

Aerosol sampling techniques using TEM grids

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TIMR, UTC, France, guided by Martin MORGENEYER

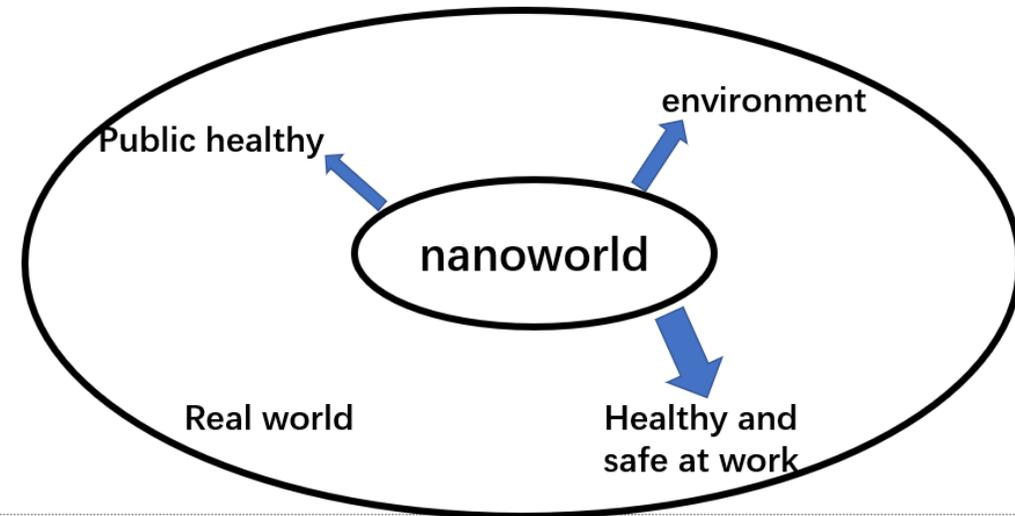
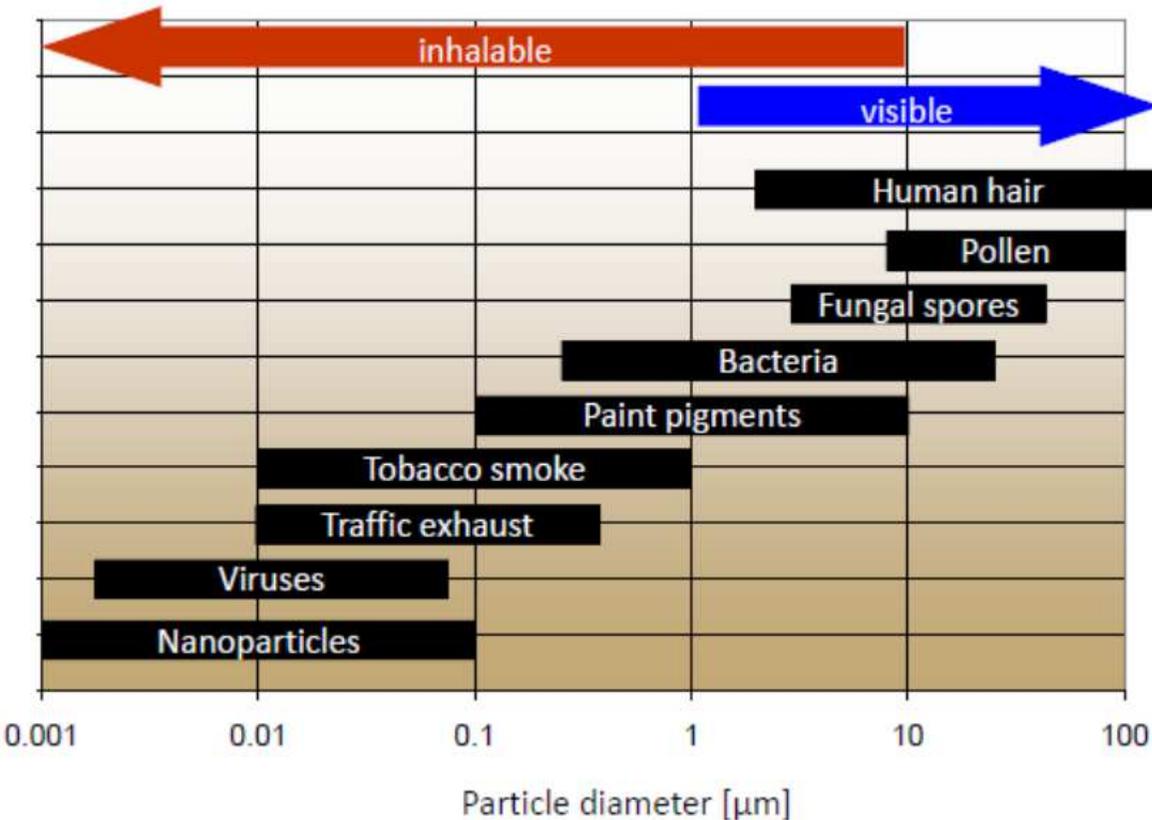
INERIS, France, guided by Christophe BRESSOT

