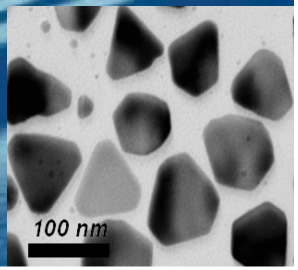
# Nanoparticle monitoring

## *State of the art and development strategies*

**François Tardif** CEA
**ftardif@cea.fr**

.

Some conclusions from Nanosafe2 project



# INTRODUCTION

*Absolute necessity to know how to measure the particles for a dynamic development of the nanomaterial industry*

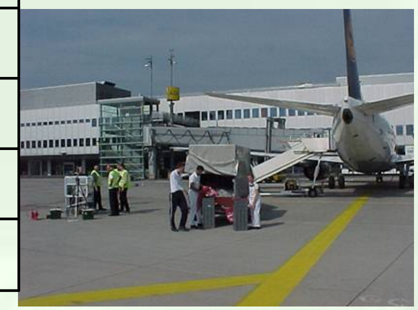
- **Decreasing worker exposition**
  - **. Qualification of confinement equipments: ventilation-filtration and individual protections: mask, gloves, suits**
  - **. Leak detections at <u>equipment</u> level**
- **Controlling the non-dissemination to the Environment**
  - **. Leak detection at <u>factory</u> level**
- **First step toward social acceptability**
  - **(Something invisible makes scared: radioactivity, etc.)**

# KNOWLEDGE ON NANOPARTICLES

## ➔ Nanosafe2 deliverable : D1.1.3

## . Very high level of already existing nanoparticles!

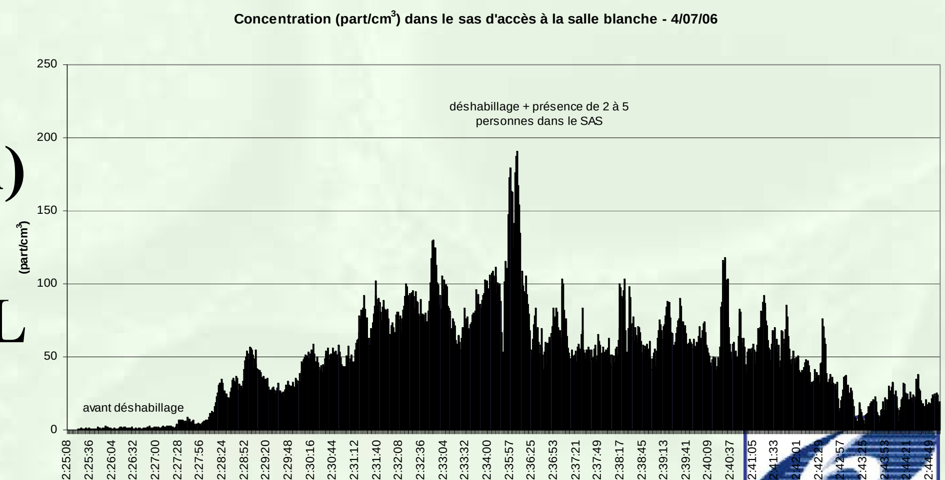
| | Particles/mL | Mean sizes |
|---|---|---|
| Outdoor, office | 10 000 | > 10 nm |
| Filtered workplaces | 0 - 2 000 | > 10 nm |
| Plasma cutting | 500 000 | > 120 nm |
| Airport field | 700 000 | < 45 nm |
| Breath after smoking | >> 100 000 000 | > 10 nm - |



## . Very fluctuant behavior of existing nanoparticles!

**Ex.: Nanoparticles measured in a clean room entrance (>10 nm)**

- **Duration: 1 hour**
- **Range: from 0 to 200 part/mL**



# SUMMARY/CONCLUSIONS

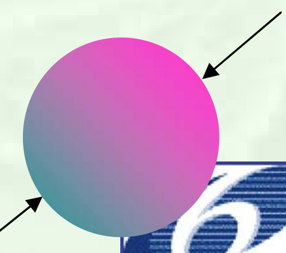
1. We need different measurement types

❖ **Airborne nanoparticules** (workers & the Environment)

2. We know perfectly how to measure the nanoparticles … at laboratory
3. Available equipments present major limitations for <u>monitoring</u>
4. Development strategy proposed in Nanosafe2

❖ **Nanoparticules in liquids and soil** (Environment)

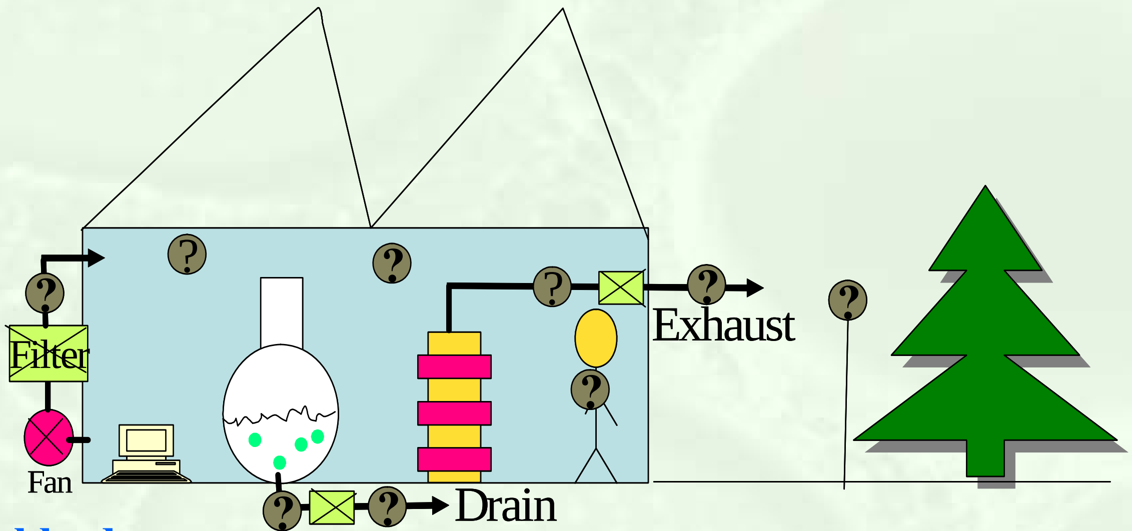
5. No (few) operational method
6. Developpement strategy proposed



