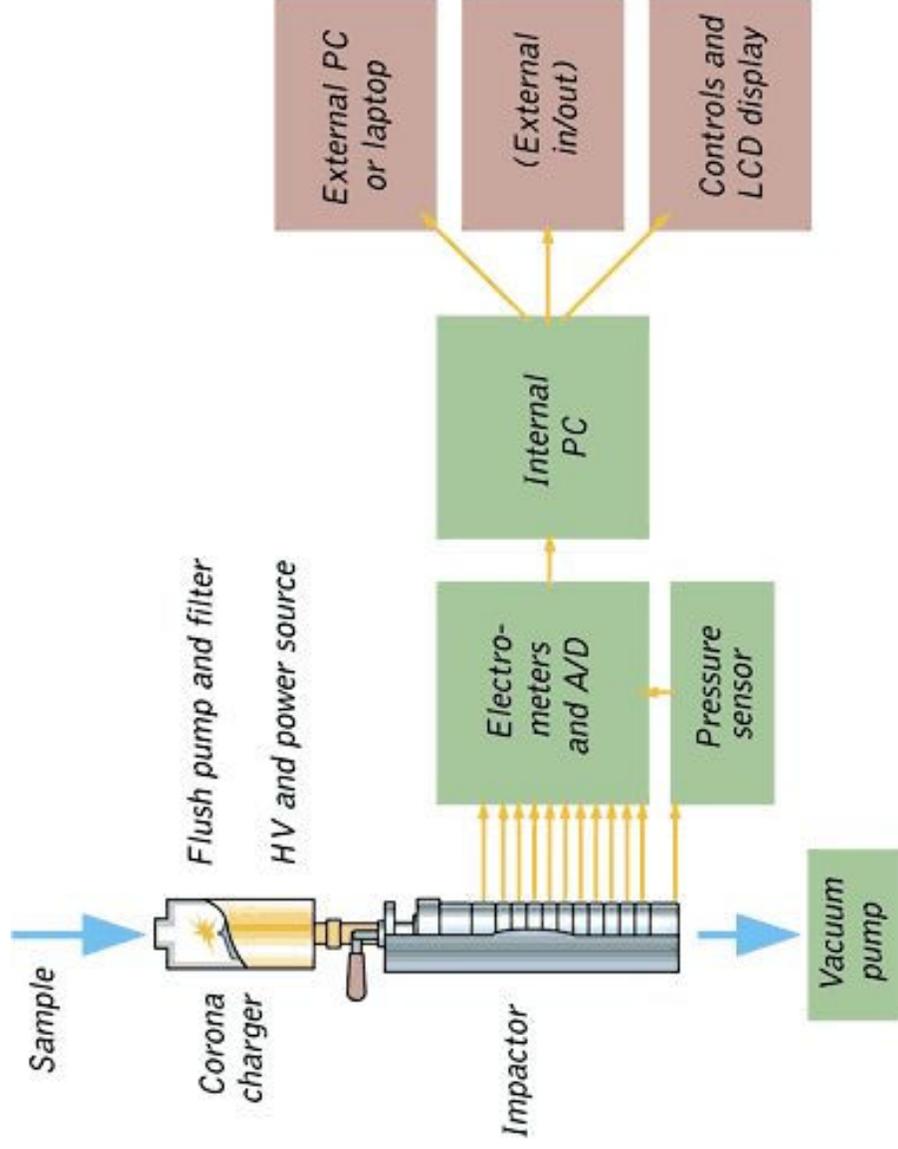
⇒ Particle diameter D_p



Example of SMPS scan

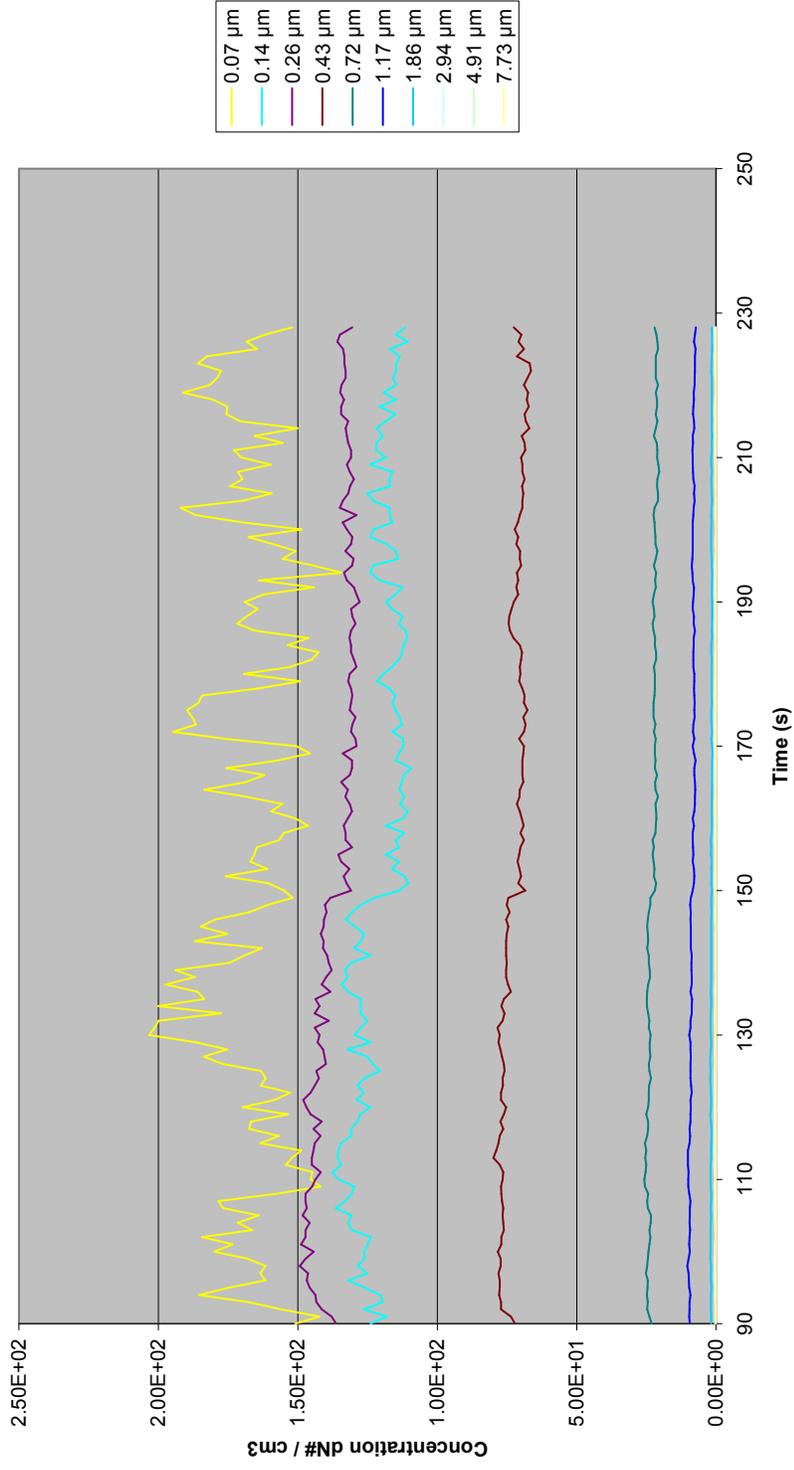


ELPI™ Electrical Low Pressure Impactor



ELPI output

T = 90 – 150 background in laboratory
T = 160 – 230 during handling in laminar extraction cabinet
Experiment 2



