

# Single Particle -ICP-MS fundamentals

**JAVIER JIMÉNEZ LAMANA**



**IPREM**

Institut des sciences analytiques  
et de physico-chimie  
pour l'environnement et les matériaux



Co-funded by the Horizon 2020 Framework Programme of the European Union  
under the grant N° 952306



# Nanomaterials and nanotechnology

- Nanomaterials and nanoparticles used in an increasing number of industrial and consumer products
- Size-related special properties: **reactivity, electrical and optical properties**



# Nanomaterials and nanotechnology

## Which are the consequences?

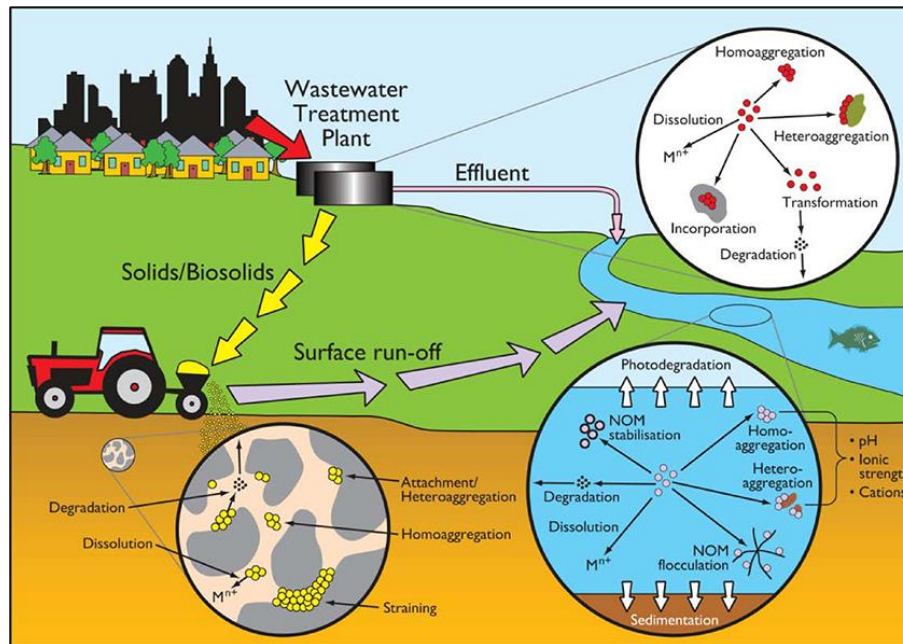
Increasingly used of nanomaterials in different fields



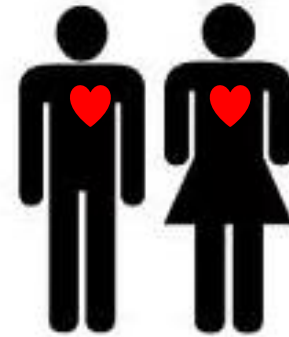
NPs Release into the environment



Interaction with environment and human being



# Nanomaterials and nanotechnology



**REGULATORY APPROACHES** that guarantee the sustainability of **Nanotechnology**

Implementation of  
regulatory approaches

Information related with detection,  
characterization and quantification  
of nanomaterials

Use and development of  
new analytical  
methodologies

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# Nanomaterials and nanotechnology

L 275/38

EN

Official Journal of the European Union

20.10.2011



## RECOMMENDATIONS

### COMMISSION RECOMMENDATION

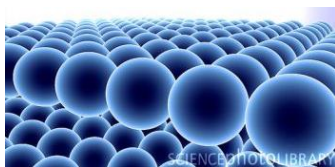
of 18 October 2011

on the definition of nanomaterial

(Text with EEA relevance)

(2011/696/EU)

'Nanomaterial' means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm.

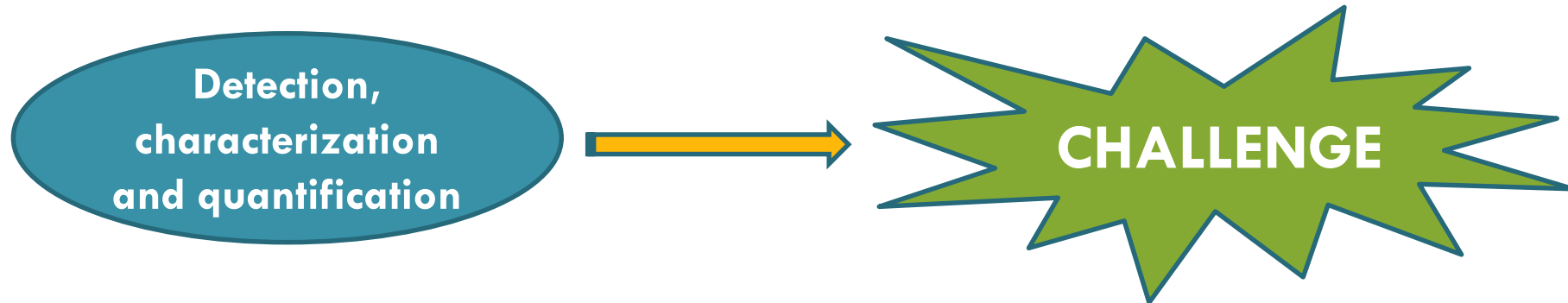


**length range approximately from 1 - 100 nm**

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# Analysis of nanomaterials



- NPs present in environmentally relevant concentrations: ppb or ppt
- Huge amount of information needed:
  - i. Detect the presence of NPs,
  - ii. Identify the type of NPs (chemical composition)
  - iii. NP characterization (size, shape, surface characteristics...)
  - iv. Number concentrations
  - v. Identify new species

**Use of (new) specific and sensitive methods of analysis**

# Analysis of nanomaterials

## Analytical techniques

### - Ensemble techniques

- Dynamic light scattering (DLS)
- Small-Angle X-ray Scattering (SAXS)
- X-Ray Diffraction (XRD)

