Methodology for assessing the impact of nanoparticles on effluents from fire

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1. Outline …

- Present situation for nanofillers
- NANOFEU Project
- Overview
- Method used to estimate the particle size distribution in fire effluents
- Preliminary results
- Conclusion
- Metrology of validation of an aerosol measurement
- Further works

2. Present situation for nanofillers …

- Everywhere, the use of nanofillers (nanoclays, carbon nanotubes) is increasing as additives in polymers.
- Their addition to polymer matrix and various additives provides new performances such as:
  - mechanical,
  - fire,
  - or electric behaviours.
- In case of combustion, Nanofillers are submitted to possible modifications of their physical and chemical properties, because of their surface treatment, dispersion and morphology (particle size).
- The present study was performed by LNE to establish a methodology to assess gases and aerosols produced during fires involving nanomaterials.

3. NANOFEU Project

❑ Partners

Project Coordinator :
Determination of heat release and toxic product yields under different fire conditions

INERIS
maîtriser le risque pour un développement durable

Molecular simulation

ISMANS

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Impact of nanofillers in terms of smoke toxicity, morphology and size distribution of their aerosols

NanoFEU

Nanocomposites & polymers producer supports

PlasticsEurope

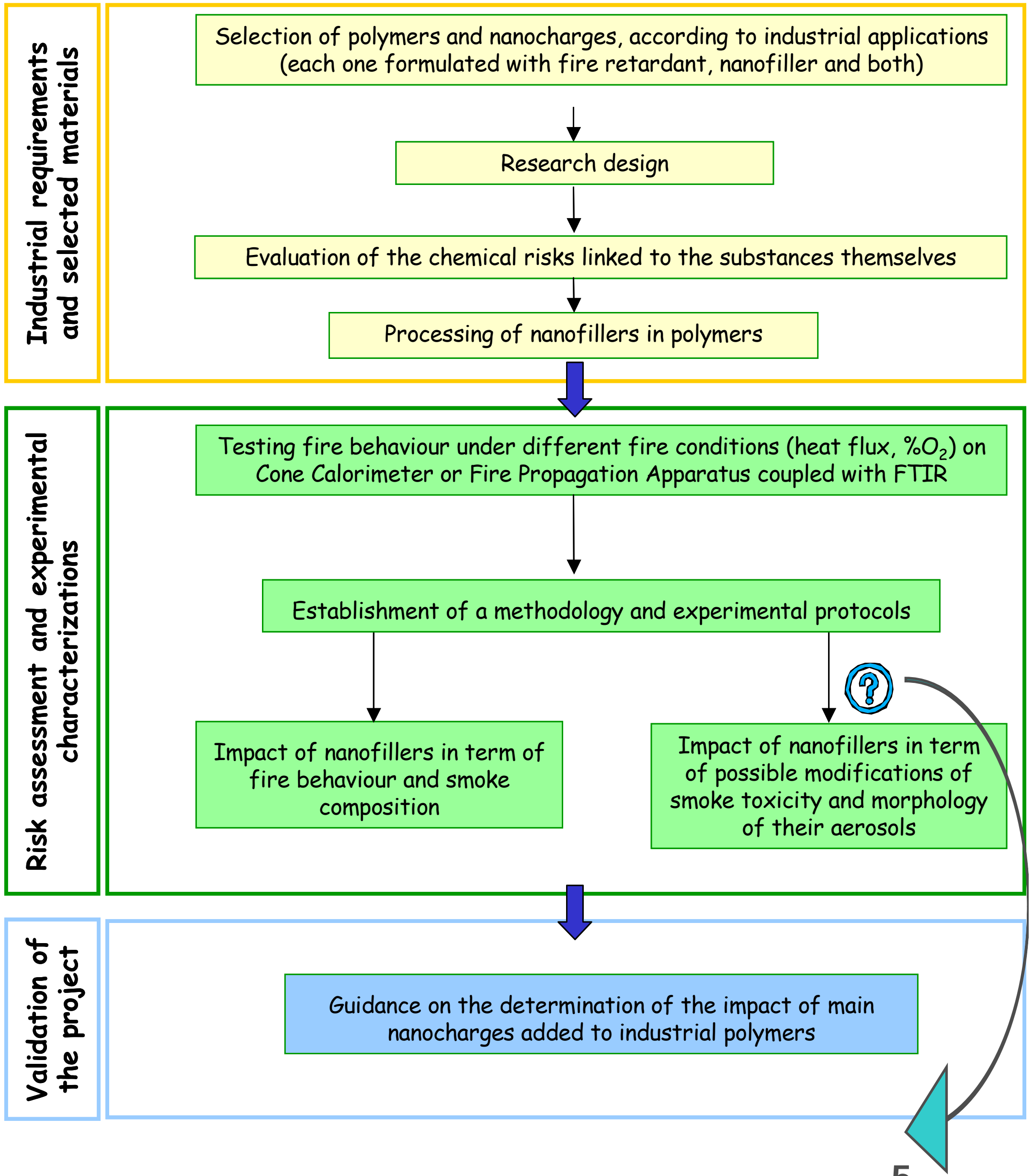
ECOLE DES MINES D'ALES

Selection of studied products and processing of nanofillers in polymers

Objectives of NANOFEU Project

This project focuses on the impact of nanofillers on the composition of smoke (gases and aerosols), by comparing polymers alone, polymers containing nanofillers and polymers containing both nanofillers and conventional flame retardant system.

Another aspect is to evaluate the morphological modifications of nanoparticles produced during combustion of such materials.



LNE is the main organization that will work on nano-aerosols measurement.