Measurement

Surface of nanoparticles

- Total surface
 - Diffusion charger
 - Nanoparticle Surface Area Monitor
(lung-deposited surface area of inhaled particles)

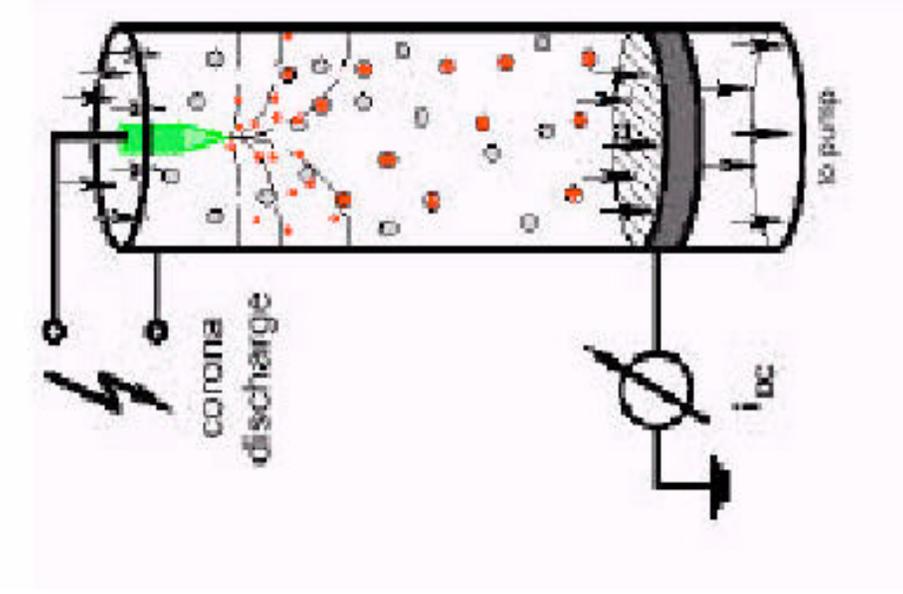


• Size distribution:

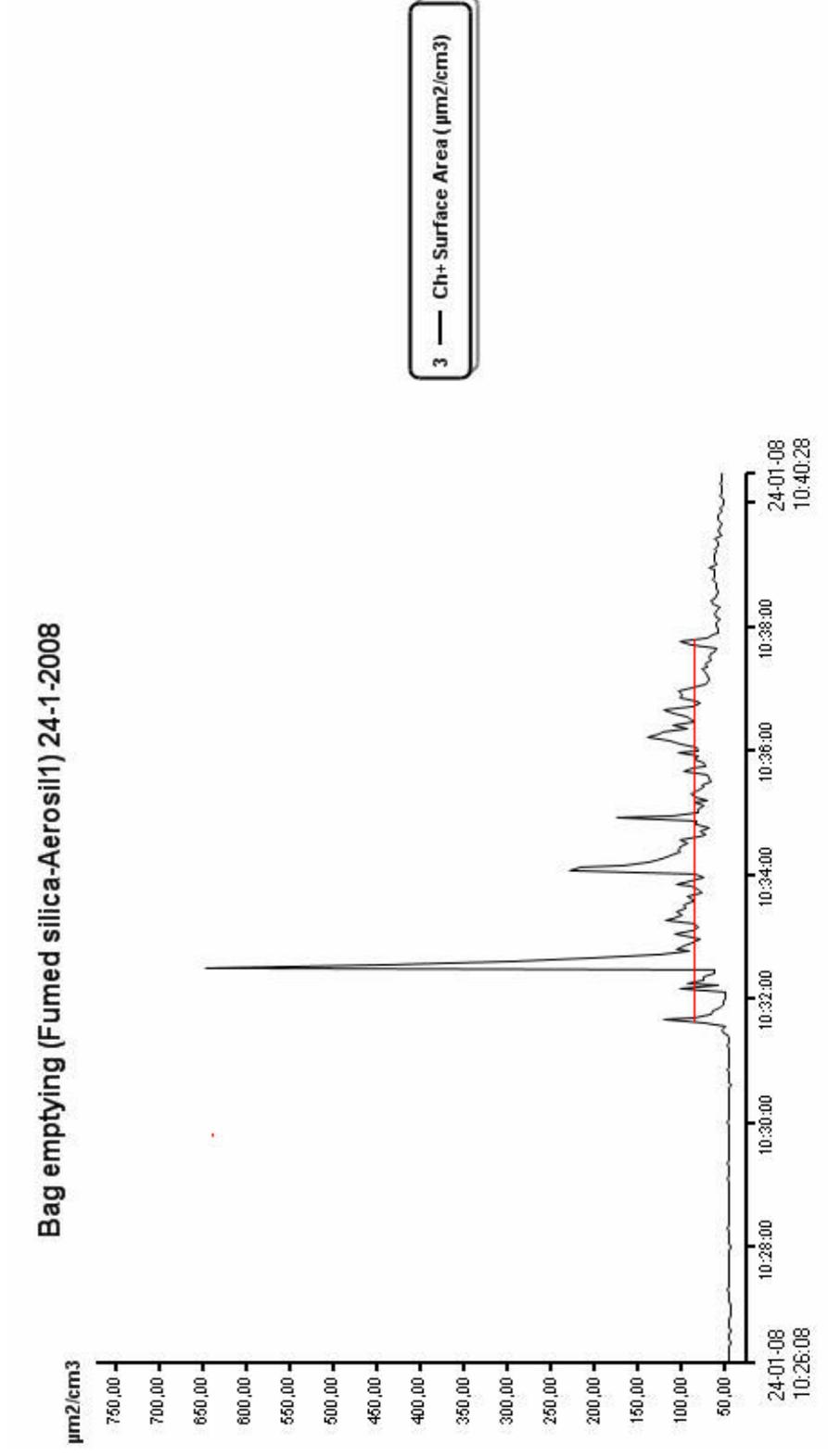
- ELPI
- Electron microscopy
- SMPS (indirect)