### - Counting techniques

- Electron microscopy (EM)
- Nanoparticle tracking analysis (NTA)
- Atomic Force microscopy (AFM)

### - Separation techniques

- Hydrodynamic chromatography (HDC)
- Size exclusion chromatography (SEC)
- Field Flow Fractionation (FFF)

# Analysis of nanomaterials

## Analytical techniques

### Ensemble techniques

- ❑ **Dynamic Light Scattering (DLS)**
- ❑ **Small-Angle X-ray Scattering (SAXS)**
- ❑ **X-Ray Diffraction (XRD)**

✓ **Information about number-based size distributions**

× **Only reliable for nearly monodisperse particles**



# Analysis of nanomaterials

## Analytical techniques

### Counting techniques

- Electron Microscopy (EM)
- Atomic Force Microscopy (AFM)
- Nanoparticle Tracking Analysis (NTA)

✓ Analysis particle by particle

× High number of measurements must be performed

# Analysis of nanomaterials

## Analytical techniques

### Separation techniques

- Hydrodynamic chromatography (HDC)
- Size exclusion chromatography (SEC)
- Field-Flow Fractionation (FFF)

✓ Separation into monodisperse fractions

× Optimization for each type of sample needed

# Analysis of nanomaterials

## Analytical techniques

### Single Particle Inductively coupled plasma mass spectrometry (SP-ICP-MS)

Different types of information that can be obtained:

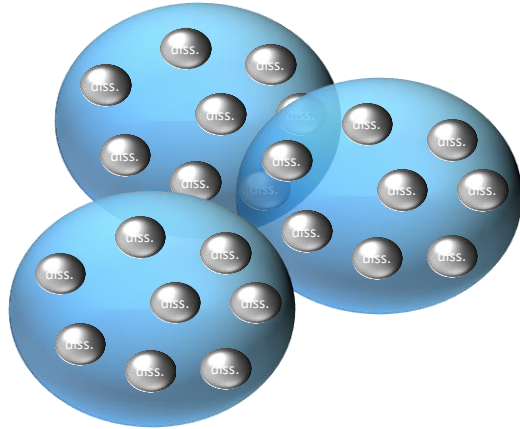
- The presence of the element in its dissolved and nanoparticulate form
- The size distribution or the mass distribution per nanoparticle
- The mass concentration of the dissolved element and nanoparticles
- The number concentration of nanoparticles



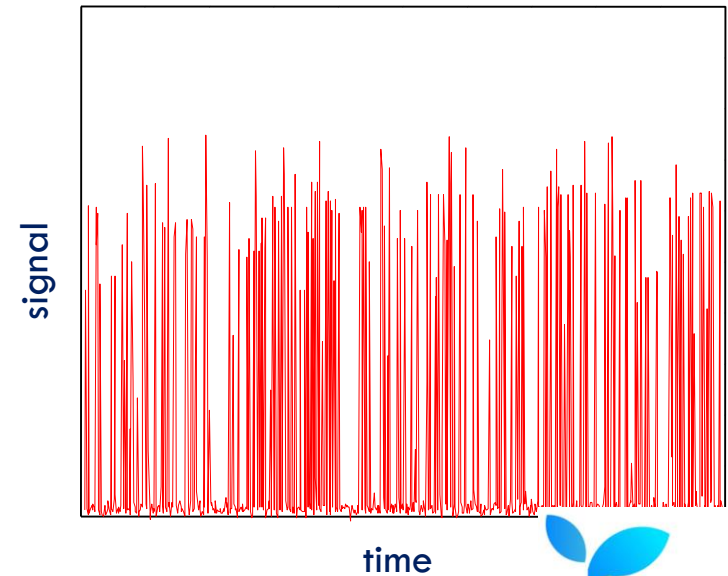
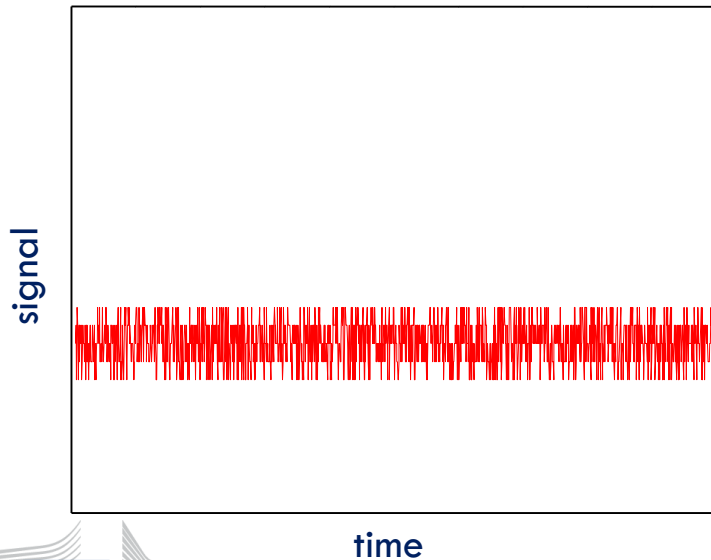
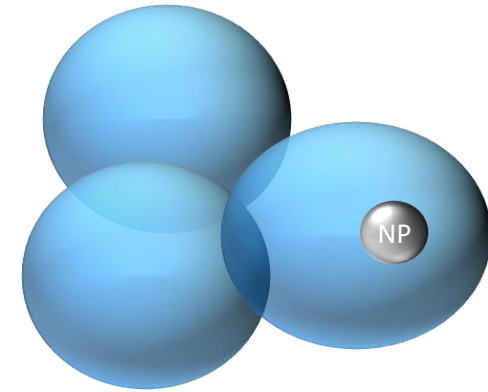
**Ultra trace metal analysis: Limit of detection at the level of ATTOGRAM:  $10^{-18}$  g**