**Nanoparticule: diameter < 100 nm (0.1 µm)**

# NEEDS IDENTIFIED IN NANOSAFE2

## Set up of a global monitoring strategy




. **Individual badge**
. **Fixed-portable equipments**
. **Real time vs. differed (+ integration delay)**
. **For Air/Liquid/Soil**

. ***Cost Constraints***
. ***Easiness to use***
. ***Robustness***

**1. Different monitoring tools will be necessary**

**➔ Nanosafe2 deliverable : D1.1.2**

# PARTICLE MEASUREMENT TOOLS

## 2. We know how to measure airborne nanoparticles … essentially at laboratory!

| | |
|---|---|
| . Particle sizes: | 2 < pd < 5 000 nm |
| . Concentrations: | 0.01 < C < $10^7$ particles/mL |
| . European companies: | Dekati (Fi), Grimm (G) |
| . N°1 supplier: | TSI (USA) |





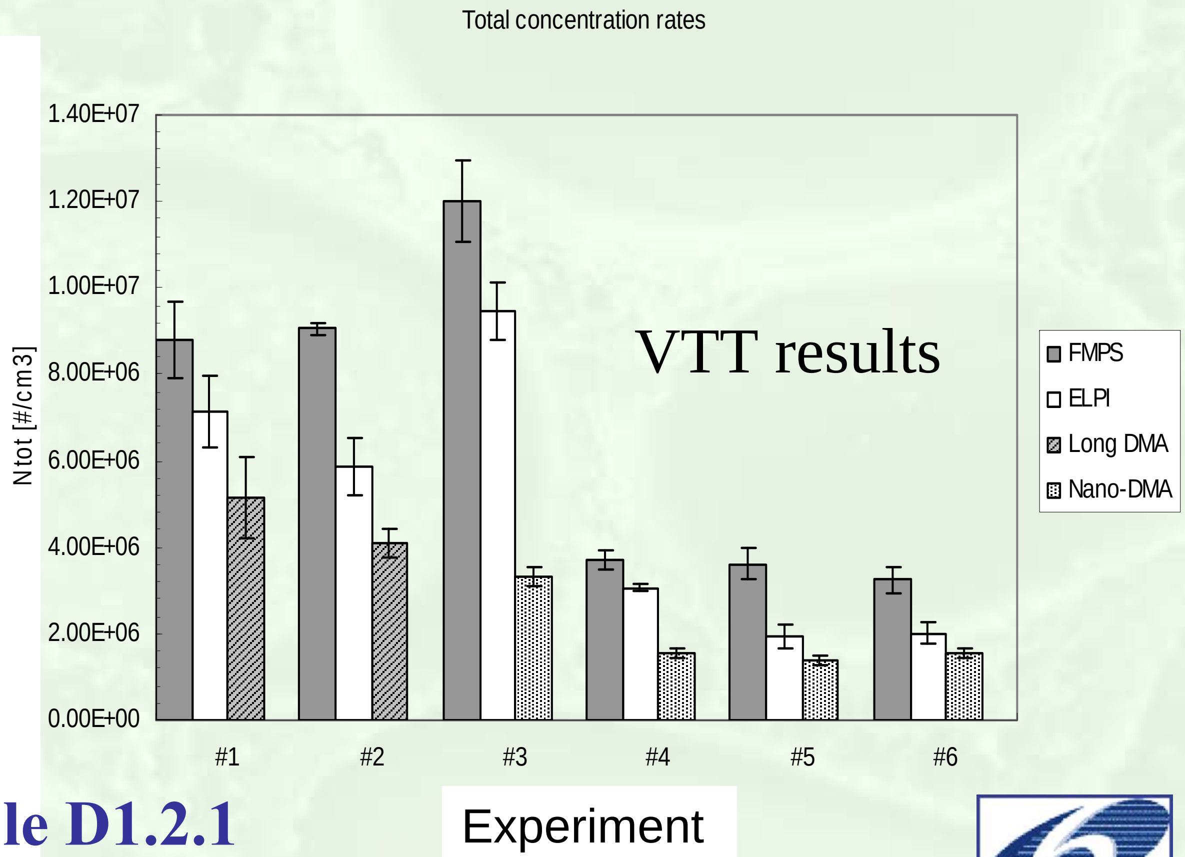

# PARTICLE MEASUREMENT TOOLS

**Nevertheless, very big differences between 2 equipments ➔ calibration tools are useful!**

## Tested tools in Nanosafe2:

- TSI 3080 series Electrostatic Classifier
- TSI Model 3007 Condensation Particle Counter
- TSI 3090 Engine Exhaust Particle Sizer Spectrometer
- DEKATI
- GRIMM SMPS
- Low pressure impactor Berner type (>21 nm)
- TSI FMPS
- NSAM
- TEOM
- . …

**➔ Nanosafe2 Deliverable D1.2.1**



# PARTICLE MEASUREMENT TOOLS

## 1. How to detect nanoparticles?

- Mass measurement
- Artificial growing of the nanoparticles + light scattering
- Electrostatic measurements

## 2. How to measure the size of the particles?

- Classification by electrical mobility + detection
- Classification by inertia + detection

# DETECTION BY MASS MEASUREMENT

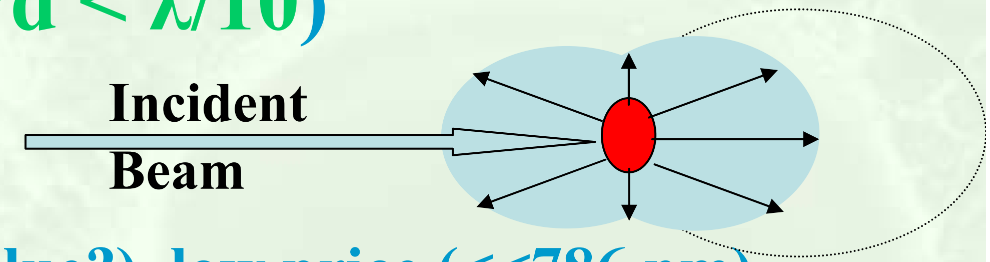
- µ-balance
- SAW (Surface Acoustic Waves)
- Filter Weight