Diffusion Charging Particle Sensor Type LQ 1-DC



Example of output Diffusion Charger



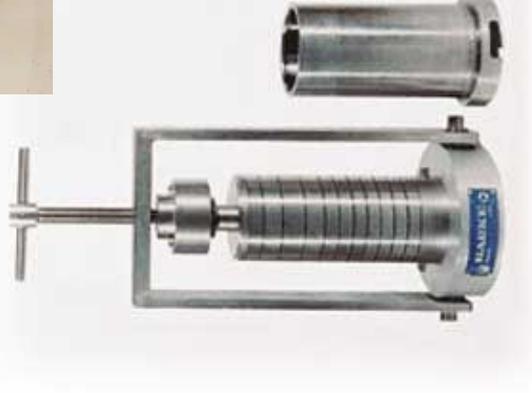
Measurement

Mass concentration

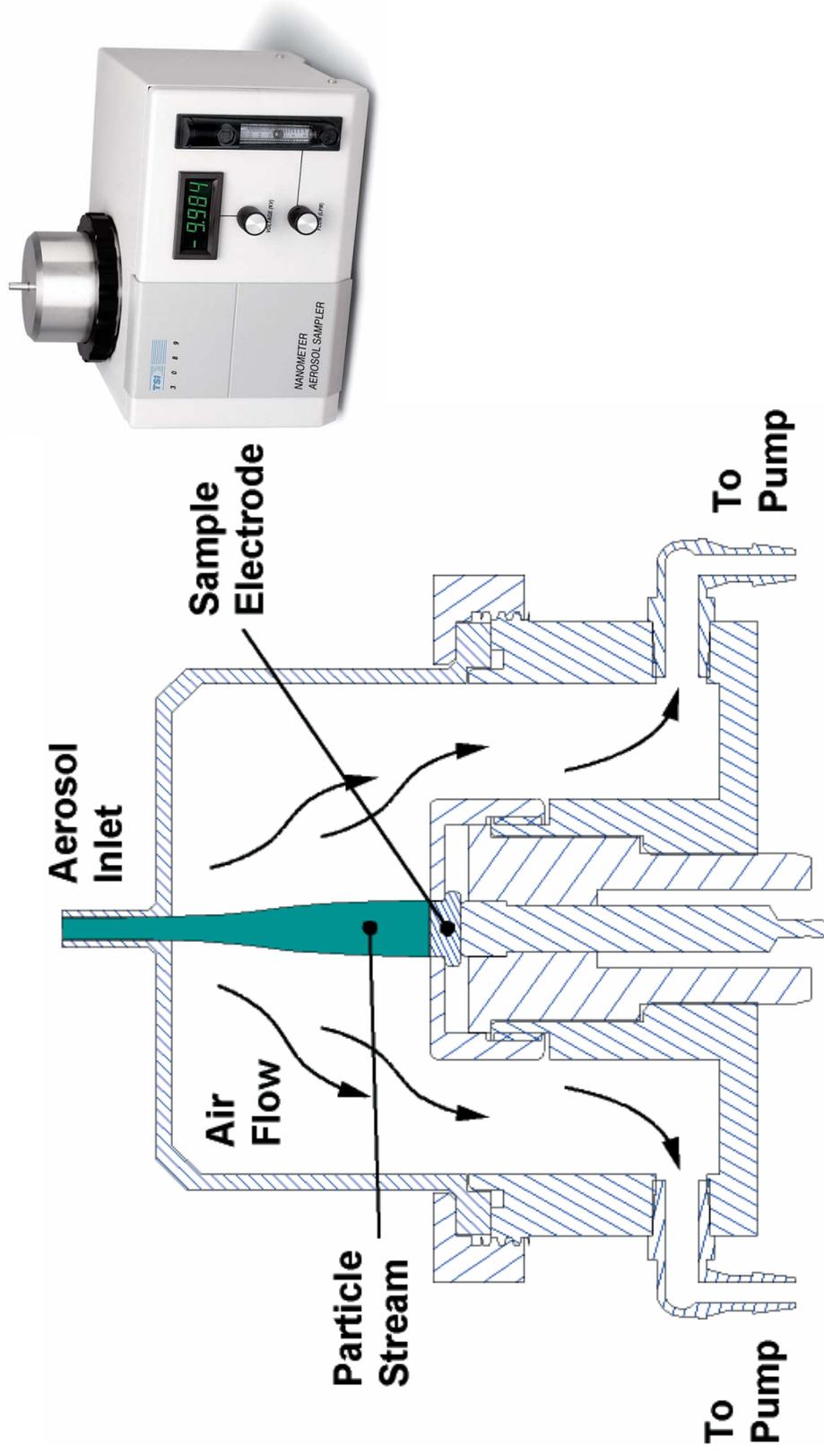
- Total conc.:
 - Personal, static samplers (respirable, 2.5 μ m, 1 μ m)
 - TEOM (online)
- Size distribution:
 - Cascade impactor
 - SMPS, ELPI (indirect)

Sampling for characterisation

- Electrostatic precipitator
- PAS with special filter/grid



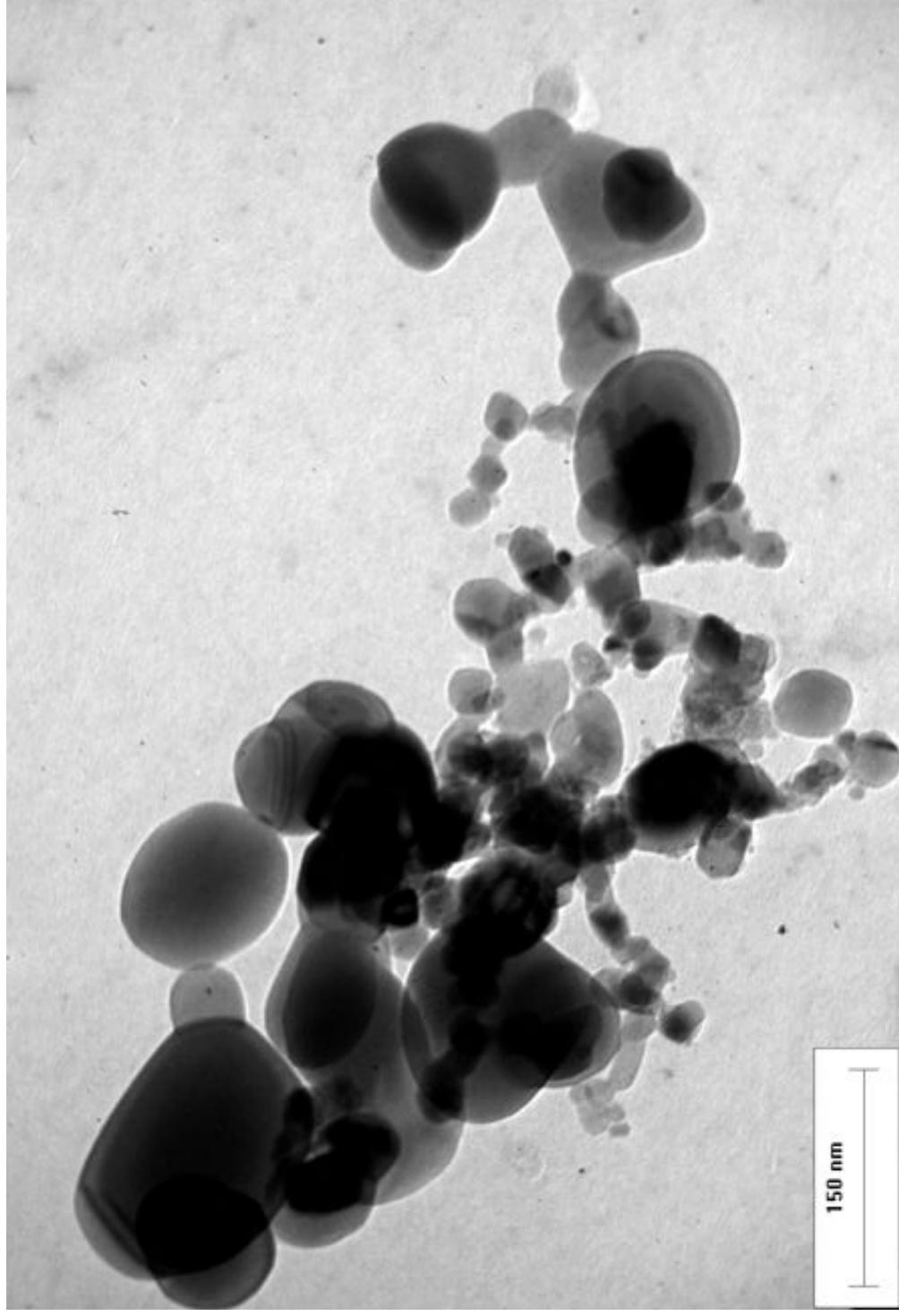
Nanometer Aerosol Sampler



Assembly TEM grids / polycarbonate filter / pre-coated gold filter for Personal Air Sampling



