FROM RESEARCH TO INDUSTRY

nanoSAFE'16

LASER INDUCED BREAKDOWN SPECTROSCOPY, A METHOD TO MEASURE AND CHARACTERIZE THE PERSONAL EXPOSURE TO AIRBORNE PARTICLES

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Toxicologie Programme Transversal

NanoSciences Programme transversal

PNS PLATE-FORME NANO SÉCURITÉ

OUTLINE

General information

- Context
- Project goal
- Principle

LIBS information

- Principle
- Interest

Results

- Qualitative analysis
- Quantitative analysis

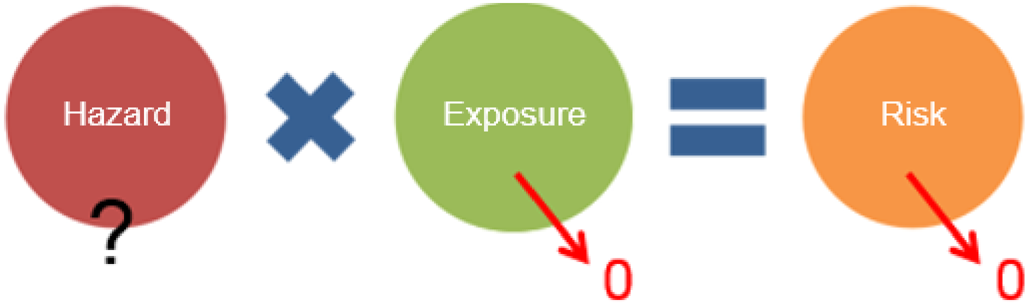
Conclusion & Perspectives

GENERAL INFORMATION

Context

- Increase of utilization and production of nanomaterials in research and industry

- Discussions on potential health impacts caused by inhalation of particles
  - Risks?



- Current scarcity of hazard data in nanotoxicology
  - Particle capacity to reach and deposit in the deep alveolar regions of lungs
  - Exposure can be hazardous
  - Studies realized on cells or on animals but complicate to extrapolate to human

- To assess the efficiency of risk management measure, it is necessary to determine the personal exposure

GENERAL INFORMATION

Project goal

- Developing a global solution to evaluate the personal exposure to particles
- Validate a collection device based on electrostatic precipitation principle, coupled with on-line and off-line particles analysis
  - User friendly
  - Sampler (off-line analysis)
  - Monitor (on-line analysis)
  - In a broad range of size particles