Funded by CSC, China

TEM spot

Background

Aerosol products are a significant part of the finished or intermediate products used in the industry. Non-intentional nanoparticle (NP) may occur due *e.g. spraying, transport* in a production process. With the development of these applications, occupational safety and environment protection are serious issues.

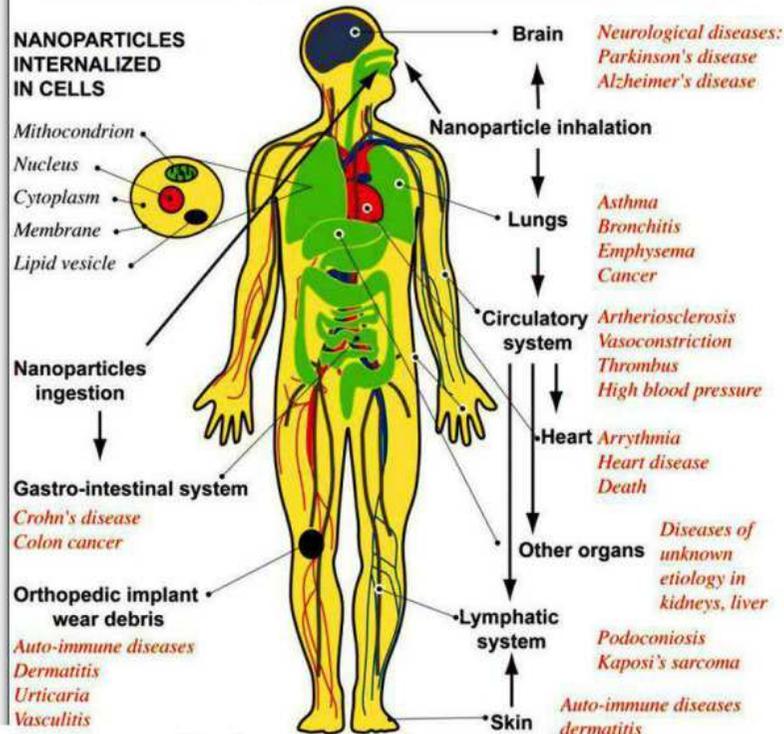


The impact of nanoparticles on human body is serious

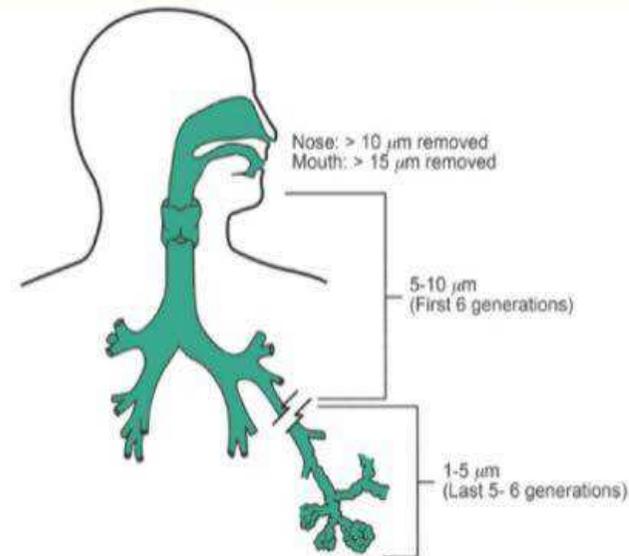
Chemtrail Geo-engineering

DISEASES ASSOCIATED TO NANOPARTICLE EXPOSURE

C. Buzeo, I. Pacheco, & K. Robbie, Nanomaterials and nanoparticles: Sources and toxicity, Biointerphases 2 (2007) MR17-MR71



The effect of aerosol particle size on the site of preferential deposition in the airways

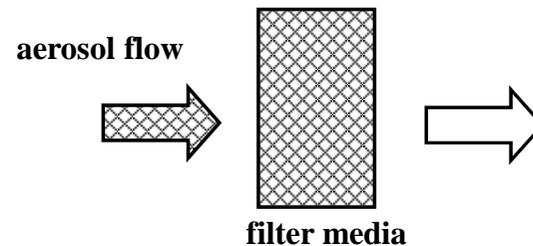


Research objectives

There is a need to develop sampling devices that will make possible speciation and quantification of nanoaerosols according to class sizes for efficient characterization. Make the measurements quantitative not only sampling airborne nanoparticles using an innovative instrument mini particle sampler (MPS) developed by INERIS and analysing particles on transmission electron microscopy (TEM) grids, but also measure by scanning mobility particle sizer (SMPS):