TEM image of particles collected during bin filling operation of TiO₂



Position of measurement devices



Challenges for personal exposure assessment of nano-aerosols

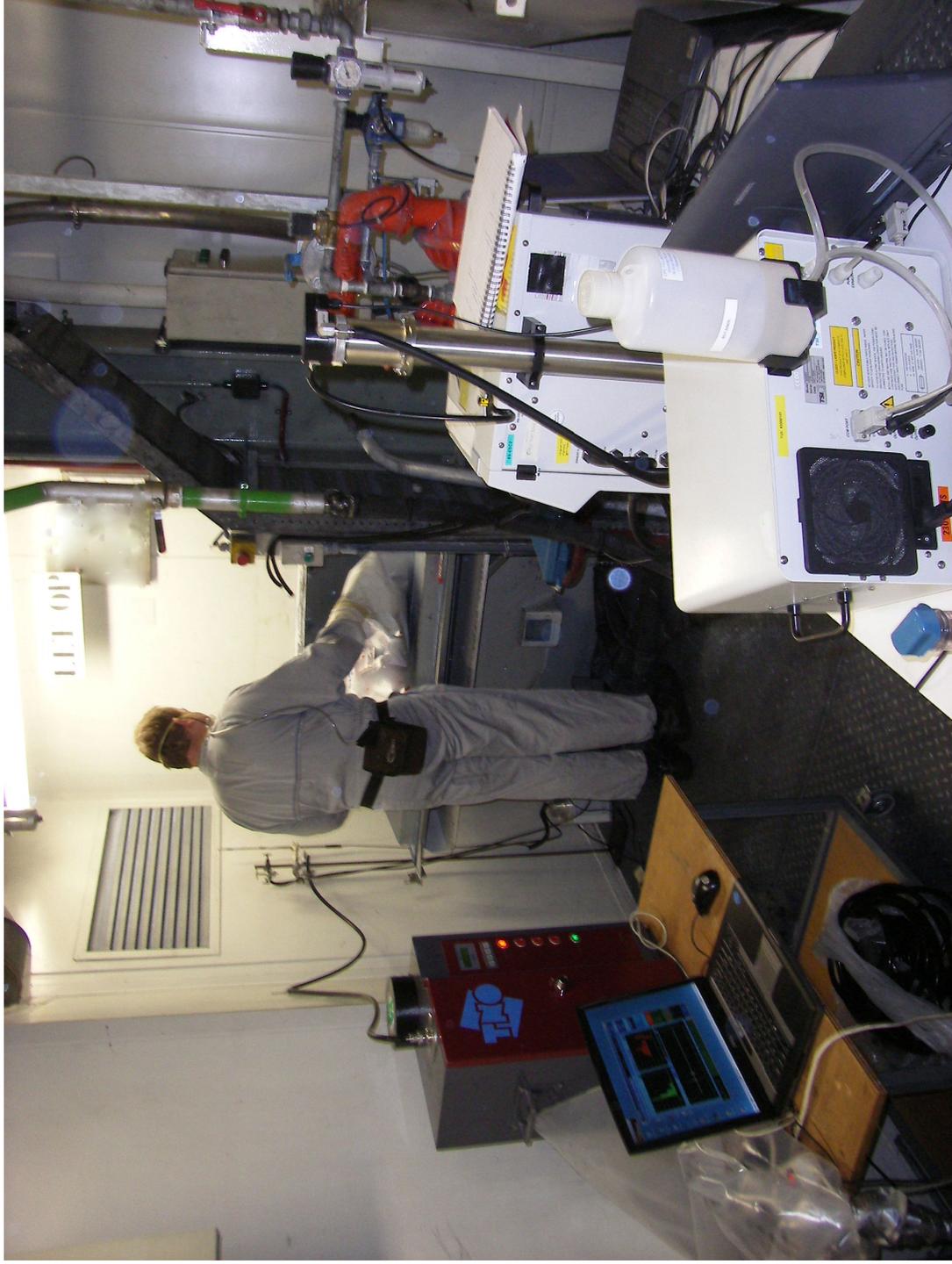
- Interpretation of output of static devices to exposure for relevant exposure metrics (mass-/number-concentration; surface area)
 - No discrimination existing NPs and MNPs
 - No discrimination ‘background’ – and MNP-aerosols
- Not taking into account temporal & spatial variation
 - Particle size distribution
 - Number and mass concentration
- Evaluation
 - (Health-based) Limit or reference values are lacking

Observations in workplace practices (1)

- Exposure scenarios very similar to 'standard' operations with conventional substances
 - In general: limited duration of MNP activities \approx exposure time