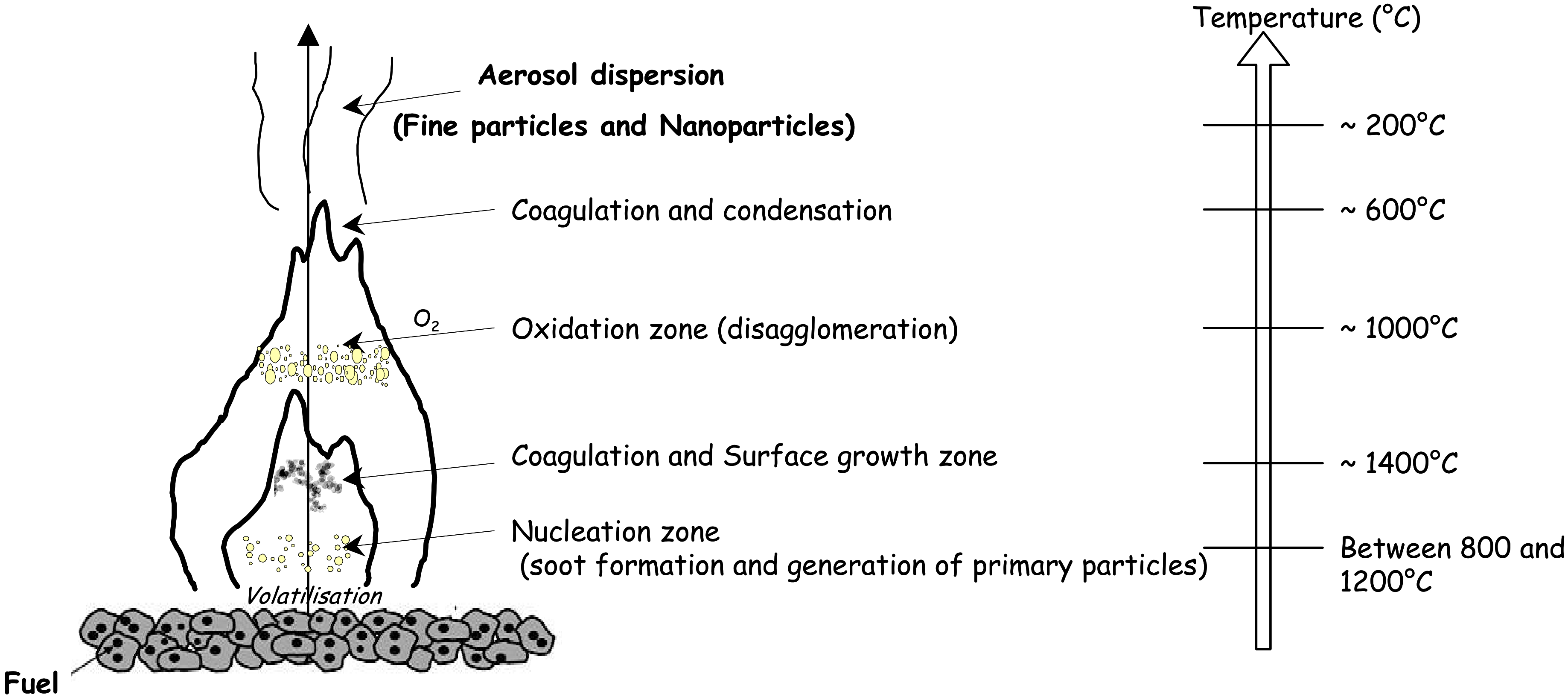
4. Overview

- During fire, three phenomena occur:
  - ✓ formation of a char (residue),
  - ✓ emission of gases that mainly depends on the evolution of the concentration during time,
  - ✓ formation of aerosol.

- Aerosols released are complex :
  - ✓ non-homogeneous mixtures of liquid droplets, of tar or water,
  - ✓ solid-phase carbonaceous agglomerated soot, with adsorbed organic compounds, or mineral particles.

Generation of aerosol in flames

Generation processes of all the different fractions of smoke aerosol can be very different, depending on many factors (concentrations, temperatures…).



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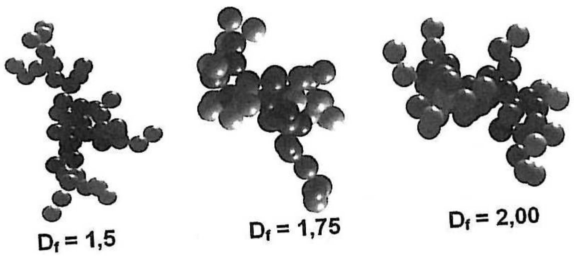