1. Interest for very high nanoparticle concentrations only, as sentivity decreases according to the 3rd power of the size: $M_{10\ nm} = M_{1\ \mu m} / 10^6$ !
2. No discrimination between natural and artificial particules

# DETECTION BY LIGHT SCATTERING

- **Rayleigh scattering ($Pd < \lambda/10$)**

  $I = f(I_0, 1/\lambda^4, Pd^6)$




➔ **Looking for low λ lasers (blue?), low price (<<786 nm)**

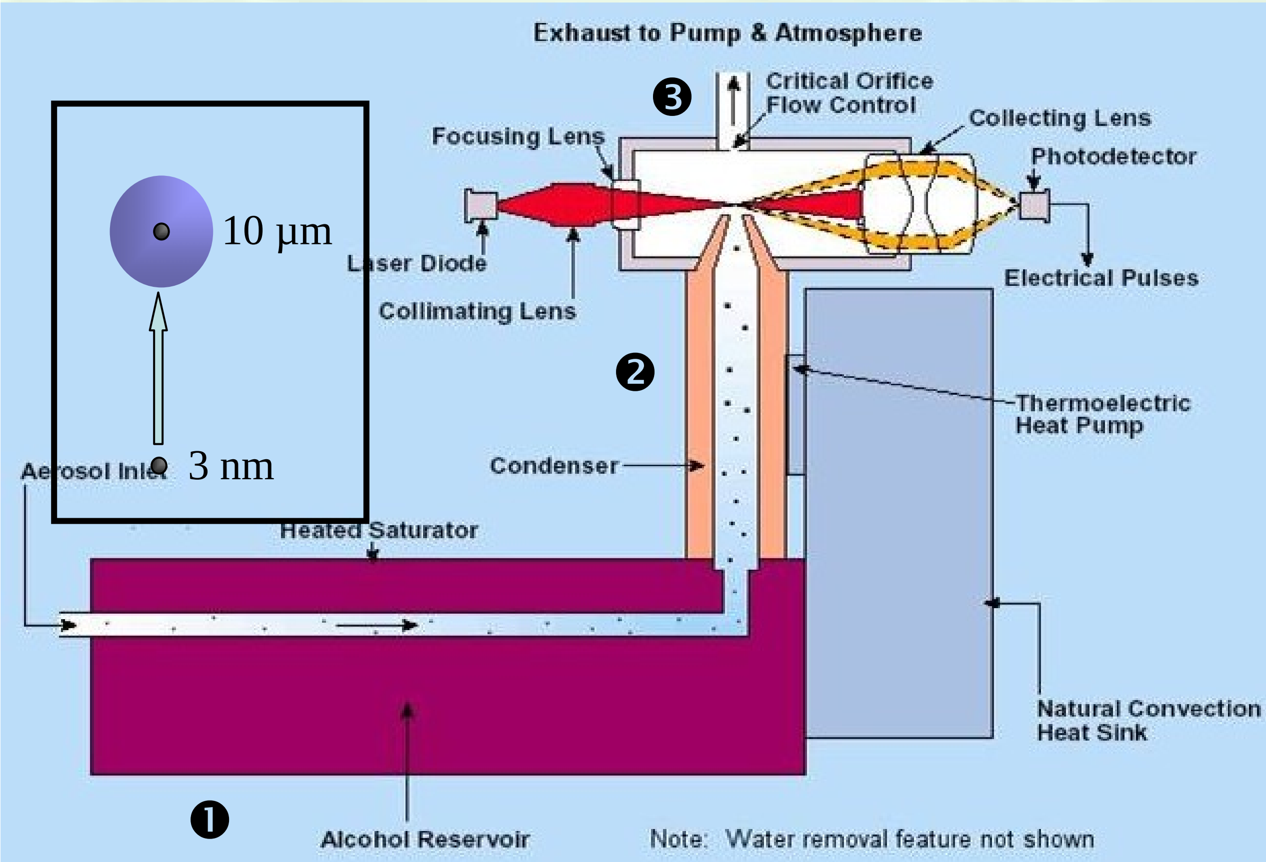
➔ **Diffusion handicapped by the 6th power on particle diameter**

- **Today's Low Limit of Detection > 50 nm**

**Too low sensitivity for nanoparticles to perform direct measurements ➔ CPC**

# CONDENSATION PARTICLE COUNTER: CPC

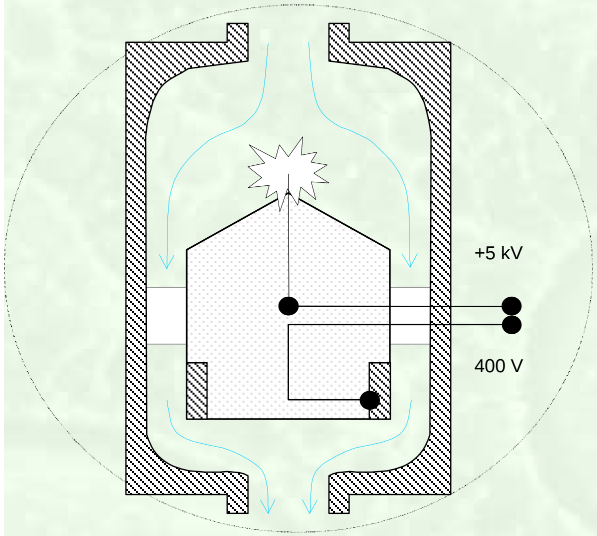
*Nanoparticles are grown in a supersaturated vapor before detection by light scattering*

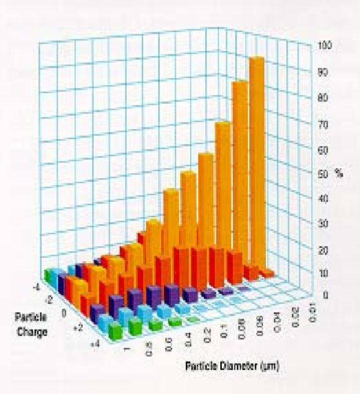



- **Very Low Limits of Detection (< 5 nm)**
- **No information on initial particle sizes**
- **Price: 15 k€**