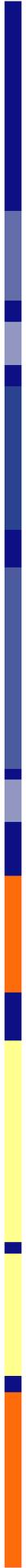
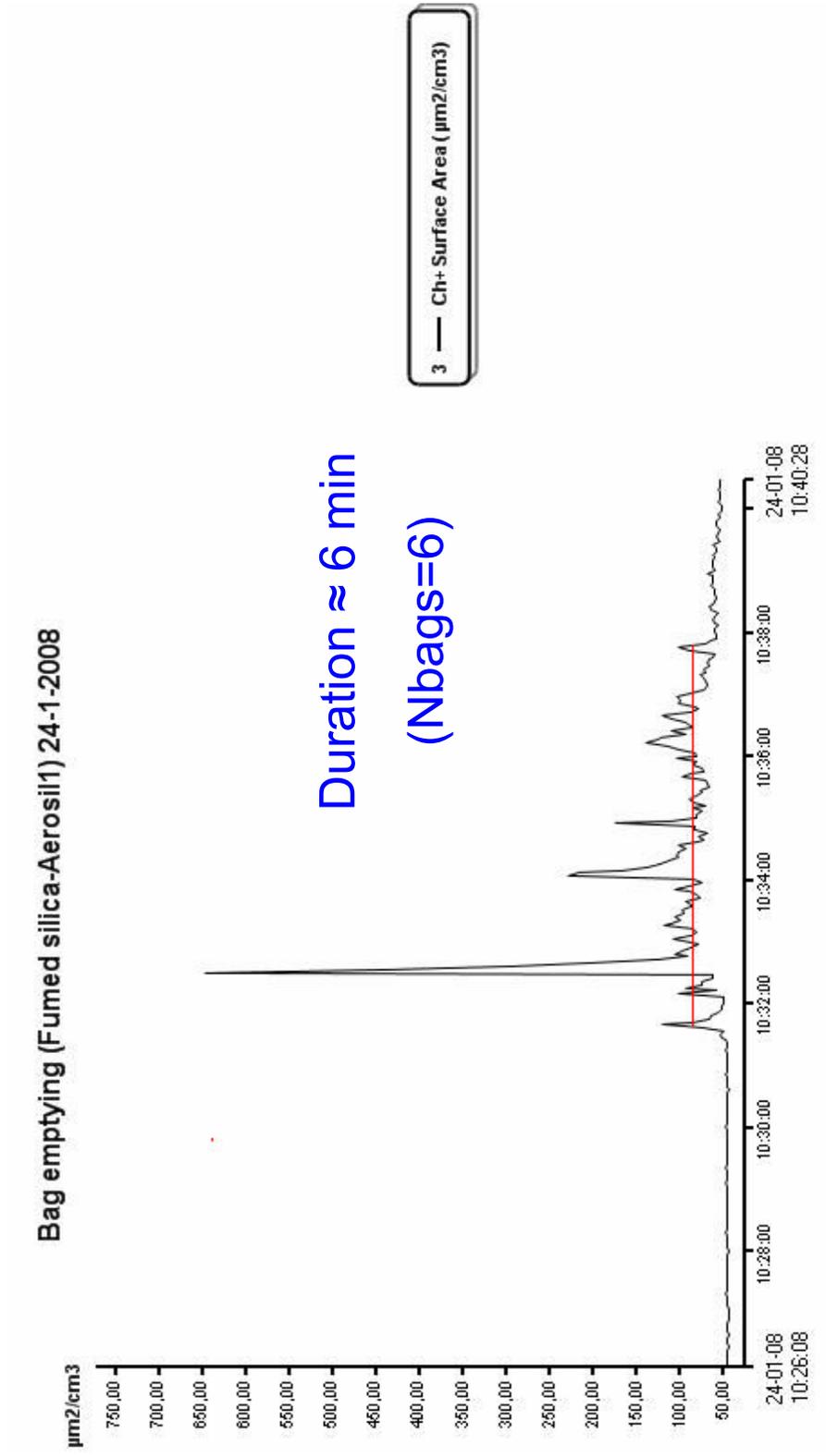


Scenario Bag emptying



Example surface area of aerosols during bag emptying

Data from NANOSH/ TNO (2008): Down-stream user MNP



Observations in workplace practices (2)

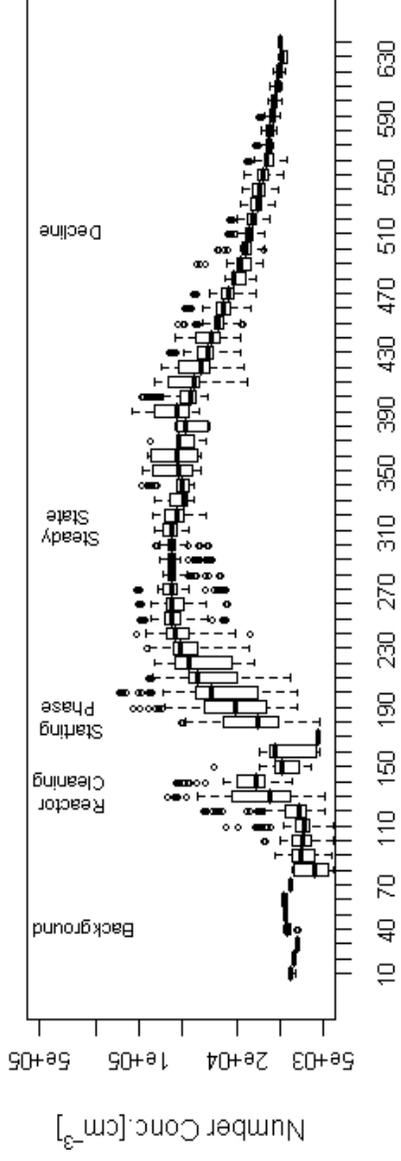
- Variable background 'exposure', e.g. Number concentration and particle identity
 - Ventilation (rate/pattern/ filtration)
 - Outdoor conditions (industrial area/ traffic) and infiltration factor
 - ????

	p/ cm ³	Mean sizes (nm)
Clean Room	0-200	>10
Lab room/ Filtered workplaces	0-2000	>10
Outdoor, office	10 000	>10
Workplace (grinding)	200 000	>120

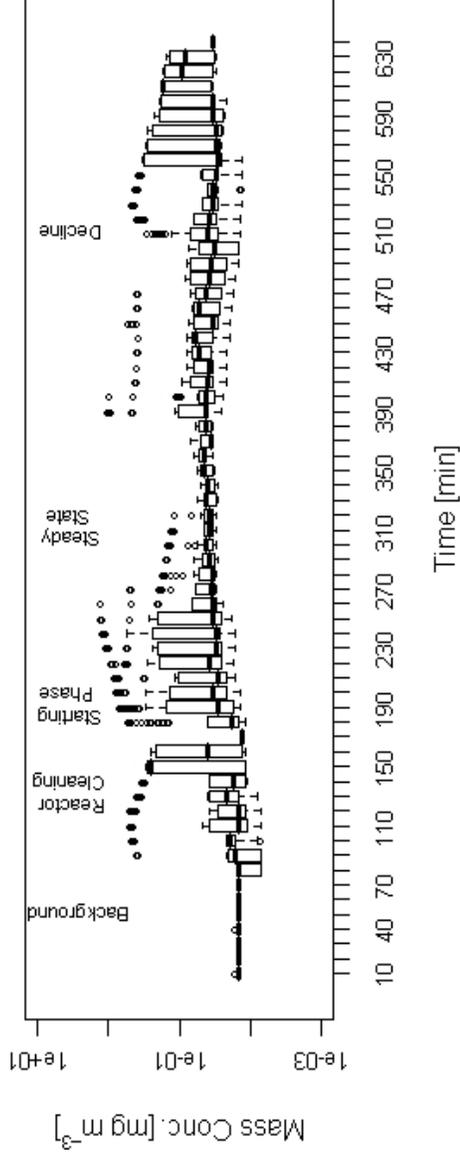
Observations in workplace practices

- In general: limited duration of MNP activities \approx exposure time
- Variable background 'exposure', e.g. Number concentration and particle identity
 - Ventilation (rate/pattern/ filtration)
 - Outdoor conditions (industrial area/ traffic) and infiltration factor
 - ????
- Indications for weak/ hardly any correlation mass/number/surface area

Number- and mass concentration in MNP production facility (Demou et al. submitted)



Time [min]