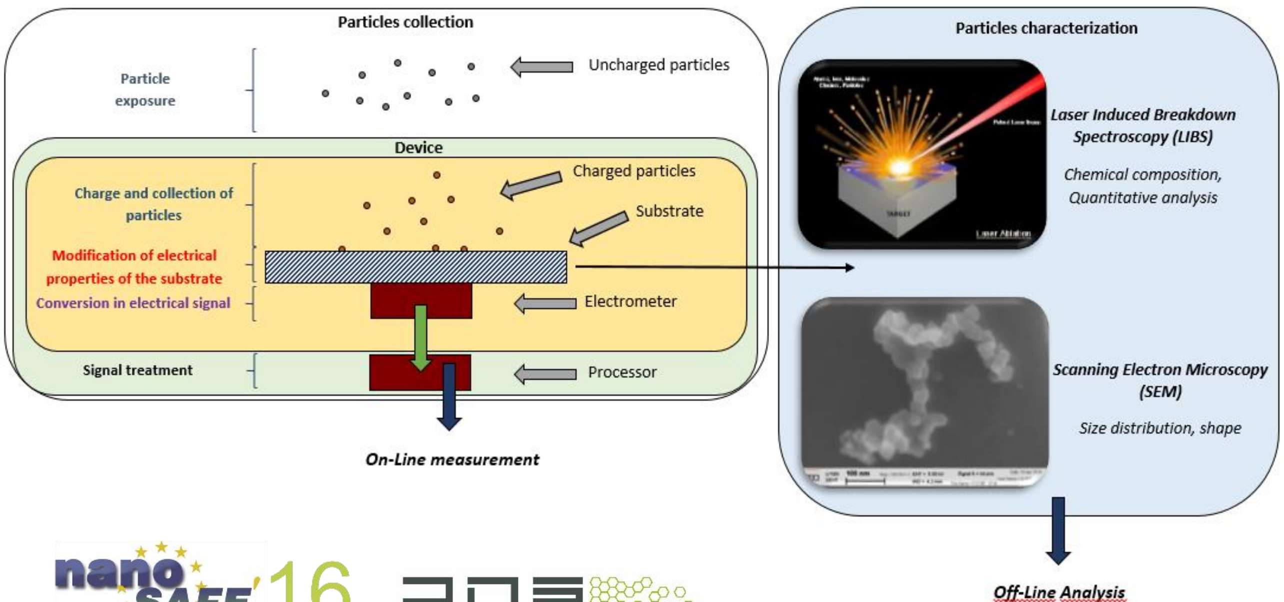
Electrostatic precipitator developed

- Wide scope
  - Environmental, Health and Safety issues
  - Worker protection
  - Inhalation toxicology

GENERAL INFORMATION

Principle

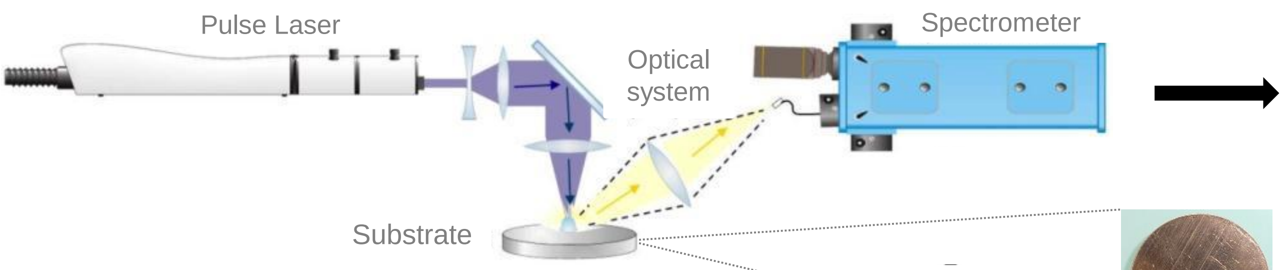
- Five stages
  - Airborne particles capture
  - Particles charge by two mechanisms (field and diffusion charging)
  - Particles collection on a metallic substrate by **size-dependent zone**
  - On line measurement of concentration
  - Off line analysis of chemical composition, spatially resolved by Laser Induced Breakdown Spectroscopy (LIBS)

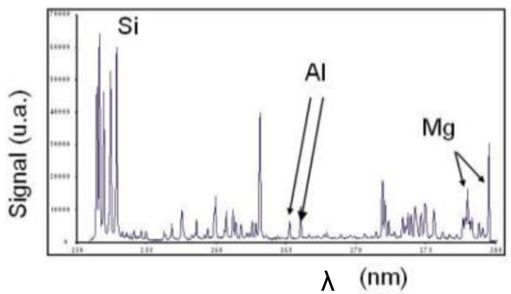


More information about device functioning in PS2-9, 8th November

LIBS INFORMATION

Principle





20 mm diameter Copper substrate

1 - Laser shot at the sample
2 - Plasma creation
3 - Plasma species excitation
4 - Radiation emissions, characteristic of chemical composition

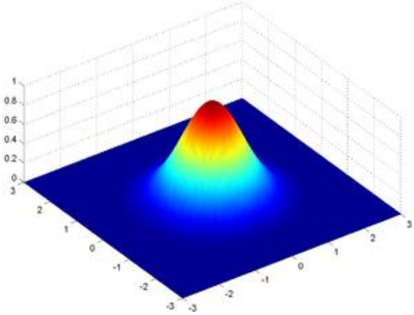
- Advantages
  - No sample preparation
  - Fast analysis
  - Spatially resolved, one spot ≈ 100 - 250 µm
- Disadvantages
  - Reproducibility and accuracy discussed
  - Destructive analysis