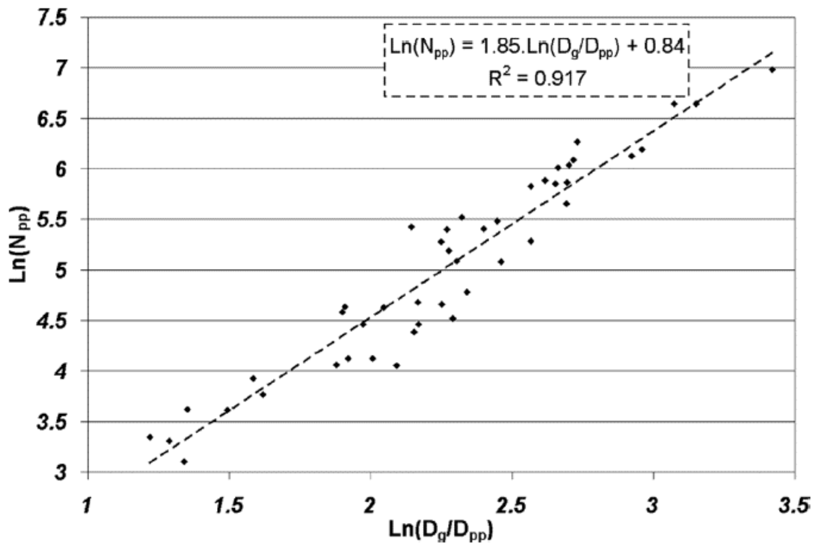
How to characterized aerosol during combustion ?

- **Concentration**
- **Mass distribution** **(aerodynamic diameter)**
- **Chemistry (locally)**
- **Morphology (locally)**
  - ✓ **D_{pp}: Diameter of primary particle**
  - ✓ **R_g: Gyration radius**
  - ✓ **N_p: Number of primary particle**

All parameters can be determined by AFM image analysis procedure

Fractal Dimension (D_f) describes the morphology of an aggregate





General representation is in log-log scale between N_{pp} and the ratio D_g/D_{pp}, in this case the slope of the linear regression applied to experimental results is the fractal dimension D_f and the intercept is the logarithm of the prefactor k_f.