# Single Particle ICP-MS: principals and theory

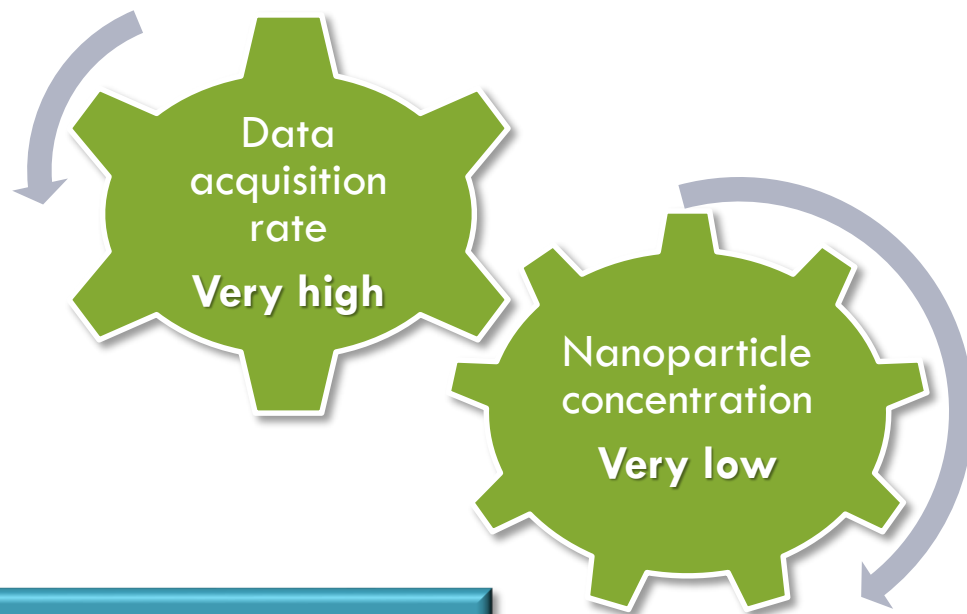
## Dissolved form



## Nanoparticulated form



# Single Particle ICP-MS: principals and theory



$< 10 \text{ ms/ reading } (> 100\text{Hz})$

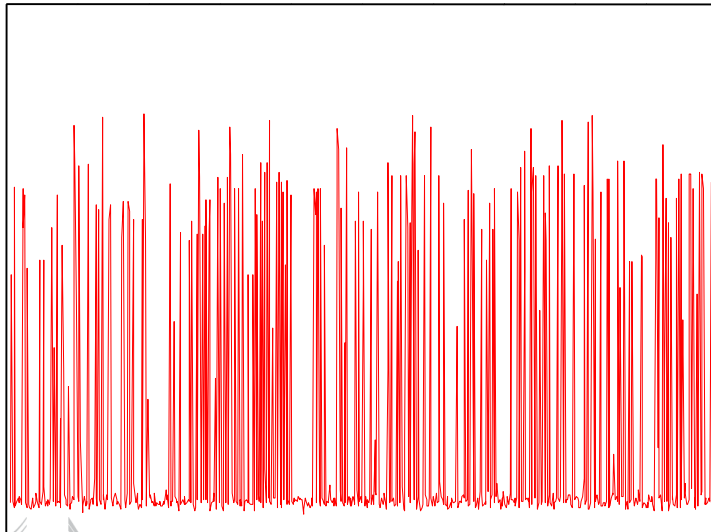
$\leq 10^8 \text{ nanoparticles L}^{-1}$

# Single Particle ICP-MS: principals and theory

1 pulse = 1 nanoparticle



←→ number of pulses =  $K$  nanoparticle concentration



pulse intensity =  $K$  atoms per nanoparticle  
=  $K'$  NP mass =  $K''$  NP size

# Evolution of Single Particle ICP-MS

2003

2011

2014

2018

??

Conception  
SP-ICP-MS

1st  
application  
nano

1st  
commercial  
instrument  
dedicated

Characterization

Maturity

## The “Prehistory”:

- Analyse ‘single particle’ mode: 90’s avec ICP-OES
- Applications: analysis of aerosols, suspended particles in air, microparticles and cells

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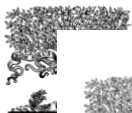


ELSEVI

Collo



ELSE'



ELSI



ELSE'



ELSEVIER

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Analytica Chimica Acta 555 (2006) 263–268

ANALYTICA  
CHIMICA  
ACTA

[www.elsevier.com/locate/aca](http://www.elsevier.com/locate/aca)

## Gold colloid analysis by inductively coupled plasma-mass spectrometry in a single particle mode

C. Degueldre<sup>a,\*</sup>, P.-Y. Favarger<sup>b</sup>, S. Wold<sup>c</sup>

<sup>a</sup> Department Nuclear Energy and Safety, Paul Scherrer Institute, 5232 Villigen-PSI, Switzerland

<sup>b</sup> Institut Forel, University of Geneva, 1290 Versoix, Switzerland

<sup>c</sup> Department of Chemistry, Royal Institute of Technology, Stockholm, Sweden

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JAAS

Cite this: DOI: 10.1039/c0ja00098a

[www.rsc.org/jaas](http://www.rsc.org/jaas)

PAPER

**Selective identification, characterization and determination of dissolved silver(I) and silver nanoparticles based on single particle detection by inductively coupled plasma mass spectrometry**

Francisco Laborda,<sup>\*</sup> Javier Jiménez-Lamana, Eduardo Bolea and Juan R. Castillo

**analytical  
chemistry**

ARTICLE

[pubs.acs.org/ac](http://pubs.acs.org/ac)