1. Assessment of the sampling efficiency and optimization of the set up;
2. TEM analysis with the following points: Reliable TEM, image analysis, development of quantification methods;
3. Adjustments / optimization of the cutoffs to collect particles according to their sizes and simulate the particles movement in MPS;
4. Assessment of particle losses in the inner parts of the sampler;
5. Tests and optimization of the developed system for various applications.

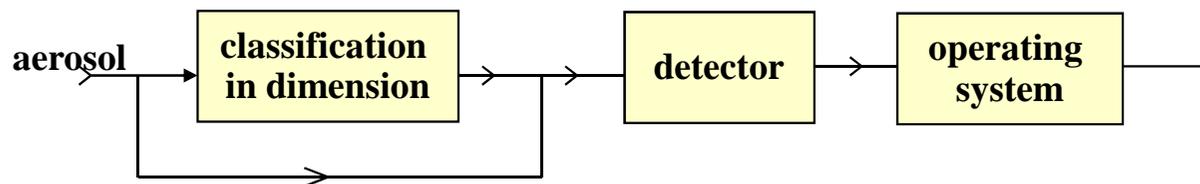
1 collect and analysis:



- ◆ Easy to analysis
- ◆ Time consuming

- Collect by filtration, electrostatic precipitators, diffusion battery.
- Off-line analysis by microscopy and microanalysis like electron microprobe or electron microscopy.

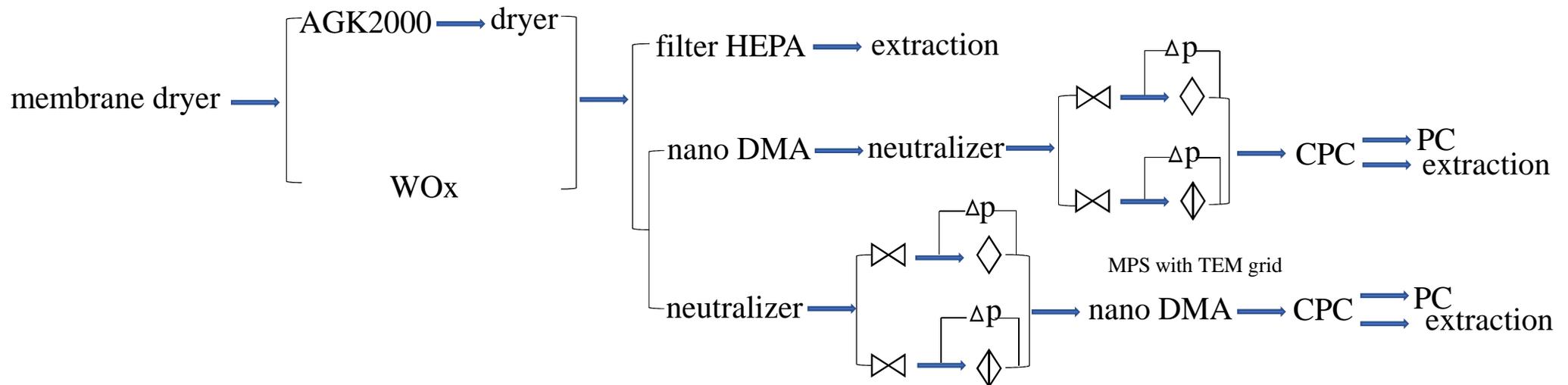
2 measure and analysis (near) real time



- Electrical mobility methods: DMA, DMPS, SEMS...
- Real-time instruments based on electrical electron of aerosols:
 - 1) EAA, DMA+CPC...
 - 2) FCE, DCS, EMS...