Interest of LIBS for this project :

Spatial resolution
Analysis for each size-dependent zones at the substrate surface

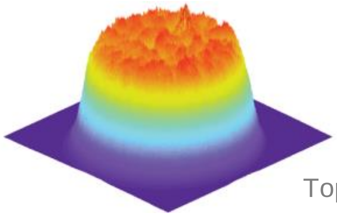
Fast analysis

Laser beam adjustment



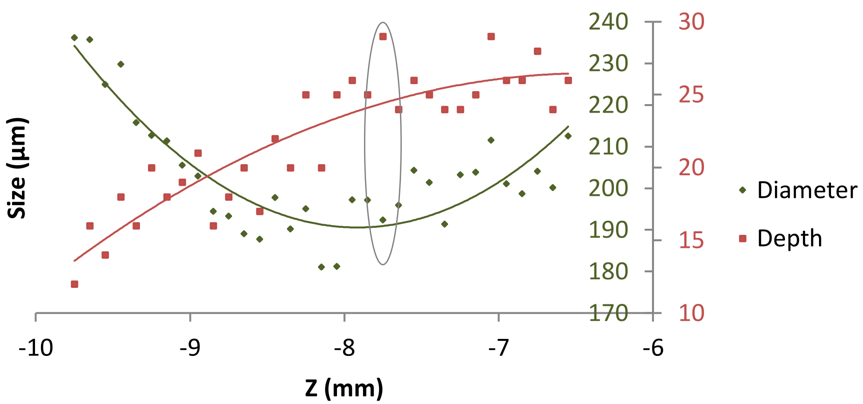
Gaussian beam

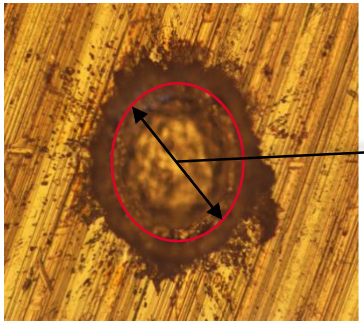
- Beam created by laser is a Gaussian beam
- Top Hat beam : Homogeneous beam
  - Important to create a homogeneous crater
  - Important to provide the same energy at any point of the substrate



Top Hat beam

- Necessity to adjustment of optical system
  - Distance sample – mirror (Z)
  - Diameter and depth measurement by microscopy
  - Max depth for min diameter