**Determining Transport Efficiency for the Purpose of Counting and Sizing Nanoparticles via Single Particle Inductively Coupled Plasma Mass Spectrometry**

Heather E. Pace,<sup>+,§</sup> Nicola J. Rogers,<sup>†</sup> Chad Jarolimek,<sup>†</sup> Victoria A. Coleman,<sup>‡</sup> Christopher P. Higgins,<sup>§</sup> and James F. Ranville<sup>\*,||</sup>

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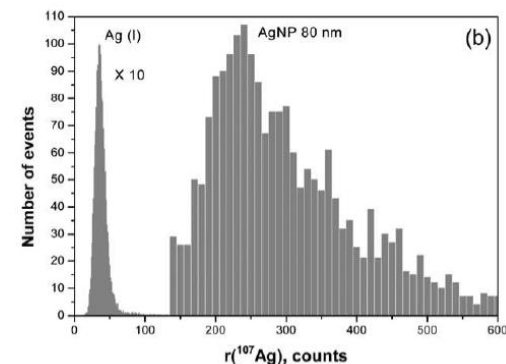
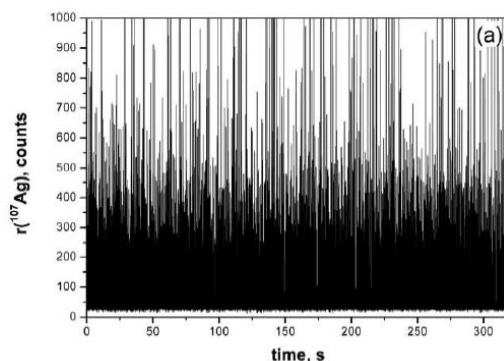
**Redefined the basis of SP-ICP-MS**

Francisco Laborda,\* Javier Jiménez-Lamana, Eduardo Bolea and Juan R. Castillo

Received 30th July 2010, Accepted 17th February 2011

DOI: 10.1039/c0ja00098a

**The first study to demonstrate one of the main advantages of SP-ICP-MS: its capability to determine selectively the analyte in its dissolved and nanoparticulate form in a single analysis and without a previous separation step**



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# Evolution of Single Particle ICP-MS

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PAPER

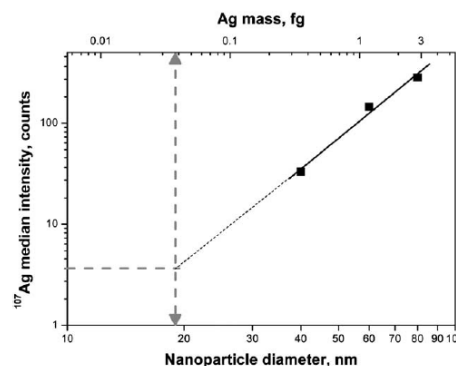
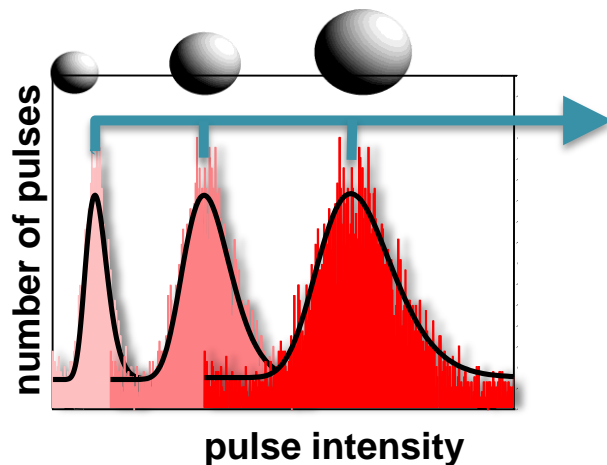
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**Use of standards with the same chemical composition to obtain the size distribution of AgNPs**

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# Evolution of Single Particle ICP-MS

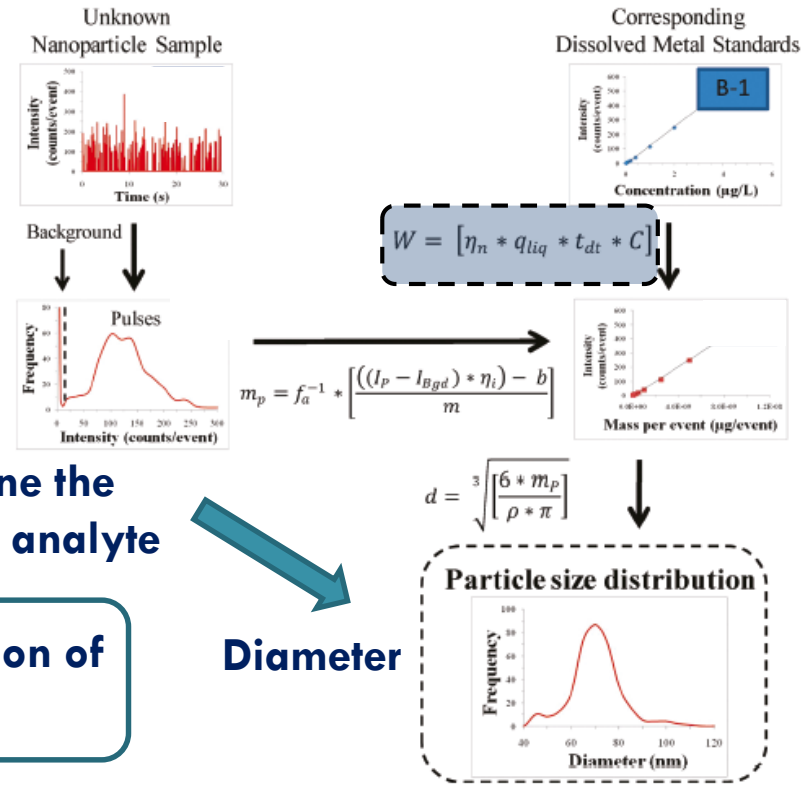


analytical chemistry

ARTICLE  
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## Determining Transport Efficiency for the Purpose of Counting and Sizing Nanoparticles via Single Particle Inductively Coupled Plasma Mass Spectrometry