- ◆ Give size distribution directly
- ◆ Expensive

Set up



Three set up (R'mili, et al.2013):

1. measurement without TEM grid
2. measurement with TEM grid
3. measurement without TEM grid again

Main instruments



AGK 2000 palas aerosol generator



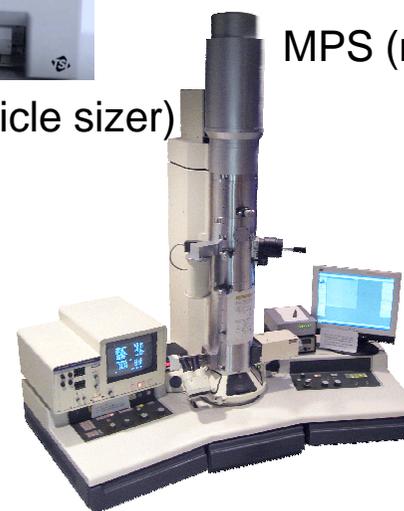
SMPS (scanning mobility particle sizer)



MPS (mini particle sampler)



WOx aerosol generator



TEM (transmission electron microscopy)

Generators

The size distribution of nanoparticles is **stable, repeatable, reproducible.**

NaCl (sodium chloride) nanoaerosol generator(atomizer): **10-130nm**

- ✓ Constant output atomizer can generate polydispersed NaCl particles
- ✓ NaCl material is mixed with fresh distilled water at different concentrations.

WO_x (tungsten oxide) nanoaerosol generator: **0.8-30nm**

- ✓ Size distribution remains steady during the experiment.
- ✓ Homogeneous deposition by WO_x generation without sample preparation.

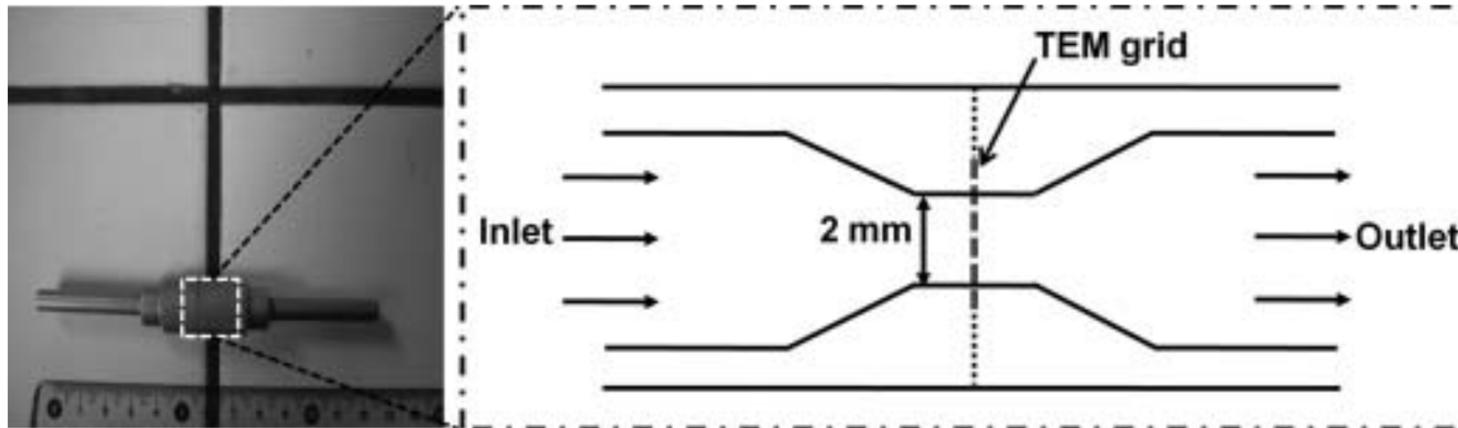
Influence factors on efficiency:

- Atomizer: applied pressure, salt concentration
- Tungsten oxide generator: carrier air flow, diluting air flow

MPS sampling system(with TEM grid)

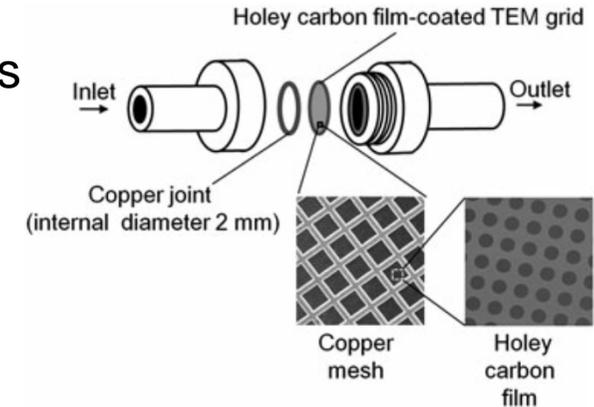
low-cost, portable, and easy to use.

- Without the difficulty sample preparation process;
- A few minutes to 30 min;
- Physical, chemical, morphological, and individual analysis;
- Easier to evaluate the collection efficiency.