**But: necessary to fill up the reservoir every week!**

# Electrometer



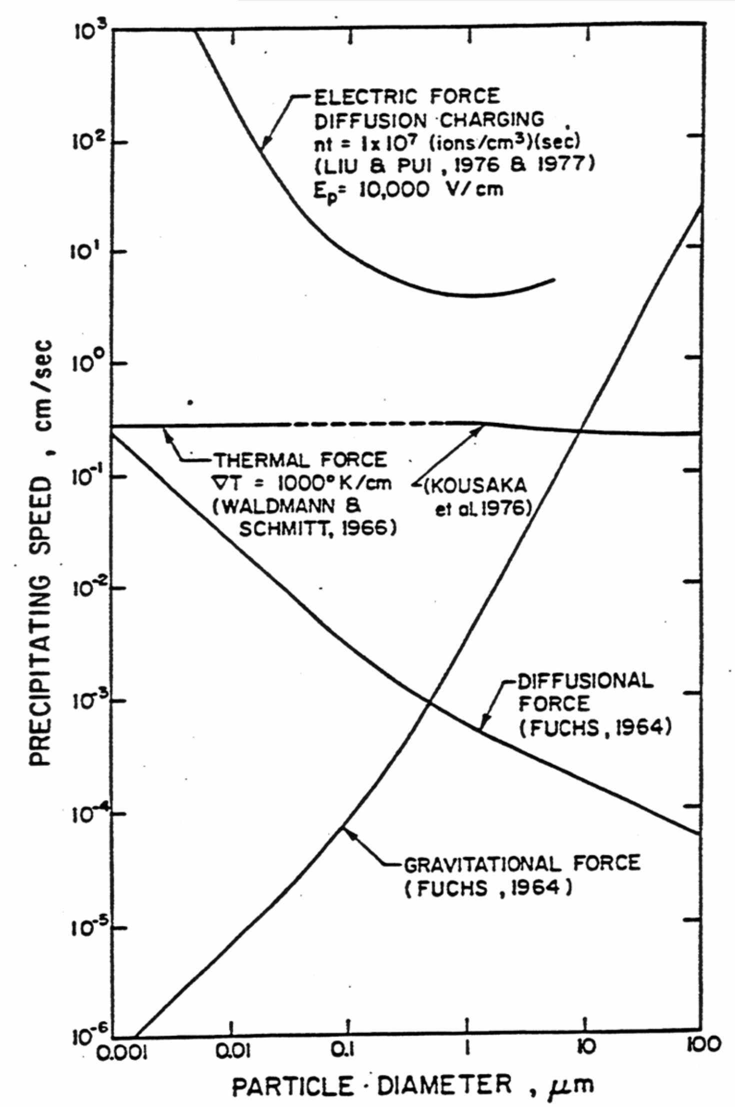

*Equilibrium-charge distribution graph*

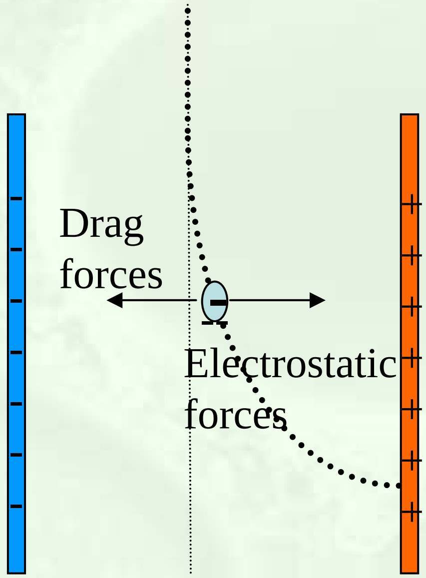
- **Very Low Limits of Detection (< 1 nm)**
- **No information on initial particle sizes, surface measurement**
- **Price: 15 k€**