Heather E. Pace,<sup>†,§</sup> Nicola J. Rogers,<sup>†</sup> Chad Jarolimek,<sup>†</sup> Victoria A. Coleman,<sup>†</sup> Christopher P. Higgins,<sup>§</sup> and James F. Ranville<sup>\*||</sup>



Dissolved Standard

Standard of the same element analysed

Determine the mass of analyte

Diameter

This procedure involves the calculation of **Transport efficiency**



Co-funded by the Horizon 2020 Framework Programme of the European Union under the grant N° 952306



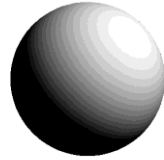
# Evolution of Single Particle ICP-MS



**Transport efficiency ( $\eta_{neb}$ ):** defined as the ratio between the nanoparticles detected with respect to the nanoparticles introduced in the nebulizer

**It requires the use of reference materials: NPs standards well characterized (known size and nanoparticle number concentration) and monodisperse**

Most used from the : U.S National Institute of Standards and Technology



NIST RM 8012 Au 30 nm  
NIST RM 8013 Au 60 nm

But also: Nanocomposix, BBI...



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# Evolution of Single Particle ICP-MS

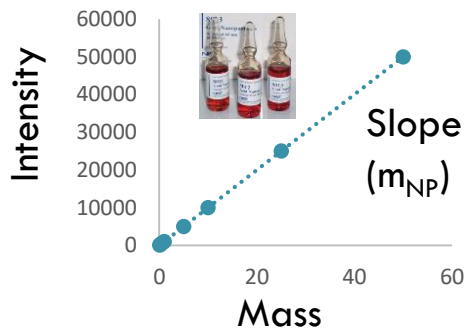


**Transport efficiency ( $\eta_{neb}$ ):** defined as the ratio between the nanoparticles detected with respect to the nanoparticles introduced in the nebulizer

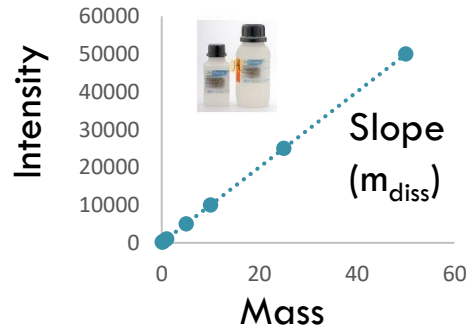
There are 3 methods: waste collection, **particle size** and **particle frequency**

**particle size method**

Calibration curve of reference NPS



Calibration curve of dissolved element



If

- Ionization efficiency of NPs = 100 %
- Atoms dissolved and atoms NP same behaviour in the plasma

$$\eta_{neb} = \frac{m_{diss}}{m_{NP}}$$



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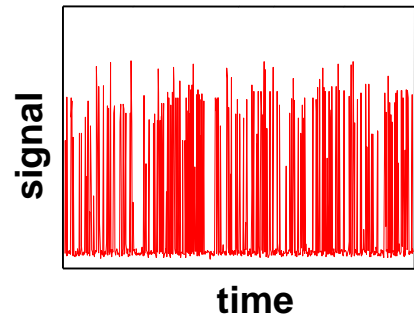
# Evolution of Single Particle ICP-MS



**Transport efficiency ( $\eta_{neb}$ ):** defined as the ratio between the nanoparticles detected with respect to the nanoparticles introduced in the nebulizer

There are 3 methods: waste collection, **particle size** and **particle frequency**

**particle frequency method**



determination of the particle frequency (particle/s) of a suspension of reference NP of known NP number concentration

$$\eta_{neb} = \frac{f_{NP}}{Q_{sam} N_{NP}}$$

$f_{NP}$ : particle frequency  
 $Q_{sam}$ : sample uptake flow  
 $N_{NP}$ : NP number conc



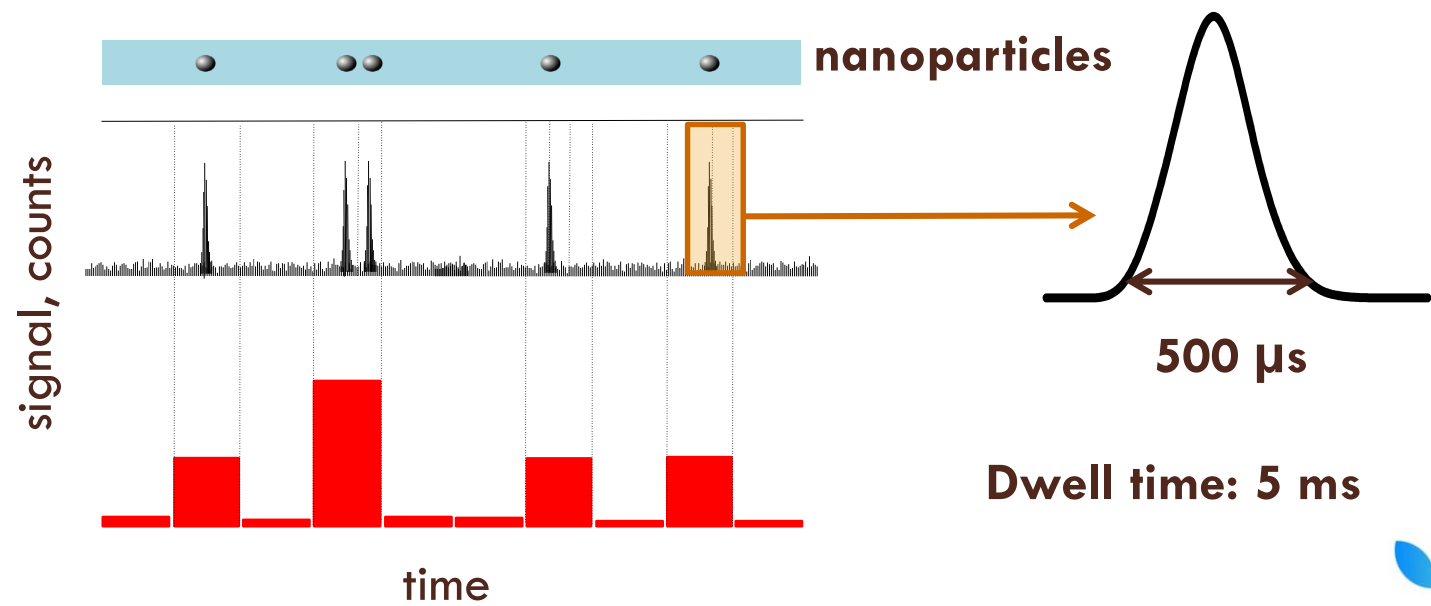
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# Evolution of Single Particle ICP-MS