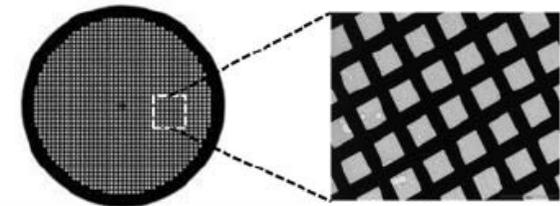
Filters for MPS sampling system

- “Lacey” type, “Holey” type, “Quantifoil” type holey carbon films
- 400 “mesh” copper, 200 “mesh” copper grid



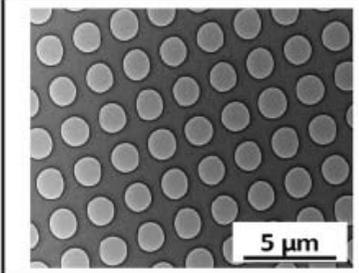
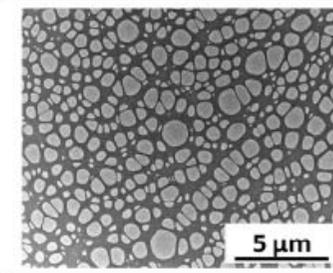
Influence factors	type				
	R1.2/1.3	R1.2/1.3	R1.2/1.3	R0.6/1	R0.6/1
Quantifoil	R1.2/1.3	R1.2/1.3	R1.2/1.3	R0.6/1	R0.6/1
mesh	200	400	400	400	400
flow rate (L/min)	0.3	0.3	0.6	0.3	0.6

(a) – TEM grid 400 mesh



(b) - Holey

(c) – Quantifoil 1.2/1.3



Influence factors on efficiency:

particle size, grid types, flow rate, residence time

SMPS 3938

SMPS 3938 measures particle concentration and size distribution.

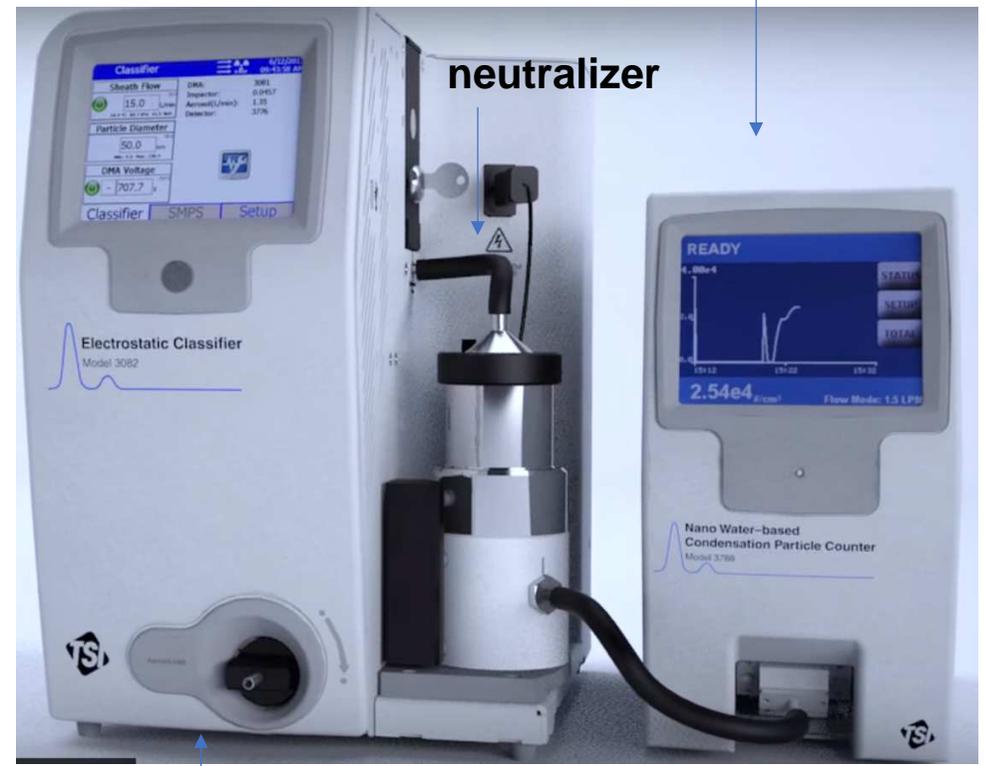
Influence factors on efficiency:

- Sheath air flow rate/sample air flow rate
- Number of channels
- DMA applied voltage
- Classifier order of particles from smaller to larger ones



Neutralizer

condensation particle counter (CPC)



differential mobility analyser (DMA)