**But: change filter-electrodes regularly to avoid clogging!**

# CLASSIFICATION BY ELECTRICAL MOBILITY

*Use of the predominant electrical forces at nano scale*



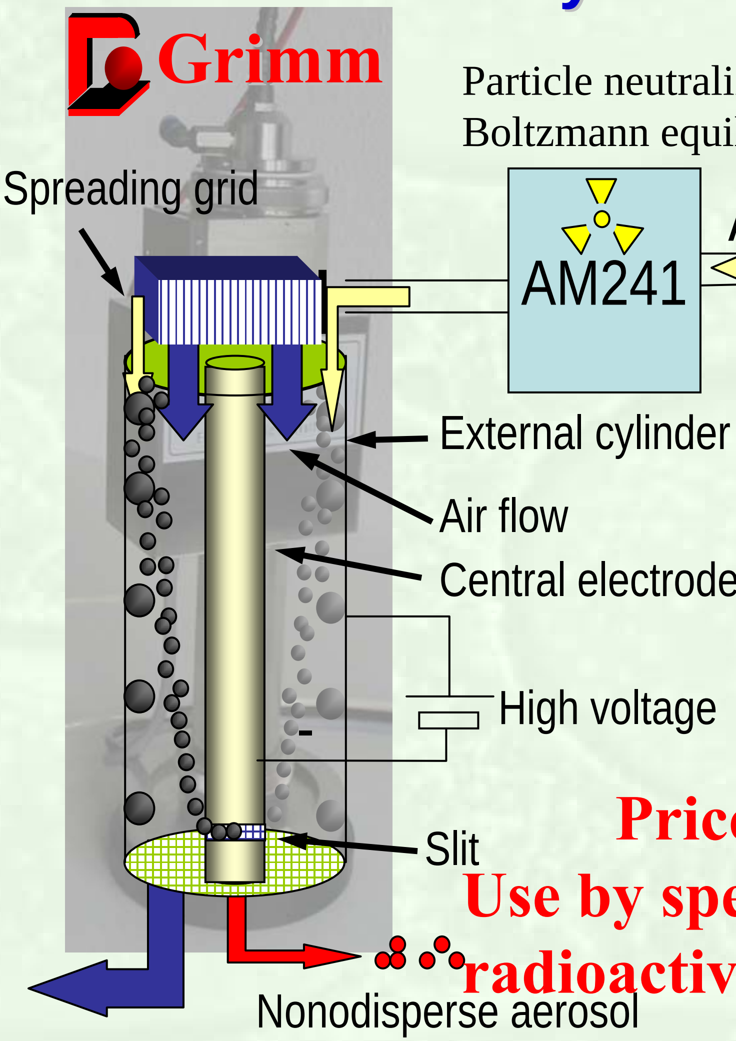



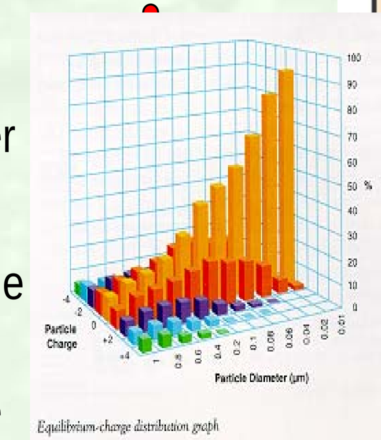

$$Zp = V/E$$
$$qE = 3\pi\mu DpV$$
$$\Big\} \; Zp = q/3\pi\mu Dp$$

# SCANNING MOBILITY PARTICLE SIZER

# SMPS

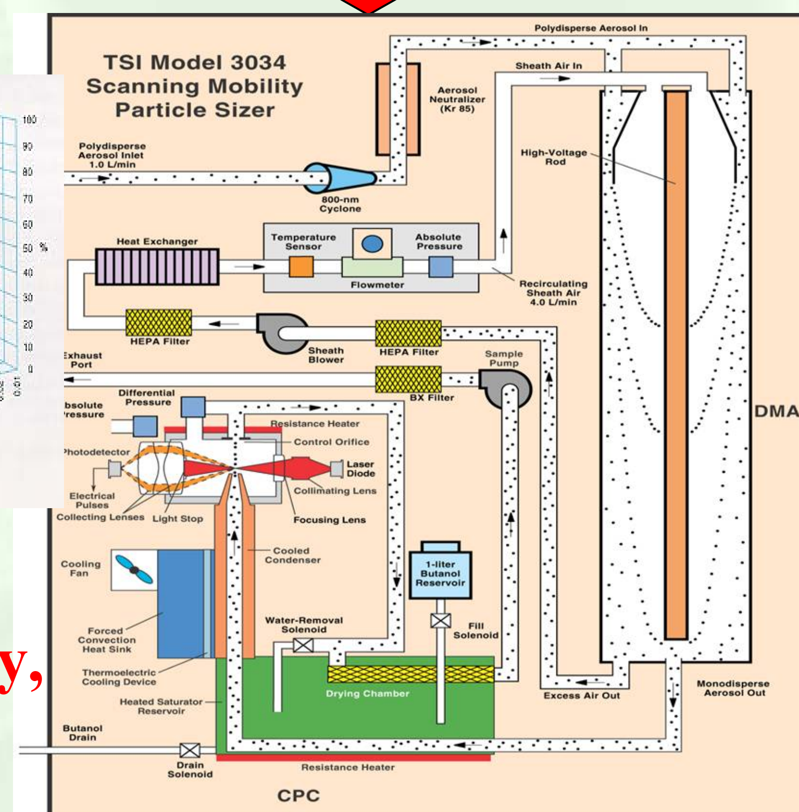
## DMA :
## Differential Mobility Analyzer




## Then detection by CPC:

## ➔ DMA + CPC = SMPS

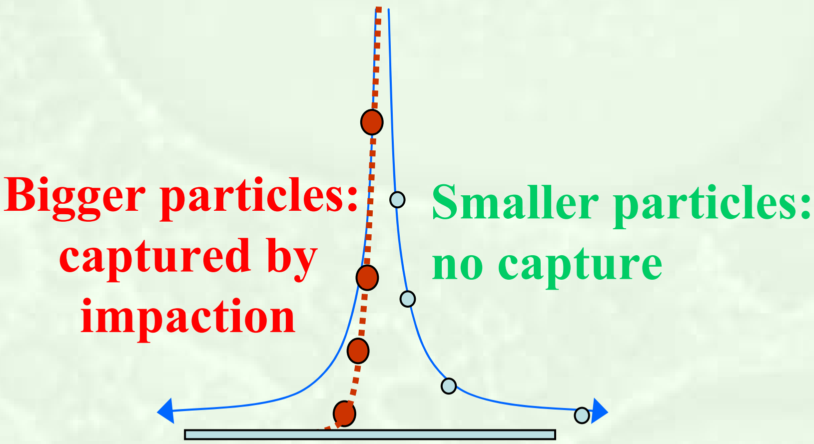



**Price > 80 k€**

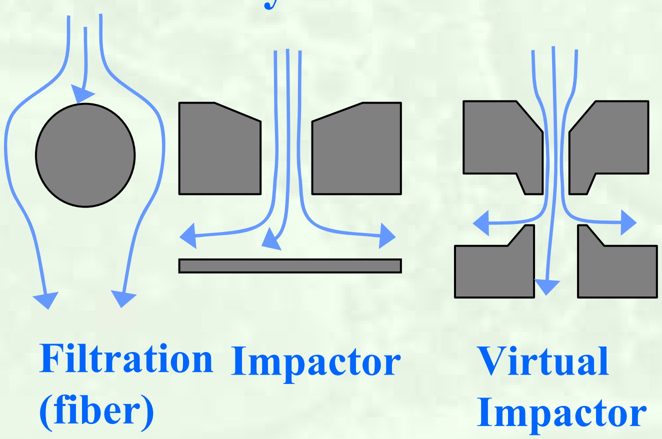
**Use by specialists only, radioactive source!**