1 pulse = 1 nanoparticle



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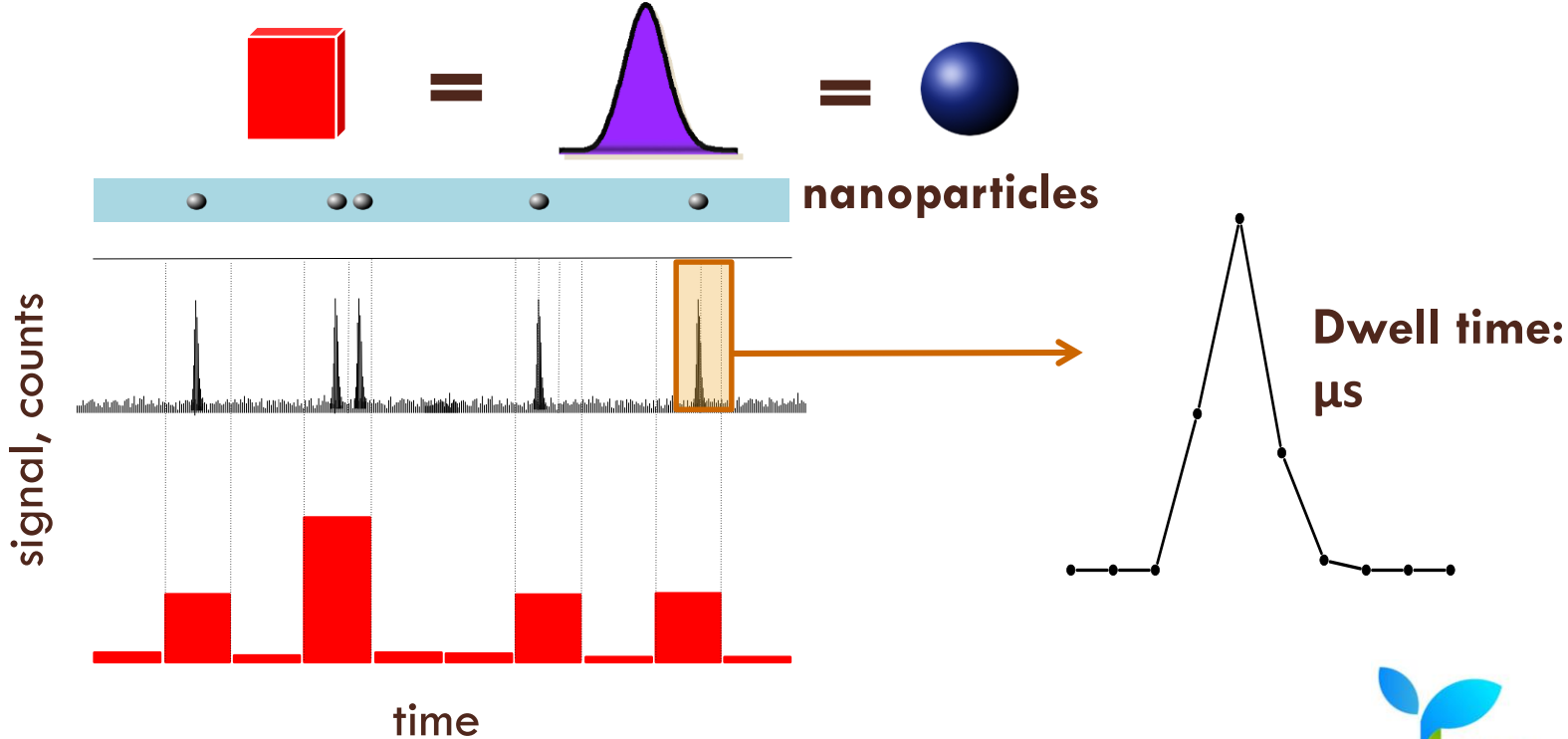




# Evolution of Single Particle ICP-MS



1 pulse = 1 transient signal = 1 nanoparticle



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# Evolution of Single Particle ICP-MS

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Anal Bioanal Chem (2014) 406:3835–3843  
DOI 10.1007/s00216-013-7559-9

RESEARCH PAPER

analytical  
chemistry

Article

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International inter  
of Ag nanoparticle

Thomas P. J. Linsinger • Ruud P

Post hoc Interlaborato  
Measurements of NIST

Antonio R. Montoro Bustos,<sup>\*,†</sup> El

<sup>†</sup>Material Measurement Laboratory, <sup>‡</sup>Inforr  
Bureau Drive, Gaithersburg, Maryland 208