Assess the Sampling efficiency by experiment

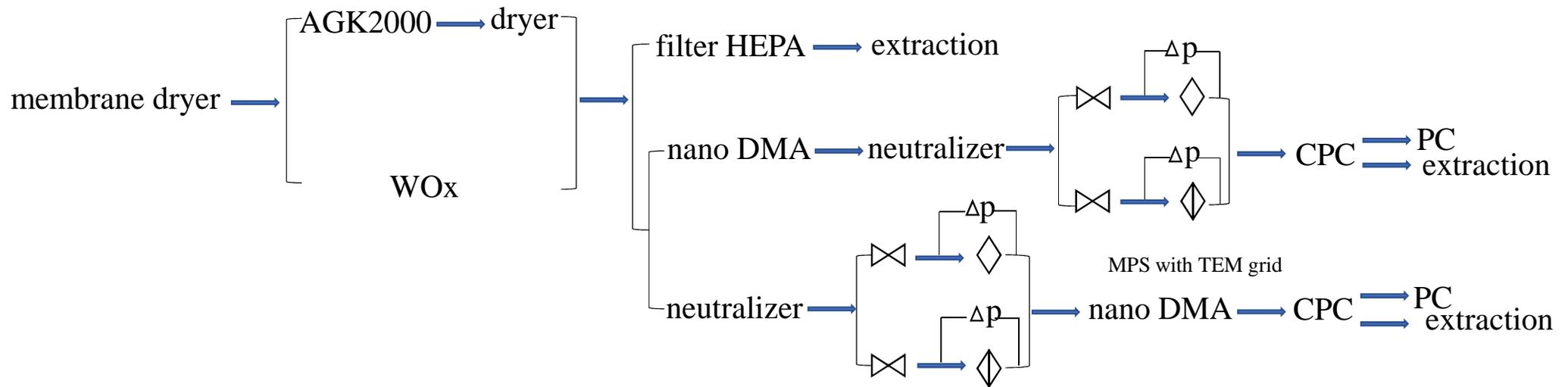
There is a interaction between influence factors and particles in the way you use the sampler.

$$E=1-P_t \quad P_t = C_{\text{downstream}}/C_{\text{upstream}} \text{ (measured by CPCs)}$$

It depends on:

- the aerosol (size, density, shape, ...)
- the flow of air (T, P, RH, ...)
- the sampling device (shape of the sensor, orientation, ...)

Set up



Three set up:

- measurement without TEM grid
- measurement with TEM grid
- measurement without TEM grid again

$$E = 1 - P_t \quad P_t = C_{\text{downstream}} / C_{\text{upstream}} \text{ (measured by CPCs)}$$

Model: **Capillary pore model**

Different expressions comparison according to different filtration mechanism: impaction on the filter surface, interception at the pore opening, brownian diffusion on the pore wall and front surface on the filter.

$$E=1-(1-E_{IR})(1-E_W)(1-E_{DS})$$

E_i (impaction), E_R (interception), E_{IR} (impaction and interception), E_W (diffusion to the pore wall), E_{DS} (diffusion to the front surface)

Characteristics parameters:

hole diameter, density of the holes, porosity, thickness, Reynold number

The flow of the carrier fluid should be **laminar(Re)**.

Calculation of E_I , E_R , E_{IR} , E_W , E_{DS}

$$E_I = \frac{2\varepsilon_i}{1+\xi} \left(\frac{\varepsilon_i}{1+\xi} \right)^2, \quad (\text{Pich 1964; Spurny et al. 1969})$$

$$\varepsilon_i = 2Stk\sqrt{\xi} + 2Stk^2\xi \exp\left[-\frac{1}{Stk\sqrt{\xi}}\right] - 2Stk^2\xi, \quad \xi = \frac{\sqrt{P}}{1-\sqrt{P}}, \quad Stk = \frac{mU_0C_c}{6\pi\eta r_0} = \frac{2C_cU_0r_p^2\rho_p}{9\eta r_0}.$$

$$E_R = \frac{4N_R^2}{1+4N_G} \left(1 + 2\frac{N_G}{N_R} \right), \quad (\text{Marre and Palmeri 2001})$$

$$N_R = N_r \left(1 - \frac{N_r}{2} \right), \quad N_r = r_p/r_0 \quad N_G = N_g \left(1 + \frac{N_g}{2} \right), \quad N_g = l_g/r_0$$

$$E_{IR} = \{N_r(N - N_r)\}^{2/(1+aN_r+bN_r^2)}, \quad (\text{Manton 1978})$$

$$a = (a_1I^2 - a_2I)/(I + a_3), \quad b = b_1I + b_2I^{1/2} + b_3I^{1/4}, \quad I = Stk'/N_r^2, \quad Stk' = \frac{2\rho_p r_p^2 U_0 C_c}{9\eta D_0} \left(= Stk \frac{r_0}{D_0} = Stk\sqrt{p} \right).$$