# CLASSIFICATION BY INERTIA

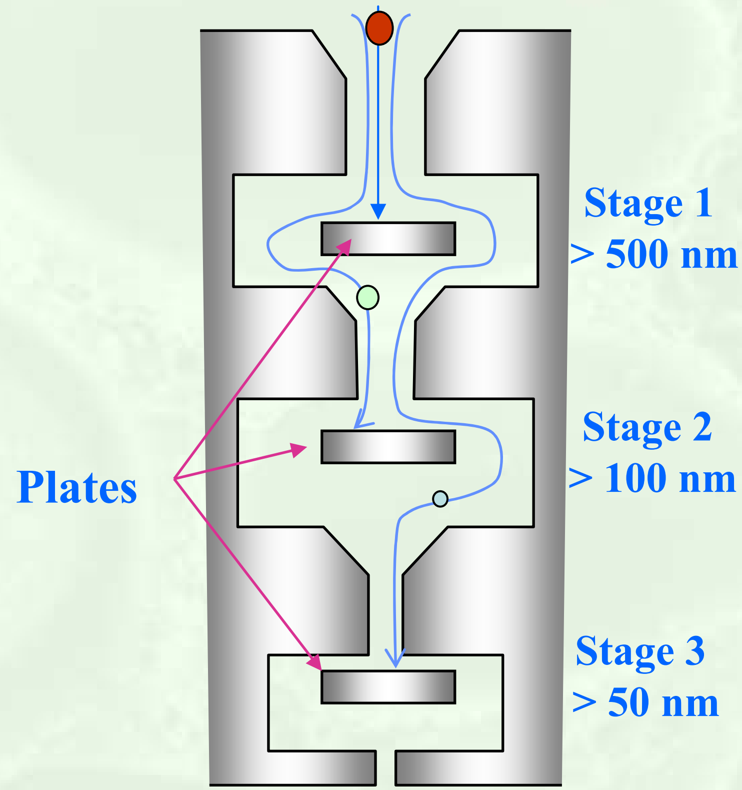
*Particles presenting sufficient inertia cannot follow the gas flow:*