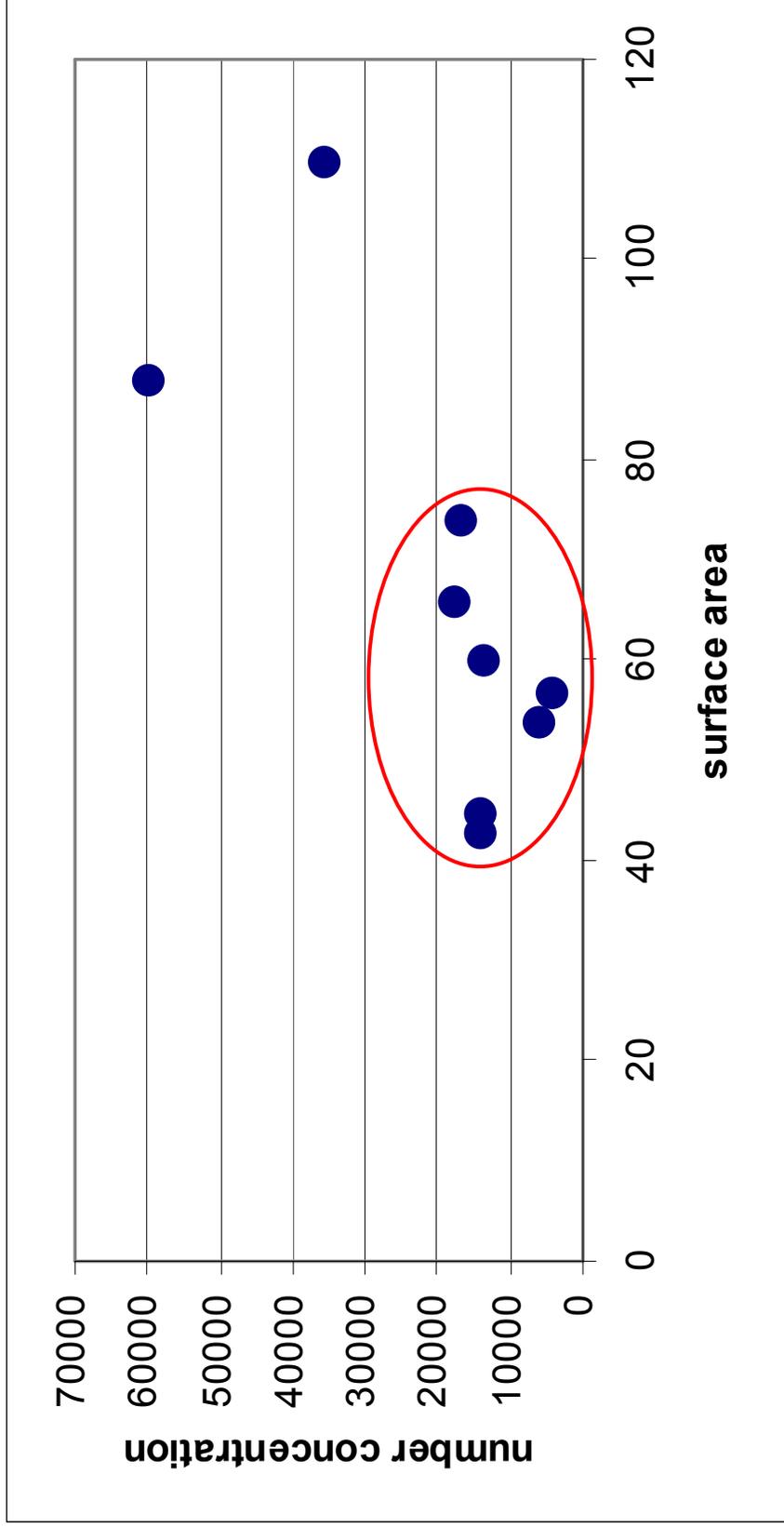


Time [min]



Lack of correlation different exposure parameters

Data from NANOSH/ HSL (2007) 3 R&D labs MNP



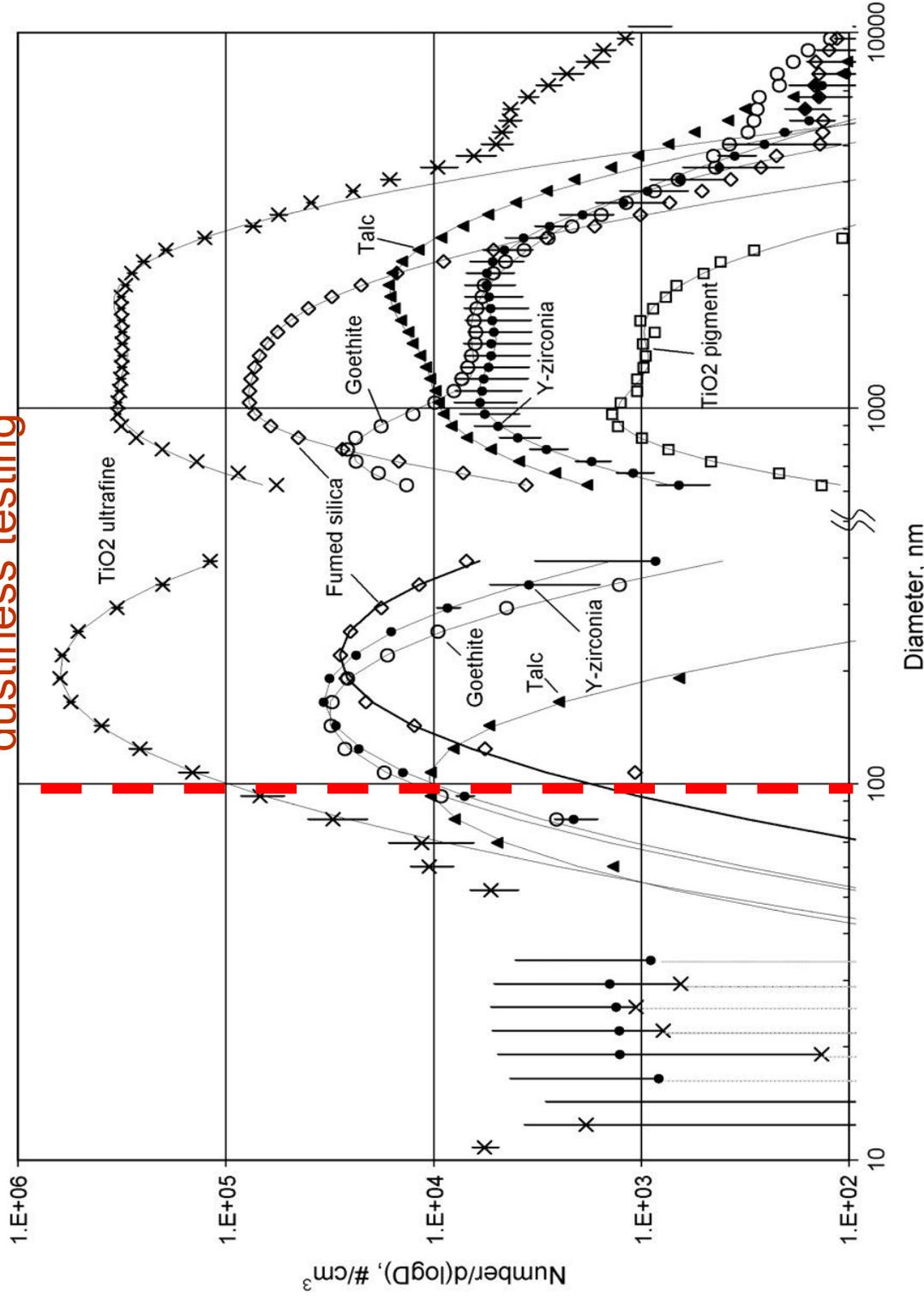
**Other considerations;
with regard to the Potential of exposure to MNPs**

- Aerosol dynamics show rapid agglomeration of NPs and attachment of NPs to larger (background) aerosols (NANOTRANSPORT)
- MNP product in package # MNP product yielded in production process

.