$$E_W = 2.56N_D^{2/3} - 1.2N_D - 0.177N_D^{4/3}, \quad \text{for } N_D < 0.01, \text{ or}$$

$$E_W = 1 - 0.81904 \exp(-3.6568N_D) - 0.09752 \exp(-22.3045N_D) - 0.03248 \exp(-56.95N_D) - 0.0157 \exp(-107.6N_D),$$

$$\text{For } N_D > 0.01 \quad (\text{Gormley and Kennedy 1949; Twomey 1962; Spurny et al. 1969})$$

$$N_D = LD_p P / r_0^2 U_0$$

$$E_{DS} = 1 - \exp\left\{ \frac{-\alpha_1 D^{2/3}}{1 + (\alpha_1/\alpha_2) D^{7/15}} \right\}, \quad (\text{Manton 1979})$$

$$D = D_p/D_0 U_0, \quad D_0 = r_0/\sqrt{P}, \quad U_0 = Q/\{(\pi/4)d_j^2\}$$

$$E_O = 1 - (1 - E_I)(1 - E_R)(1 - E_W)(1 - E_{DS}) \text{ or } E_O = 1 - (1 - E_{IR})(1 - E_W)(1 - E_{DS}).$$

Measurement uncertainty

The uncertainty of the measuring procedure for the present research mainly from **uncertainty of sampling efficiency**.

Two methods to calculate **expanded uncertainty** from the experimental data:

Polygonal approximation method and curve-fitting method: (NF EN 13205)

methods	Polygonal approximation method	curve-fitting method
monodisperse	√	√
polydisperse	×	√

Referenced literatures

- R'mili, Badr, et al. "Particle sampling by TEM grid filtration." *Aerosol science and Technology* 47.7 (2013): 767-775.
- Ogura, Isamu, et al. "Aerosol particle collection efficiency of holey carbon film-coated TEM grids." *Aerosol Science and Technology* 48.7 (2014): 758-767.
- Givehchi, Raheleh. "Filtration of NaCl and WOx nanoparticles using wire screens and nanofibrous filters." (2016).
- Bressot, Christophe, et al. "Exposure assessment of Nanomaterials at production sites by a Short Time Sampling (STS) approach: Strategy and first results of measurement campaigns." *Process Safety and Environmental Protection* 116 (2018): 324-332.
- Bressot, Christophe, et al. "Exposure assessment based recommendations to improve nanosafety at nanoliposome production sites." *Journal of Nanomaterials* 16.1 (2015): 342.
- Nanotechnologies – Measurements of Particle Size and Shape distributions by Transmission Electron Microscopy.
- NF EN 13205 Workplace exposure-assessment of sampler performance for measurement of airborne particle concentrations.

Thank you for attention!

*Any
suggestions
or questions?*

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E_{IR} E_I and E_R

$$E = 1 - (1 - E_{IR})(1 - E_W)(1 - E_{DS})$$

E : E_{IR} replace E_I and E_R :

The impaction process is calculated without accounting for the finite size of a particle, while the interception process ignores the inertia of a particle relative to the flow. (Manton, 1978)

TEM quantification analysis

Descriptor: size descriptor

Parameters: mean and spread

Goal: to get low RSE(relative standard error) and uncertainty

Case study examples should illustrate:

- identification of touching particles and artifacts,
- selection of size and shape descriptors with high repeatability,
- estimation of measurement uncertainties for distribution parameters, i.e., mean and spread,
- use of data visualization tools to augment measurement uncertainty results.

Particle analysis and image analysis: Image J

Data analysis: average, SD, Cv, U

Statistical analyse methods:

- AVONA(boxplots, P value)/ pairwise-AVONA
- K-S test (D(n,m))
- Bivariate analysis: bivariate plots
- Curve-fitting:
 - Histogram, **cumulation distribution**, quantile plots
 - Three reference models : normal distribution, **lognormal distribution**, and Weibull
 - two methods : **nonlinear regression model or maximum likelihood model**