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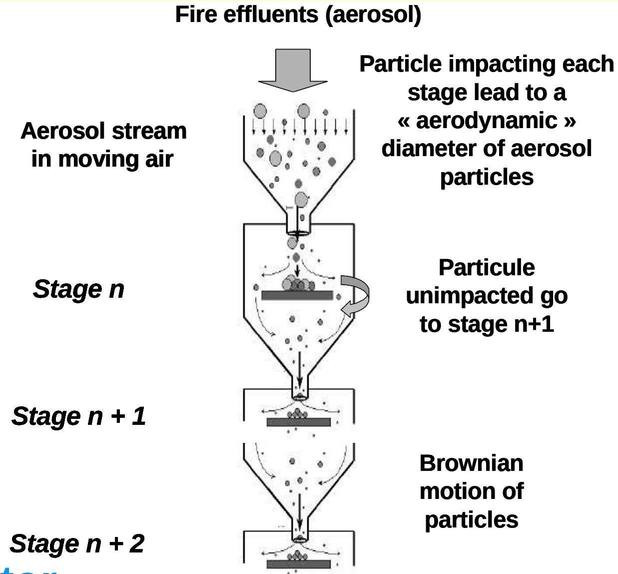
5. Method used to estimate the particle size distribution in fire effluents

FIRE MODEL

Low Pressure Impactor (DLPI) coupled with modified Cone Calorimeter

Stage	D50% [µm]
13	10
12	6.8
11	4.4
10	2.5
9	1.6
8	1.0
7	0.65
6	0.40
5	0.26
4	0.17
3	0.108
2	0.06
1	0.030
Filter	~ 0

Heated Impactor



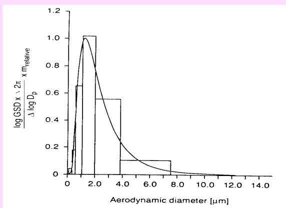
Multi-stage cascade impactor system

PARTICLE ANALYSIS

Mass distribution

(Mass Median Aerodynamical)

Mass distribution analysis (example of histogram of particle size distribution)



Selection of aerosols size < 30 nm

< 100 nm

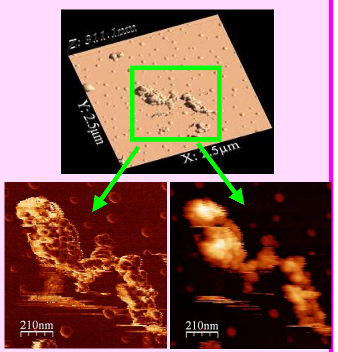
Chemical analysis

(X-Ray)

Morphology analysis

(Definition of collection substrate)

Morphology analysis using Atomic Force Microscope (AFM)



Phase and topographic images of nanometric morphology of an aerosol

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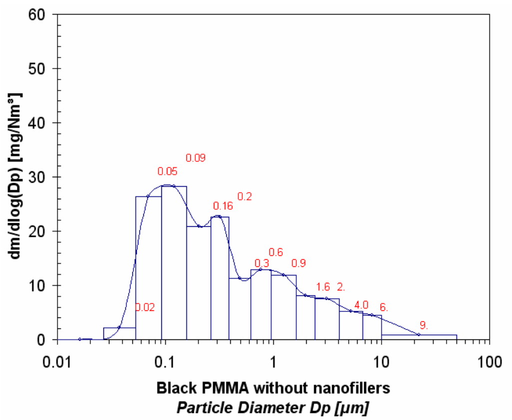
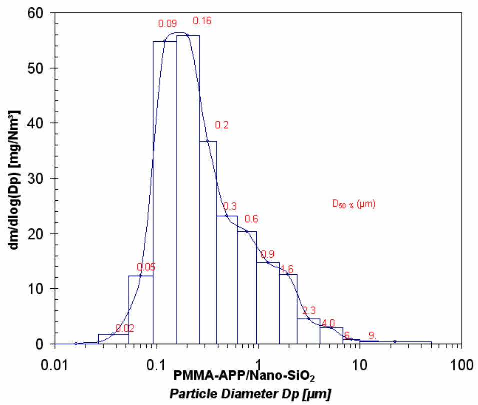
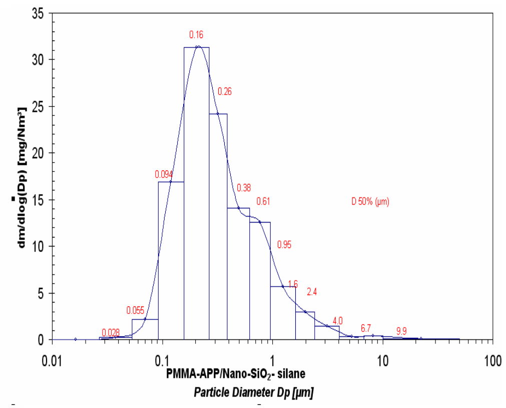
6. Preliminary Results