Characterization of 'bulk'/packaging MNP dustiness testing



Schneider, T. et al. Ann Occup Hyg 2008 52:23-34; doi:10.1093/annhyg/mem059



Additional OH tools

- OH Observations/ monitoring of
 - ✓ Work activities patterns
 - ✓ Worker behavior
 - ✓ Emission/ sources
 - ✓ Workplace ventilation patterns



Challenges for personal exposure assessment of nano-aerosols

- Interpretation of output of static devices to exposure for relevant exposure metrics (mass-/number-concentration; surface area)
 - No discrimination existing NPs and MNPs
 - No discrimination ‘background’ – and MNP-aerosols
- Not taking into account temporal & spatial variation
 - Particle size distribution
 - Number and mass concentration

→ ADEQUATE MEASUREMENT STRATEGY

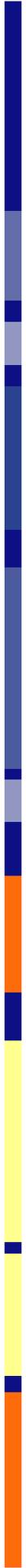
MEASUREMENT STRATEGY (1)

Selection of appropriate metric and measure(s)	Simultaneously measurement of mass concentration ($\mu\text{g}/\text{m}^3$), number concentration (p/cm^3), total particles surface area concentration ($\mu\text{m}^2/\text{cm}^3$)
Activity observation and time registration	Measurement over pre-activity- activity -post-activity time periods



MEASUREMENT STRATEGY (2)

<p>Discrimination MNP from other sources</p>	<p>Identification of possible sources of emission</p> <p>Determination of air stream patterns (macro= plant; micro= work station)</p> <p>Simultaneously measurement of particle concentration up-stream and work station</p> <p>Activity observation and time registration</p> <p>Split up pre-activity-activity-post- activity time periods</p> <p>Sampling for identification during Pre-post activity and activity</p>
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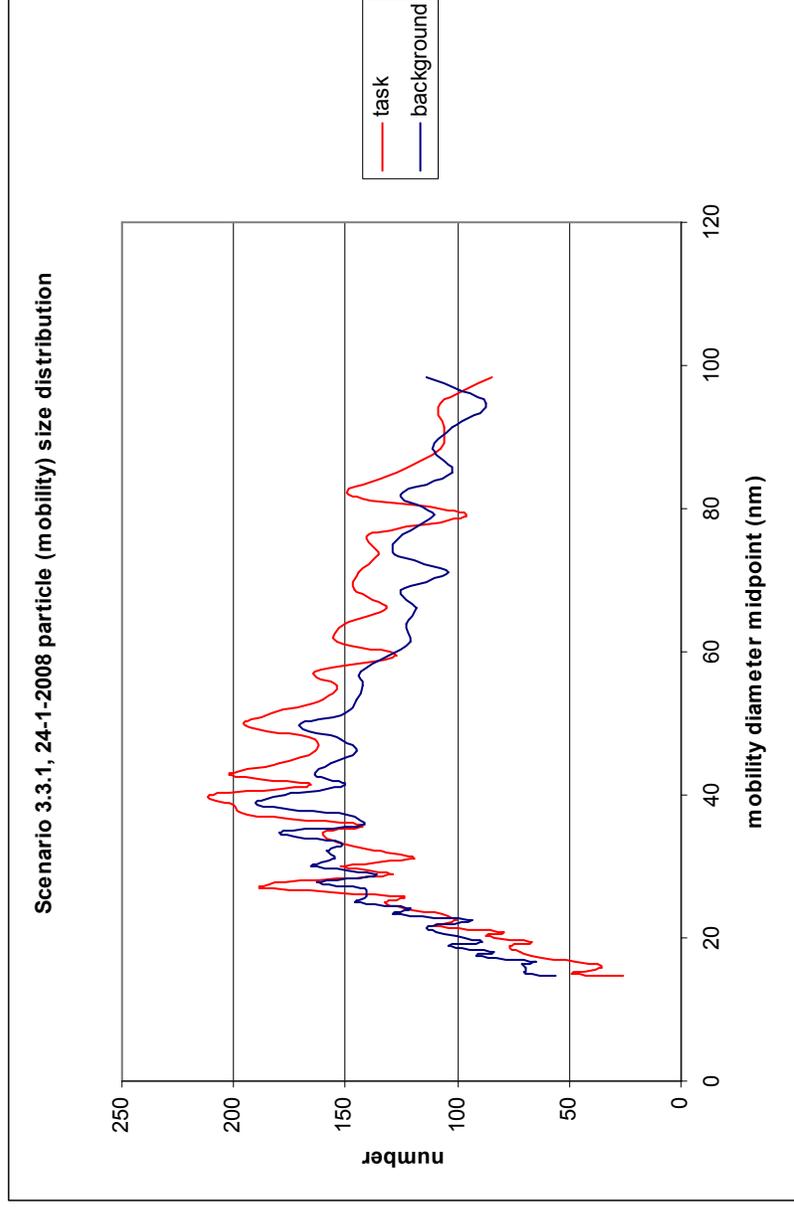


MEASUREMENT STRATEGY (3)

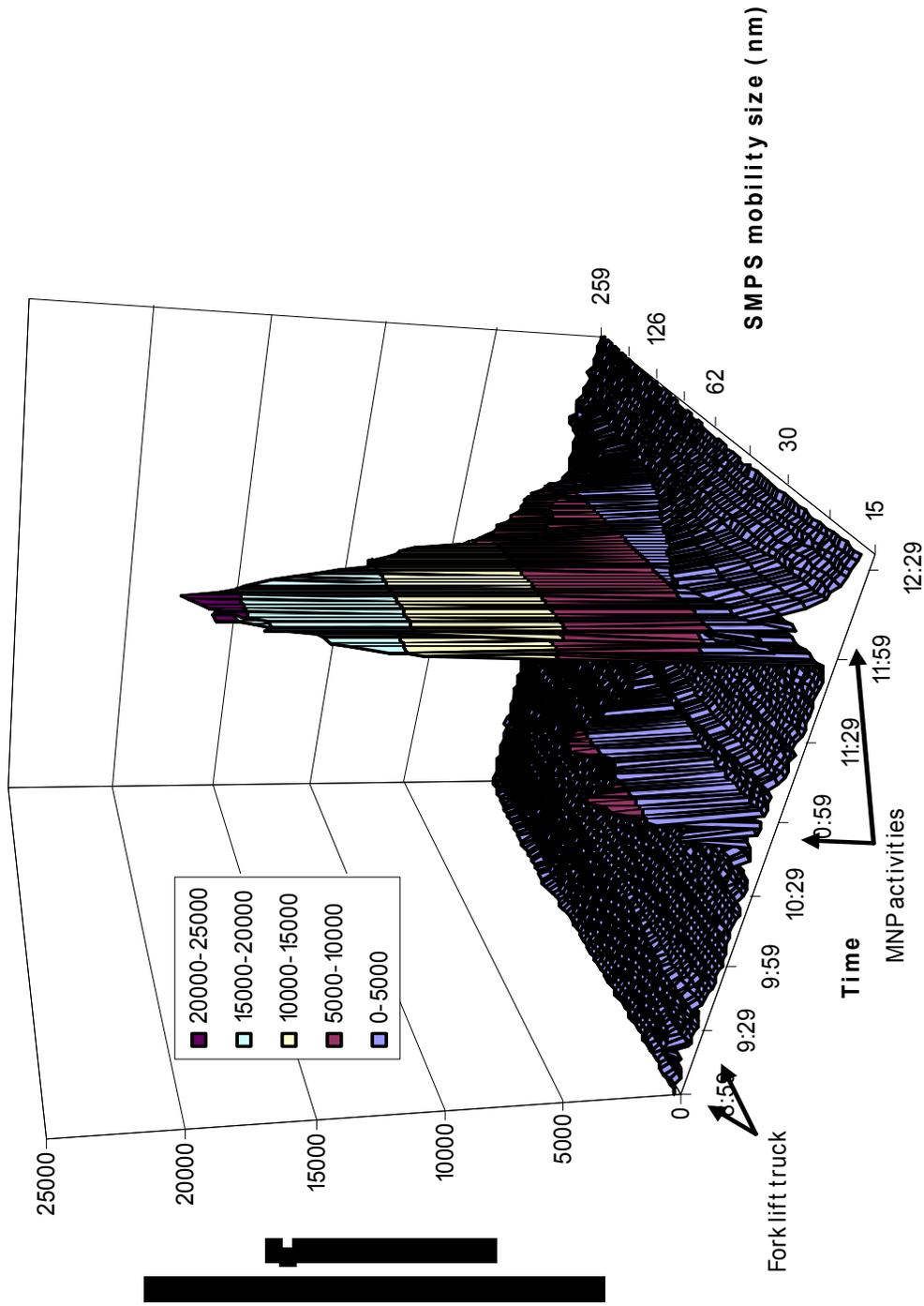
Spatial variations	
	Determination of air stream patterns (macro= plant; micro= work station)
	Dedicated positioning of measurement device
	Activity observation and time registration
	Both personal and static sampling for identification