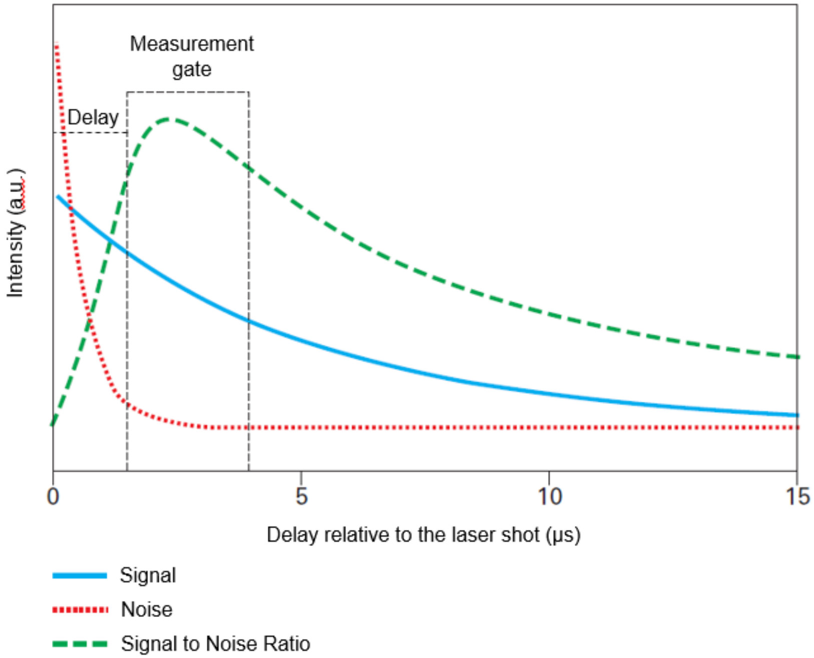


Typical crater

Spatial resolution
Diameter : 192 µm
Depth : 29 µm

RESULTS

Signal optimization – SNR improvement

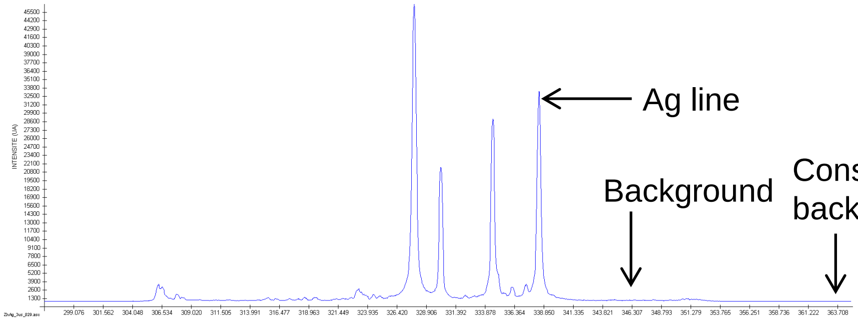


- Delay optimization
  - Delay : time between the end of laser shot and the signal acquisition
- 50 ns ≤ Delay < some µs
- If Delay ↑, signal intensity ↓

- First selection of five metallic materials for substrate – Cu, Ti, Al, Zn, Ni
- Selection of five particulate materials for deposit – TiO_2, ZnO, SiO_2, Ag, Al_2O_3
- Choice of 16 couples “substrate / particles” without spectral interferences from databases