Anal Bioanal Chem (2017) 409:4839–4848  
DOI 10.1007/s00216-017-0427-2

RESEARCH PAPER

Results of an interlaboratory method performance study  
for the size determination and quantification of silver  
nanoparticles in chicken meat by single-particle inductively  
coupled plasma mass spectrometry (sp-ICP-MS)

Stefan Weigel<sup>1,2</sup> • Ruud Peters<sup>1</sup> • Katrin Loeschner<sup>3</sup> • Ringo Grombe<sup>4</sup> •  
Thomas P. J. Linsinger<sup>4</sup>

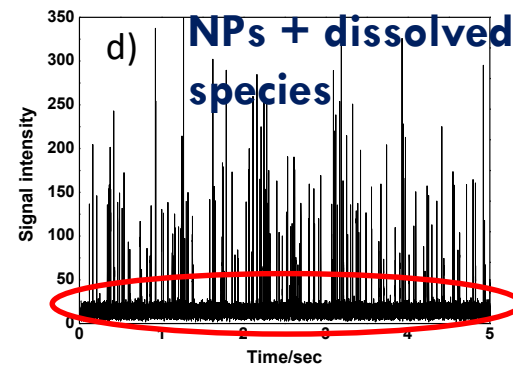
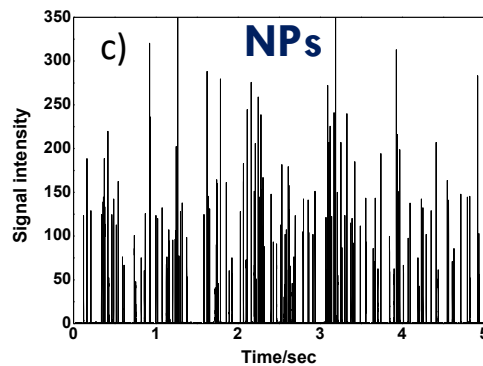
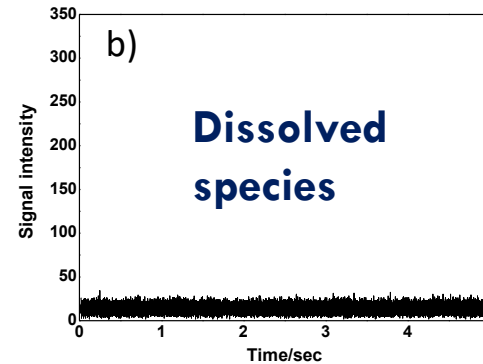
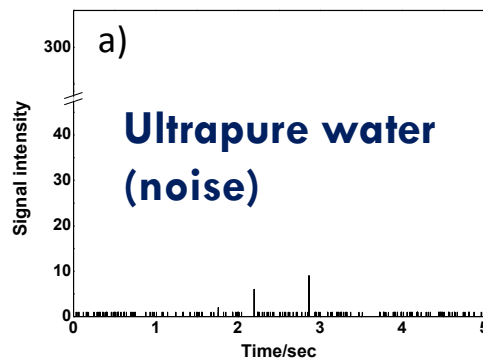


Co-funded by the Horizon 2020 Framework Programme of the European Union  
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# Information obtained by Single Particle ICP-MS

each sample containing nanoparticles is measured by monitoring the element of interest according to the corresponding mass-to-charge ratio ( $m/z$ ) during several seconds or minutes

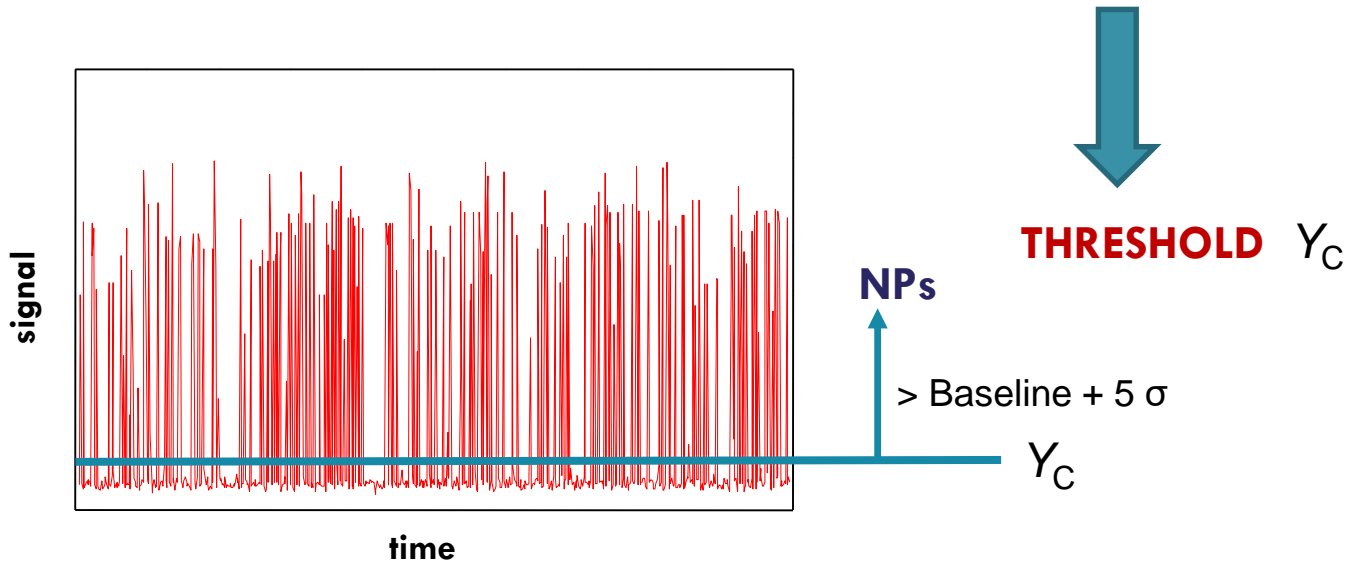


**Very useful for screening purposes!**

Co-funded by the Horizon 2020 Framework Programme of the European Union under the grant N° 952306