- Particle size analysis by cascade impactor experiment

<table>
<tr><th></th><th>PMMA
Without nanofillers</th><th>PMMA/APP+Nano-SiO_2</th><th>PMMA/APP+Nano-SiO_2-silane</th></tr>
<tr><td rowspan="2">Median aerodynamic diameter of the aerosol

(µm)</td><td rowspan="2">0.094

One population
</td><td>0.094 and 0.16
(Two populations)</td><td>0.16 and 0.26
(Two populations)</td></tr>
<tr><td></td><td></td></tr>
</table>

✓ Surface treatment of the nanofiller play an important role on particle size distribution and nano-aerosol production

Chemical analysis by X- Ray Fluorescence of the soot obtained after combustion of the mixtures

- ✓ **PVDF membrane were used**

	New filter (blank)	PMMA/APP/ SiO_2-silane	PMMA/APP/ SiO_2	PMMA without nanofillers
Filters (aerosol sampling)	not detected	traces	not detected	not detected
Silica Residues (%)	-	18.5	25	not detected

- ✓ **Presence of nanofillers in aerosol after combustion is not evident, depending on the surface treatment of the filler.**

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- **Microscopic images of the soot obtained after combustion of the mixture PMMA/APP+Nano-SiO_2-silane**
  - ✓ **Glass slip provides an ideal surface, having a very reduced background topographical noise.**
  - ✓ **Stage number 1 of the cascade impactor having a cut-off-diameter of 30 nm.**

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AFM images of soot obtained after combustion of the PMMA/APP+Nano-SiO_2-silane (stage impactor number 1)