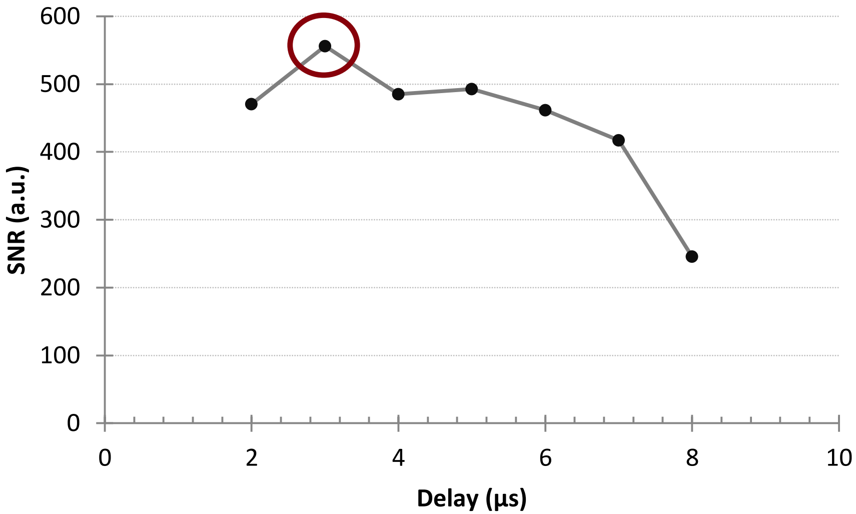
Signal optimization – SNR improvement

Ag deposit on Zn substrate



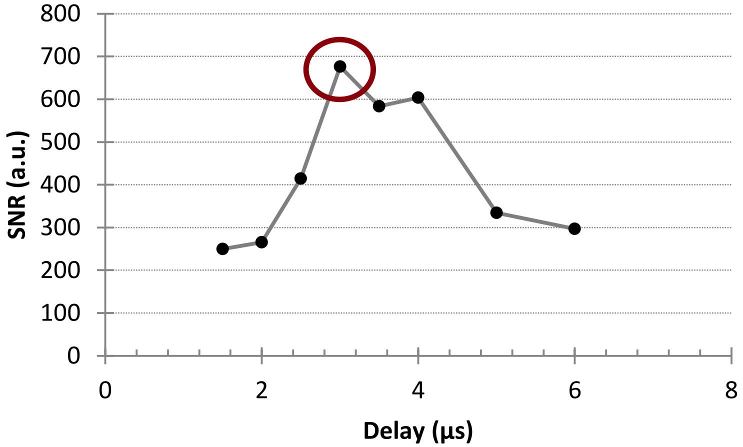
- Ag : 338.3 nm
- Background : 346.7 nm
- Electronic background 825 a.u.

- Optimal delay : 3 µs
- SNR max : 555 a.u.



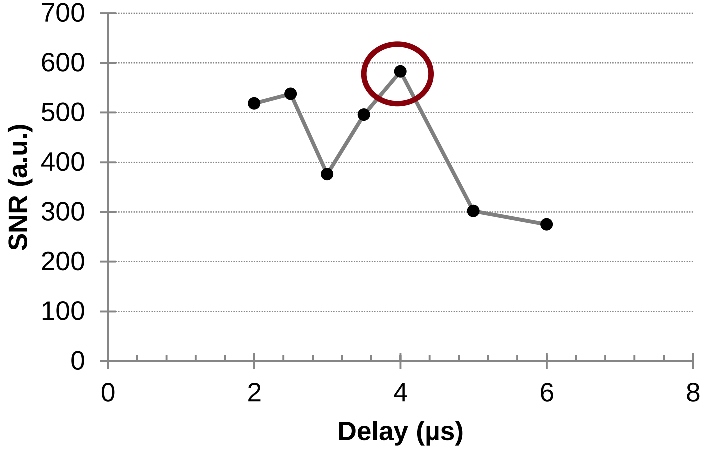
Signal optimization – SNR improvement

Ag deposit on Cu substrate



- Ag : 338.3 nm
- Optimal delay : 3 µs
- SNR max : 676 a.u.

Ag deposit on Al substrate



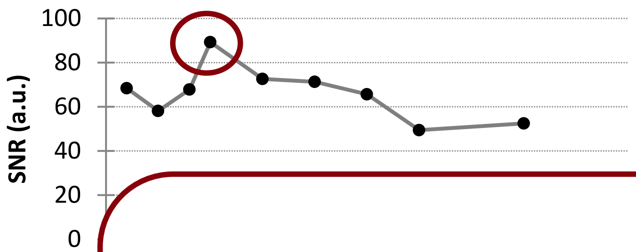
- Ag : 338.3 nm
- Optimal delay : 4 µs
- SNR max : 582 a.u.

→ Optimal delay for Ag deposit : **3 - 4 µs**, for three different substrates

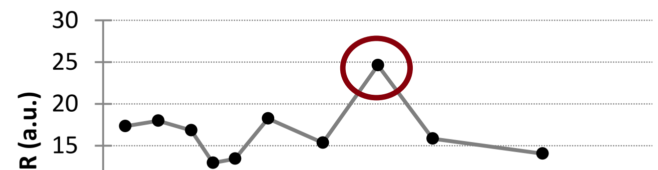
RESULTS

Signal optimization – SNR improvement

SiO_2 deposit on Cu substrate



SiO_2 deposit on Ni substrate

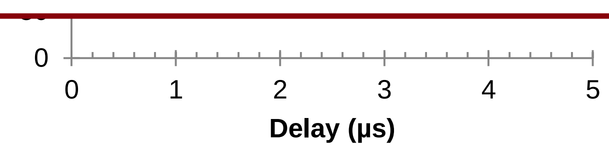


- Optir
- SNR

Determination of optimal delay necessary for each new sample (deposit / substrate)

Optimal delay reusable for same samples (deposit / substrate)

2.5 µs
.u.