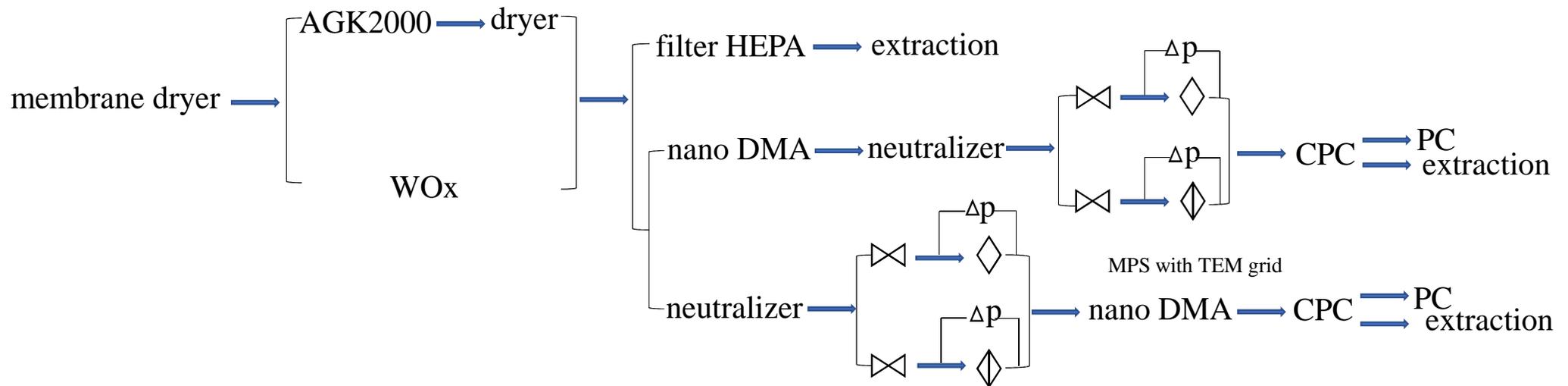
Nanosafety requirement

1. Collective protection: **HEPA(H14) filters, a closed conformity of a fume hood.**
2. Individual protection: **Type FFP3 mask, Type Tyvek suits, ...**
3. All the storages of nanomaterials should be **clearly labeled.**
4. Using the method of dilution-cracking based procedure for **destroying the nanostructure of the nano-objects.**
5. Wrap materials during transport.
- ...

SMPS

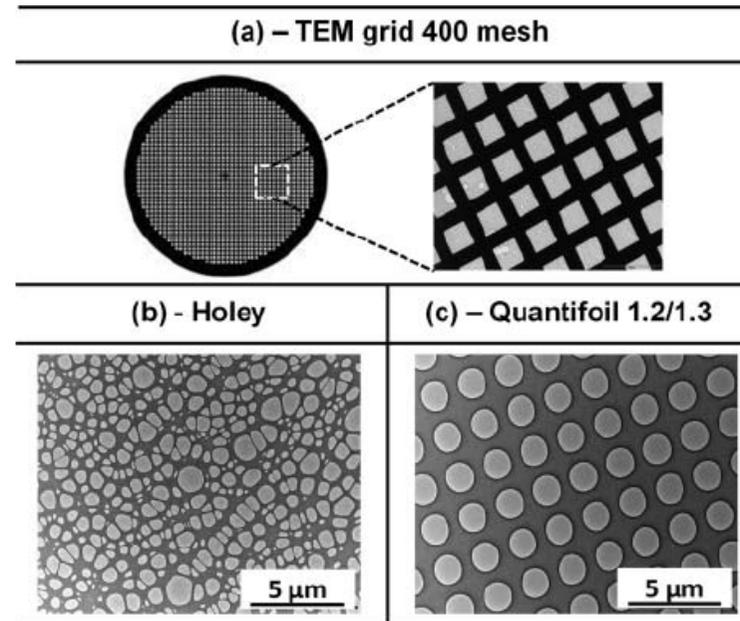
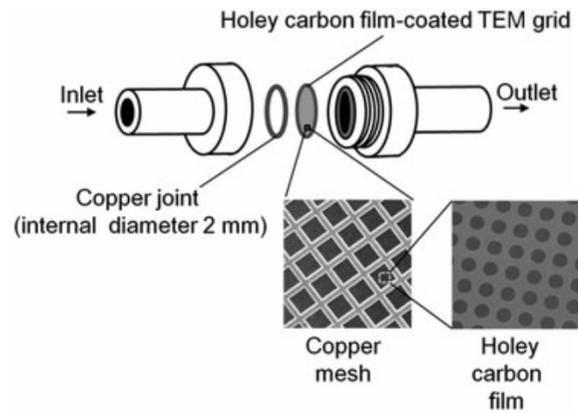
- The **electrostatic classifier** is used to inhale the particles with certain diameter range from air and measures flow.
- The **neutralizer** create a well-characterized charge distribution on the particle.
- In the **DMA** , the charged particles experience an electrical field that causes them to move through the gas in which they are suspended.
- The **CPC** counts single particles to provide accurate counts, even at low concentrations.

Set up



Membrane dryer: provide dry, filtered compressed air at a regulated pressure.
Pressure-drop checked by sampling clean air before can check the uniformity of pore sizes.

Filters for MPS sampling system



Holes generally calibrated in diameter, evenly spaced and uniformly distributed.