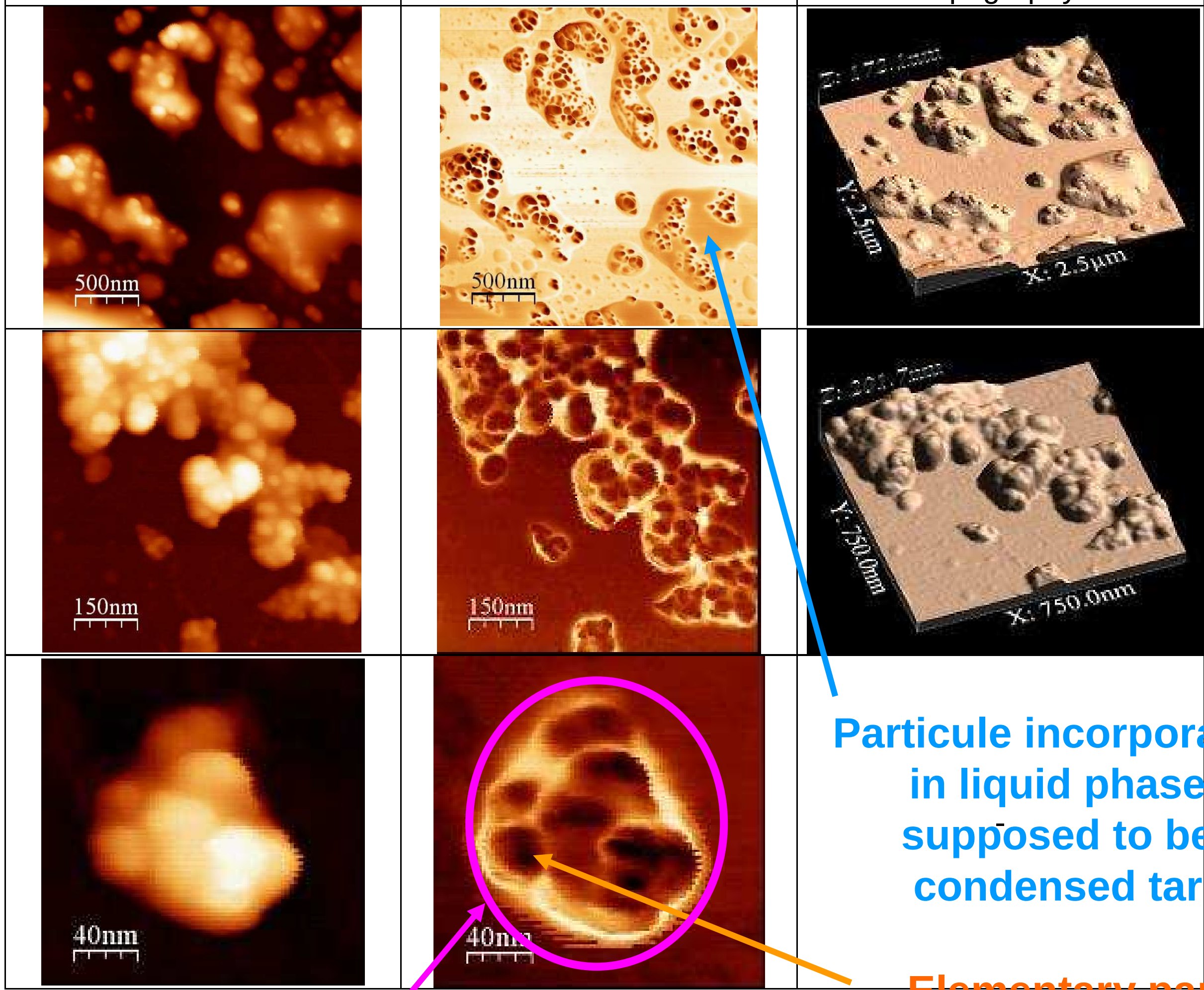
✓ Morphology of nano-aerosol that is different from usual fractal form of carbon aerosols and similar to a more compact structure.

✓ One hypothesis explaining this morphology is the presence of silane around nanoparticles of silica that have fixed carbon core on the surface to create a compact structure.

✓ Large amount of Tar is imaging.

AFM images of soot obtained after combustion of the PMMA/APP+Nano-SiO_2-silane (stage impactor number 1)

Topography image	Phase image	3D representation of the topography

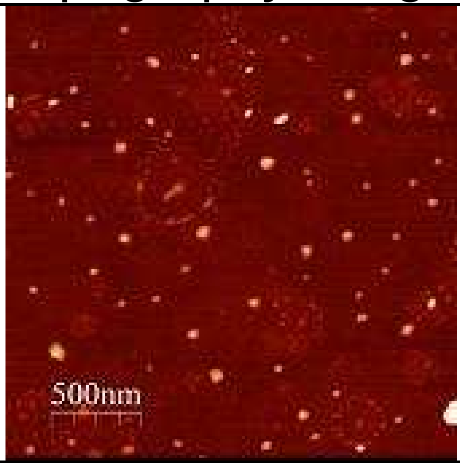
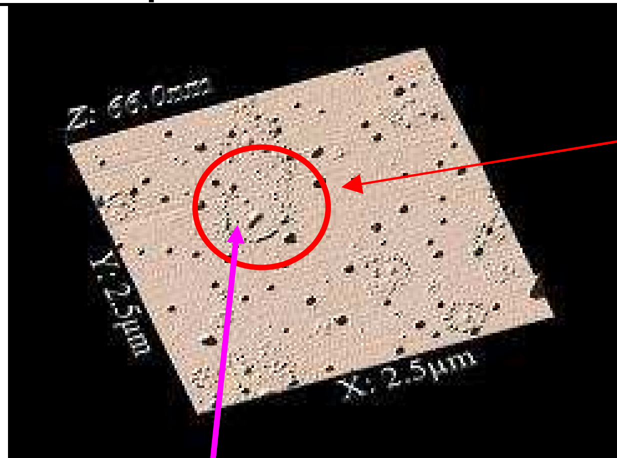