- Optimal delay : 3 µs
- SNR max : 205 a.u.

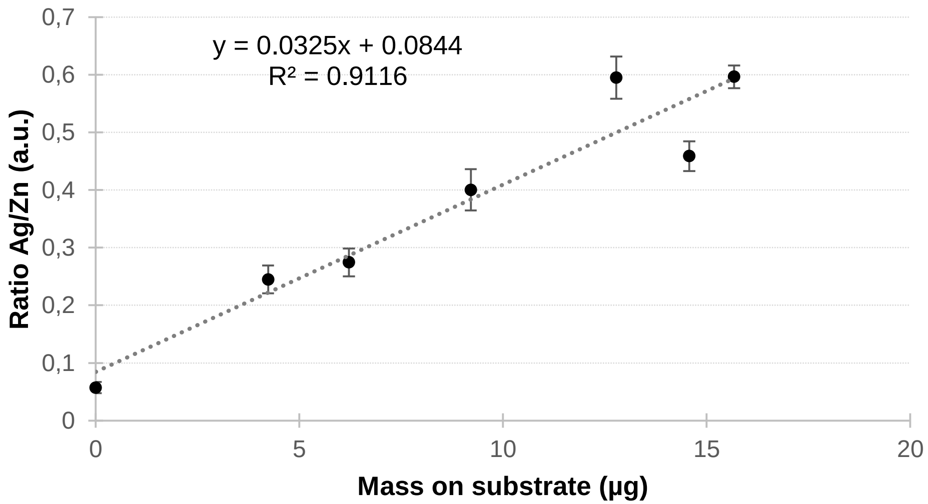
→ SiO_2 three different substrates / three different optimal delays

Calibration – Ag example

- Realization of controlled deposits (0.25, 0.5, 1, 2, 2.5 & 3 hours)
  - Ag particles
  - On Cu substrate and Zn substrate
- First quantification of deposit by XRF analysis using existing calibration
- Calibration by LIBS
  - Normalization
  - Determination $I_{Ag}/I_{Substrate}$
- Determination of LOD and LOQ
  - LOD 3σ/a
  - LOQ 10σ/a

Calibration – Ag example

Ag deposit on Zn substrate



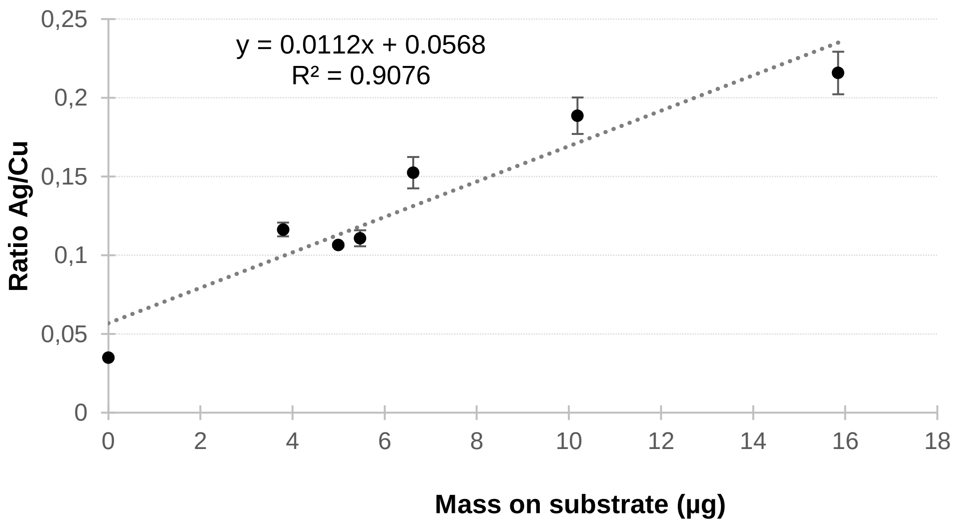
- LOD $3\sigma/a$ = 1.8 µg
- LOQ $10\sigma/a$ = 6 µg
- Substrate area = 3.14 cm²
- LOD = 0.57 µg/cm²
- LOQ = 1.9 µg/cm²