➔ **Possibility to separate particles by inertia !**



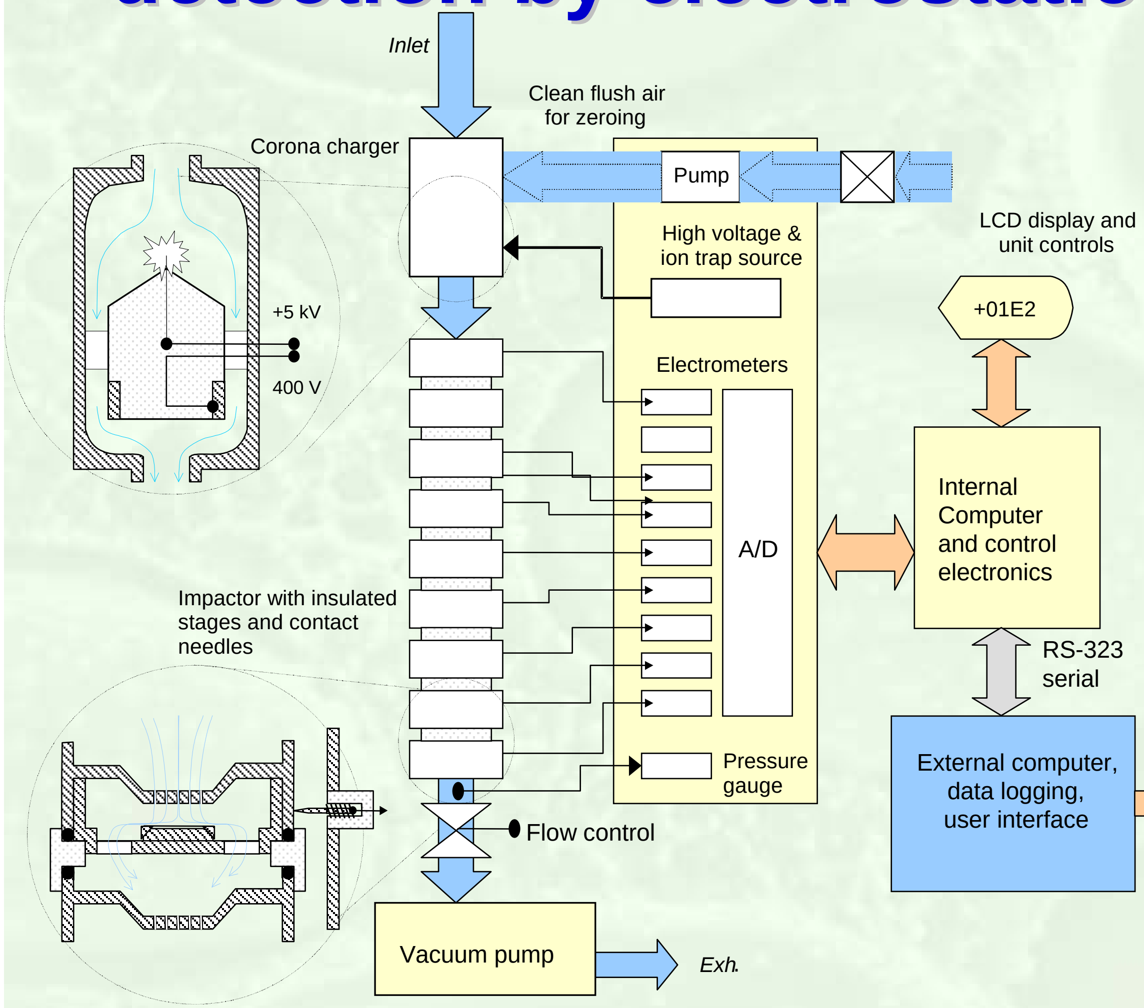

**Cascade impactor**



# LOW PRESSURE IMPACTOR

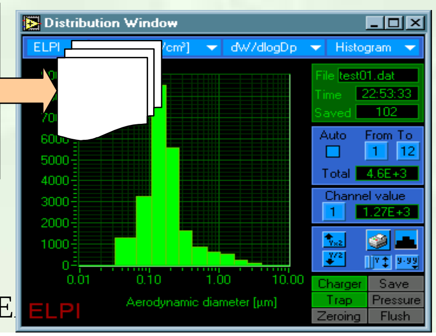
# LPI

## Classification by inertia, detection by electrostatics




**Price > 80 k€**

**Use by specialists only**



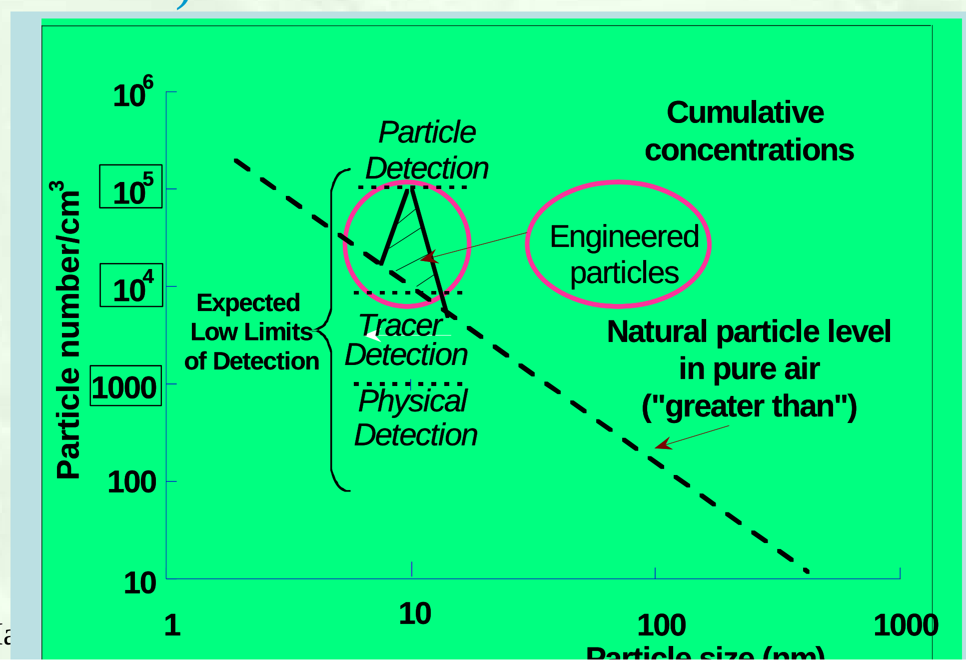
# LIMITATION OF TODAY'S TOOLS

## 3. Today's measurement tools present important limitations for industrial monitoring

. Available particle measurement tools are not adapted for industrial monitoring as they require: specialists, maintenance, even sometime radioactive source, high price, etc.

. Measurement of engineered nanoparticles limited by the fluctuant and very high nanoparticle levels (interest to work in clean rooms)

**Necessity to design other techniques specific to engineered nanoparticles based on other approaches: elemental analysis, tracing, etc.**

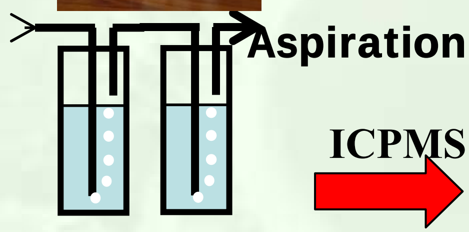


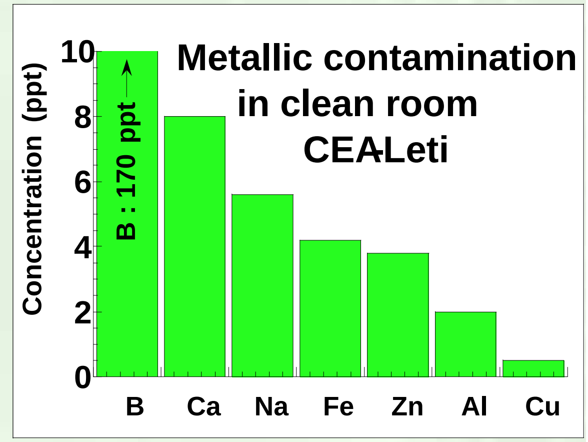
# SPECIFIC TECHNIQUES

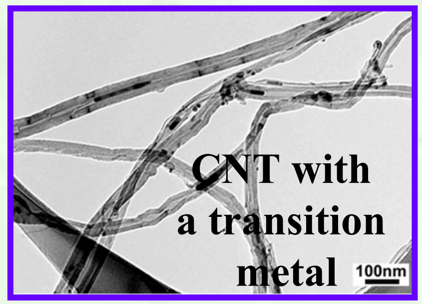
Some examples:

## Elemental analysis

- . Mass spectrometry
- . Atomic Absorption
- . Ionic Chromatography
- . Fluorescence X
- . TOF SIMS (Organics)
- . Laser spectrometry LIBS



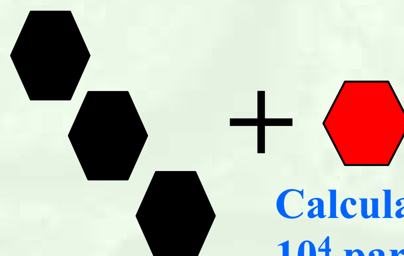



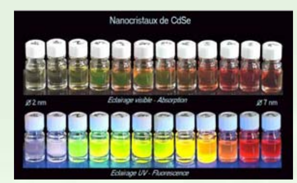




**Low Limit of Detection 24H00 : 0.1 ppt !**

## Tracing techniques

**Adding fluorescent tracers easily detectable since the production of the nanoparticles: "Nanotracers"**






**Calculated Low Limit of Detection: $10^4$ part/mL**

**Nanomaterial + Nanotracers**

# Nanosafe2 STRATEGY PROPOSAL FOR

# AIR MONITORING

**1. <u>Short-term:</u>** **industrialialisation of the most promising existing particle detection tools for a fast survey of workers in labs and industry. Example of objectives: price < 5000 €, maintenance > 6 months.**

**. Proposition of methods enabling to use particle type detection in actual fluctuant ambiances**

**. Design of transportable calibration methods**

**2. <u>Middle-term:</u>** **design in parallel of:**

**. Industrial detection tools specific to engineered nanoparticles**

**. Individual badges**

**. Low cost detection for environmental survey**

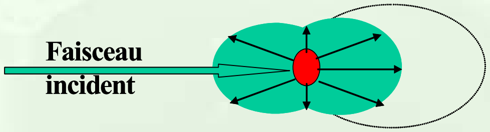
**3. etc.**

# PARTICLES IN LIQUIDS AND SOILS

. The background noise due to natural nanoparticles is extremely high in liquids and soils (>> air) !

. Some laboratory equipment to measure nanoparticles in liquids and soils:

- Photon Correlation Spectroscopy – PCS- 0.6 nm< Pd < 6 µm but limited to 2 granulometric picks
- Light scattering Pd > 10-50 nm limited to very diluted particle concentrations (microelectronics)




➔ Detection specific to engineered nanoparticles seems more adapted for liquids and soils (ICPMS , etc.)