Particule incorporated in liquid phase supposed to be condensed tar

Agglomerated structure

Elementary particle with a median diameter size of 40 nm

AFM images of the soot obtained after combustion of the mixture PMMA-APP / nano- SiO_2 - silane surface treatment (stage impactor number 9 – D50% : 1.60 µm)

Topography image	3D representation of the topography
	 Structure of supposed evaporation

Central particle surrounded by smaller ones

✓ **Evaporation is due to the temperature and the different pressures of each stages of the cascade impactor.**

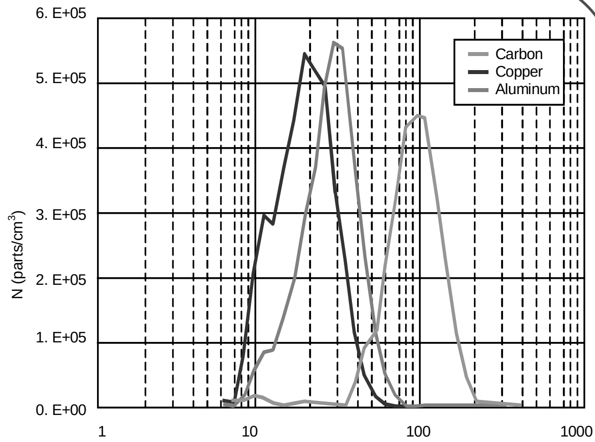
7. Conclusion

- **Preliminary results can be summarized as follow :**
  - ✓ **Fire behaviour is clearly influenced by the presence of nanofillers.**
  - ✓ **Particle size distribution are significantly different comparing to an aerosol realised by black PMMA without nanofillers, and those obtained on the same matrix coupled with silica, or silica-silane nanofillers.**
    - **In the case of PMMA containing nanofillers, amounts of particles produced is greater, and enriched in particles in the range 0.094 to 0.26 µm (aerodynamic diameter).**
  - ✓ **X-ray fluorescence analyses of residues and sample of soot tends to demonstrate that nanofillers are not systematically present in fire effluents, depending on the surface treatment (the addition of silane) in the formula for example.**
  - ✓ **Particles imaged during this study using AFM highlight the complexity of the aerosol, which involves not only particles but large amount of tars and post-deposition coagulation phenomenon. This brings information on the fact that sampling conditions are important, having an influence on measurements.**

8. Metrology of validation of an aerosol measurement

Spark discharge generator

✓ **Generator is able to produce a nanostructured aerosol of particles by electrical discharge between two electrodes**



Nano-aerosol generator with calibration in Diameter and Morphology

Granulometric distribution N(dm) for different chemical nature of electrodes

Validation of the particles measurement

✓ Generator + cascade impactor

⇨ Aerodynamic diameter

✓ Generator + SMPS (Scanning Mobility Particle Sizer)

⇨ Electrical mobility diameter -> Number of particles -> Mass

Comparison in term of granulometric distribution

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9. Further works

- **Comparison with other technique**

Fire Model

(Cone Calorimeter)

Cascade impactor
(DLPI)

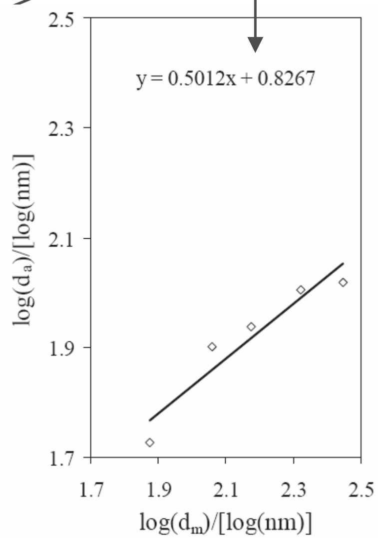
DLPI, brings number size distribution in terms of aerodynamical diameter

SPMS (**Scanning Mobility Particle Sizer**)

+ CPC (**Condensation Particle Counter**)

SPMS produces monodispersed aerosol in terms of electrical mobility diameter

Relationship between log (D_a) and log (D_m)



Morphology ← The slope of this relationship is proportional to the fractal dimension

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