Differentiation activity and non-activity

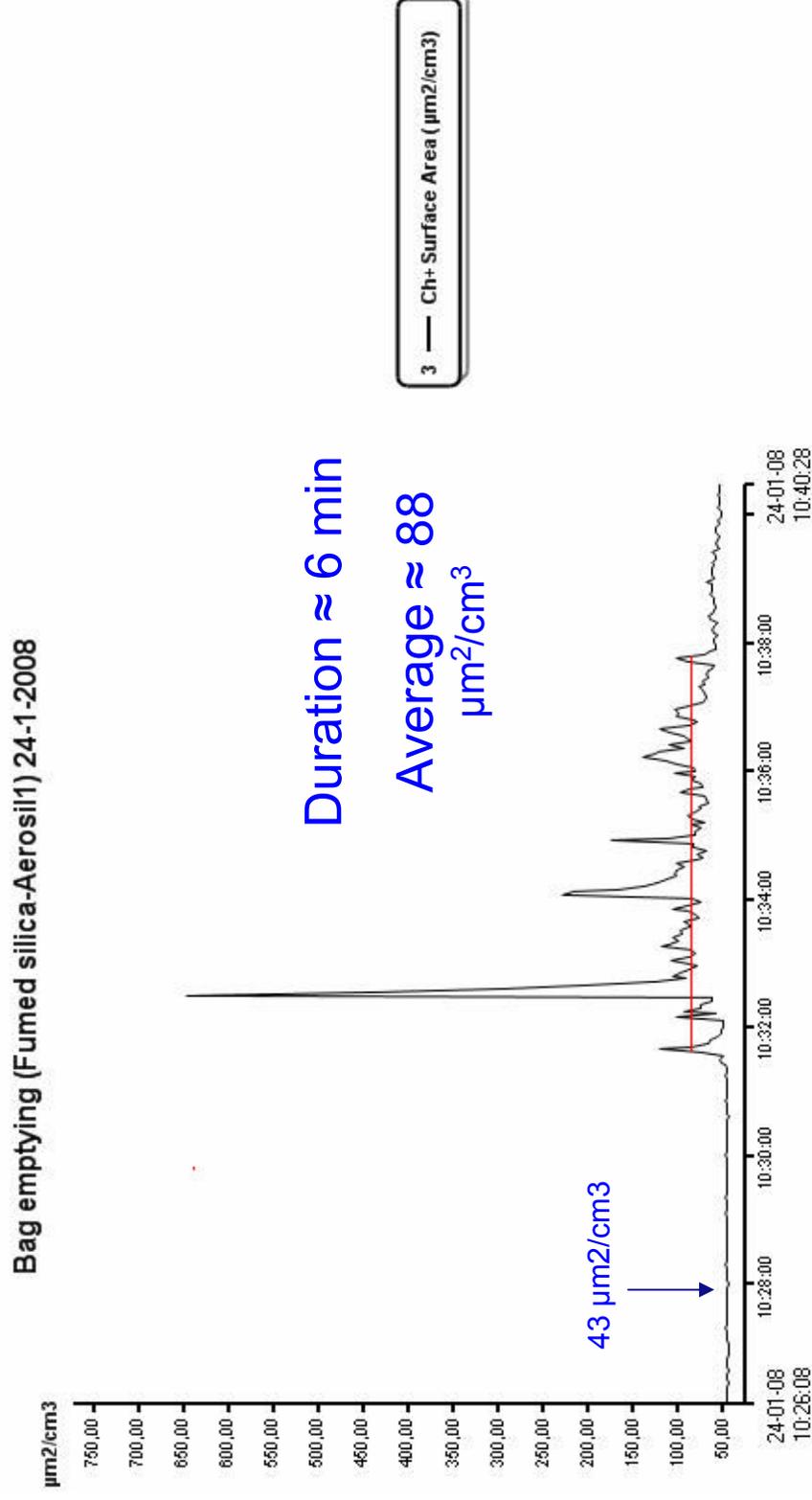


Example of combining real-time size selective monitoring (SMPS) with OH observations



Example surface area of aerosols during bag emptying

Data from NANOSH/ TNO (2008): Down-stream use of MNP



Example of interpretation of measurement results

Bag emptying		MNP (fumed silica) Confirmed by TEM analysis	
Measurement		Estimate of exposure (per person/shift)	
	Average ($\mu\text{m}^2/\text{cm}^3$)	Duration (min)	Cumulative Total surface area($\mu\text{m}^2/\text{cm}^3$)
Activity	88.4	12	± 1060 ($\pm 5.6\%$)
Background	43.6	408	± 530 ($\pm 2.8\%$)

Conclusions

- Activities related to production and use of MNP may result in exposure to nano-aerosols (and dermal exposure to NPs dispersion)
- To estimate exposure
 - All exposure metrics should be considered
 - An adequate measurement strategy should be designed
 - All exposure measures should be considered
- To evaluate exposure
 - Standard and specific exposure scenarios should be identified
 - Good practices should be defined AND Quantified!
 - Benchmarking as a first step in exposure evaluation

Relevant information

- ISO, OECD, ASTM, BSI report/guidelines
 - Example ISO TR 229 WG 3 (draft) TR Health and Safety Practices in Occupational Settings relevant to Nanotechnologies
- SZW/ Arbo-unie-Hogeschool Zuyd: state-of-the-art/ safe practices in the Netherlands (release report spring 2008)
- More info?: please contact
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 - dick.brouwer@tno.nl

THANK YOU for YOUR ATTENTION