**5. No operational methods for liquids and soils**

# Nanosafe2 STRATEGY PROPOSAL FOR

# LIQUIDS AND SOILS MONITORING

1. Design of adapted sampling tools (filtration, …)

2. Adaptation of the specific measurement techniques set up for air

3. …

# SUMMARY/CONCLUSIONS

1. We need different measurement types

❖ **Airborne nanoparticules** (workers & the Environment)

2. We know perfectly how to measure the nanoparticles … at laboratory
3. Available equipments present major limitations for monitoring
4. Development strategy proposed in Nanosafe2

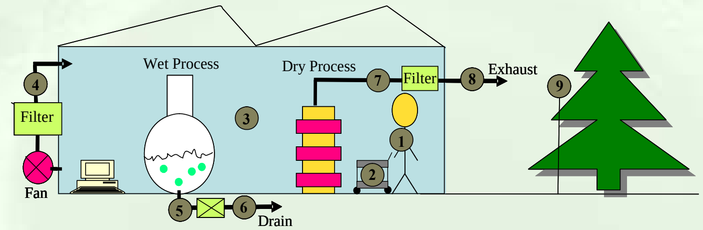
❖ **Nanoparticules in liquids and soil** (Environment)

5. No (few) operational method
6. Developpement strategy proposed

*Special thanks to:*
*DEKATI, GRIMM, PMS, TSI, ECCOMESURE, INTERTEK, EC financing Nanodafe2 project*

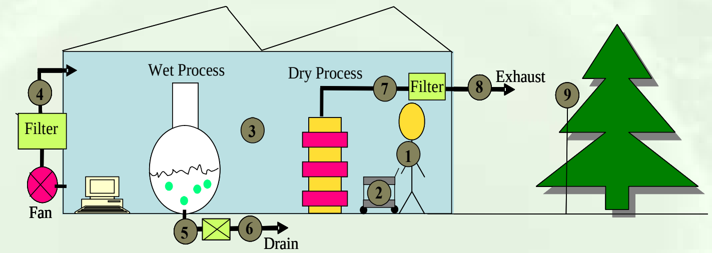
# Thanks for your attention …

# Monitoring Strategy




| Location | Interest (High /Medium / Low) | Fixed vs Portable | On-line vs Off-line | Monitoring Frequency | Monitoring Duration | Acceptable Cost k€ | Use |
|---|---|---|---|---|---|---|---|
| 1 | High | Portable | Off-line | 1 / month | 1 month | 0.1 / badge | Each worker to wear a personal monitoring badge for one month to measure level of exposure. (Analogous to radiation badges worn in the nuclear industry). |
| 2 | High | Portable | On-line | Monitoring frequency to be dependent on state of operation, e.g. start-up or capable on-going operation. | up to 15 min | 15 | Monitoring equipment to be used to confirm that engineering design and controls are adequate during start-up or following a process change and also to ensure ongoing effectiveness of design and controls during normal operation. Monitoring equipment to be placed on a mobile cart to allow monitoring in a number of defined locations. Monitoring frequency to be dependent on state of operation, e.g. start-up or on-going operation. |
| 3 | High | Fixed | On-line | Equipment to take measurements at 5 min to 30 min intervals depending on the toxicity of the nanoparticle and required reaction time. | 5 min – 30 min | 10 | Fixed piece of equipment to be located close to potential release points to alert worker of any leaks. The optimum location in the workplace to be defined by modelling leak scenarios. The monitoring equipment could be connected to an alarm to alert workers of a leak. The alarm could then initiate risk management measures to minimize exposure and release to the environment, e.g. emergency evacuation and emergency shutdown and containment. |
| 4 | Low (Measurement of filter efficiency. Location 3 is more relevant for workers). | Portable | Off-line | 1 / month | 15 min | 5 | A portable piece of equipment to be used to determine if there are any releases from the air filtering system. Other equipment such as differential pressure measurements over the filter could be used to determine the general integrity of the filter and the monitoring equipment could be used to ensure that the air re-circulated back into the room is within defined limits. The monitoring frequency could be increased or decreased following the filter manufacturers advice. |
| 5 | Low (Control before filter interesting for process only). | Portable | Off-line | 1 / 6 months | 1 hour | 5 | A portable piece of equipment to be used to measure the presence of nanoparticles in liquid waste. To get a representative reading a number of grab samples could be taken over a certain period of time (so as to include normal operation, wash-out, etc. The purpose of the equipment would be to understand the concentration of nanoparticles leaving the process through the liquid waste stream. The data could then be used to ensure that the liquid filter is working efficiently and also to determine if process changes are required to reduce the total quantity of nanoparticles being lost from the process through liquid waste. |

# Monitoring Strategy

| Location | Interest High / Medium / Low | Fixed vs Portable | On-line vs Off-line | Monitoring Frequency | Monitoring Duration | Acceptable Cost k€ | Use  |
|---|---|---|---|---|---|---|---|
| 6 | High (Exhaust measurement). | Fixed | On-line or Off-line | When tank is full | 5 min | 15 | The monitoring equipment in the liquid waste stream can be either on-line or off-line. If the liquid waste enters a positive release tank where the concentration of nanoparticles must be measured prior to release and the tank has a large capacity compared with the amount of liquid waste generated then the analysis can take place off-line whereas if the tank fills regularly then an on-line measurement would be required to test the waste before allowing the waste to be released. The sample duration would ideally be quite short and the tank should be mixed prior to taking a sample to ensure a homogeneous mixture. |
| 7 | Low (Control before filter interesting for process only). | Fixed | On-line | Continuous to allow the process to be continuously monitored. | < 1 min | 15 | Monitoring equipment to be used for process control. Therefore the monitoring should be close to continuous so that any changes could be detected as soon as possible to allow corrective actions to be taken. |
| 8 | High (Exhaust measurement). | Fixed | On-line | Equipment to take measurements at 5 min to 30 min intervals depending on the toxicity of the nanoparticle and required reaction time. | 5 min – 30 min | 10 | A fixed piece of equipment to be used to determine if there are any releases from the process filtering system. Other equipment such as differential pressure measurements could be used to determine the general integrity of the filter and the monitoring equipment could be used to ensure that the air released to the environment is within defined limits. |
| 9 | Medium (Useful for communication in addition of measurements in location 8). | Fixed | Off-line | 1 / month | 1 month | 1 | A fixed piece of equipment which allows the level of nanoparticles outside the process to be determined and allows the impact of the process on the environment to be determined. |