Estimation of airborne concentration :
During **8h** sampling at **1L/min**, it is possible **to detect** a particle aerosol of **3.9 µg/m³** and **to quantify** an aerosol of **12.5 µg/m³**

RESULTS

Calibration – Ag example

Ag deposit on Cu substrate



- LOD 3σ/a = 0.28 µg
- LOQ 10σ/a = 0.93 µg

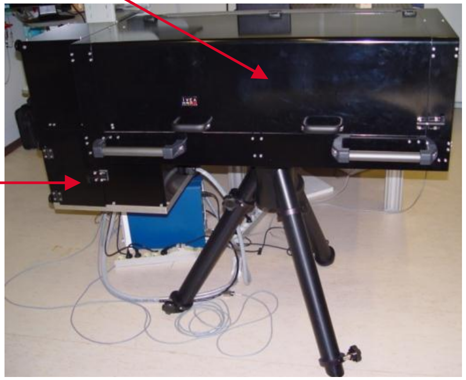
- Substrate area = 3.14 cm²

- LOD = 0.089 µg/cm²
- LOQ = 0.298 µg/cm²

Estimation of airborne concentration :
During **8h** sampling at **1L/min**, it is possible **to detect** a particle aerosol of **0.6 µg/m³** and **to quantify** an aerosol of **1.9 µg/m³**

CONCLUSIONS

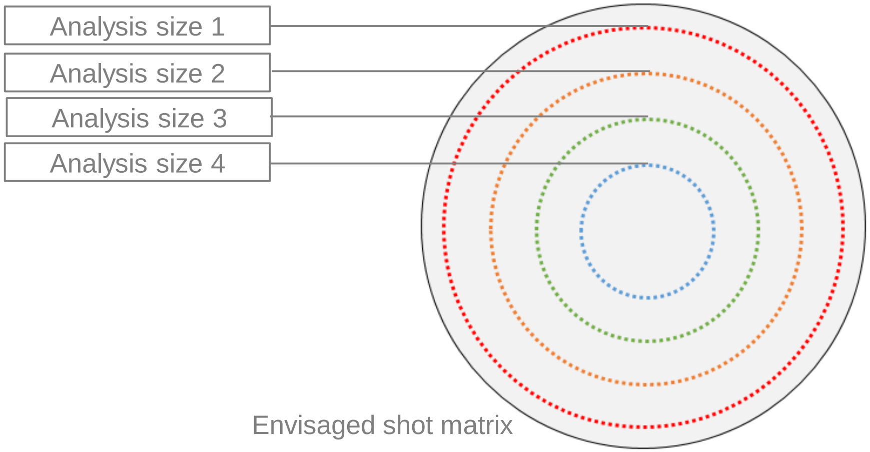
- Determination of the spatial resolution
  - Top Hat beam
  - ≈ 200 µm
- Identification of the different noise sources
  - Electronic noise (825 a.u.)
  - Shot noise (below 1500 a.u.)
- SNR optimization by the delay modification
  - Convergence for some samples but…
  - For measurement quality, necessity to do this optimization for each new sample
- Studies of the shot energy, the substrate materials, the substrate rugosity, …
  - Determination of reference material for substrate (Cu or Zn)
- Calibration and determination of LOD and LOQ
  - ≈ µg/m^3



LIBS system

PERSPECTIVES

- Final precipitator permits to collect particles along concentric circles with a size dependent radius
  - A radius = A particle size
- With LIBS, possibility to shot along concentric circles
  - A LIBS analysis by radius, so by size
  - Quantification and chemical composition determination for each size
- Provide a global analysis of the deposit
  - Size distribution
  - Chemical composition
- Extrapolation to the aerosol



Envisaged shot matrix

Thank you for your attention !

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PLATE-FORME NANO SÉCURITÉ

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