# Information obtained by Single Particle ICP-MS

- The frequency of the detected pulses is directly related with the NP concentration in the sample
- We need to discriminate between signals coming from the nanoparticle and signal due to the background/dissolved element



Counting the number of pulses > the threshold



$$C_{NP} = \frac{N}{Q_{sam} \eta_{neb} t_i}$$

$\Sigma$  signal > the threshold



Mass concentration of NPs

< the threshold



Mass concentration of dissolved element

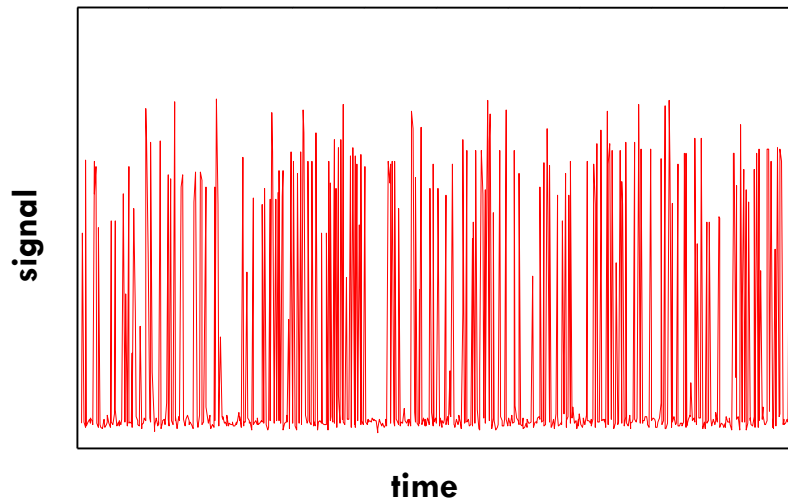
Co-funded by the Horizon 2020 Research and Innovation Programme of the European Union under the grant N° 952306

# Information obtained by Single Particle ICP-MS

Time scan

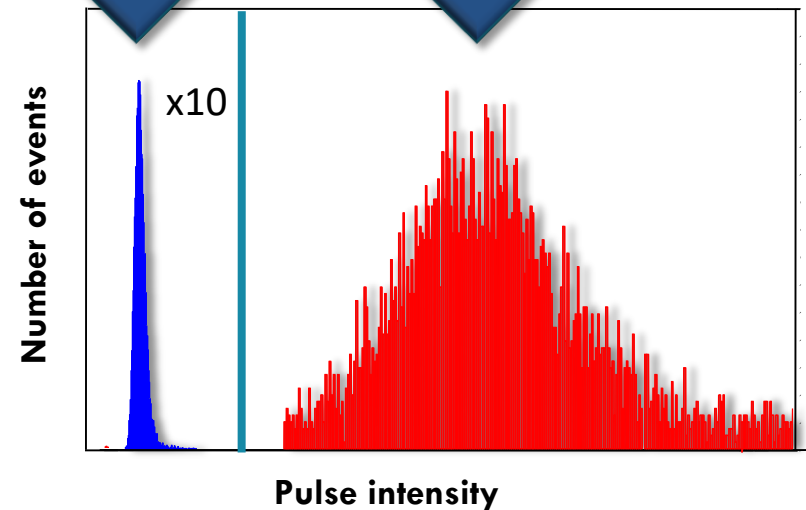


histogram

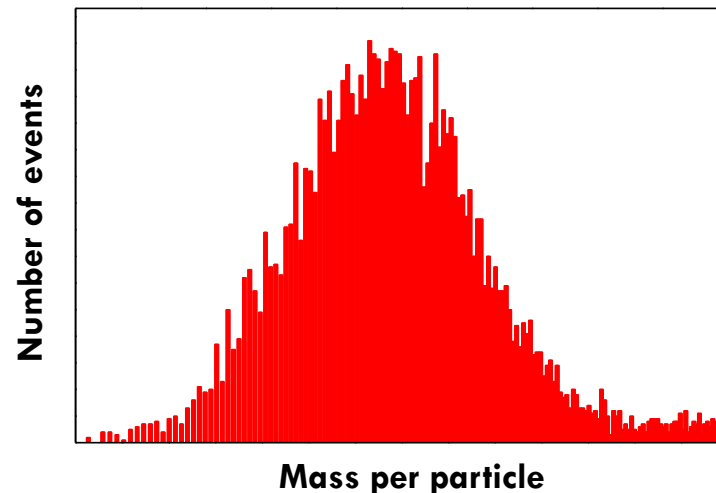
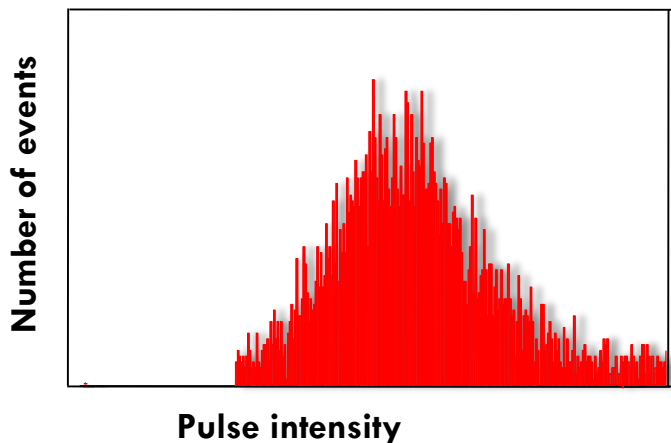


Background/  
Dissolved  
analyte

nanoparticles



# Information obtained by Single Particle ICP-MS



dissolved standard

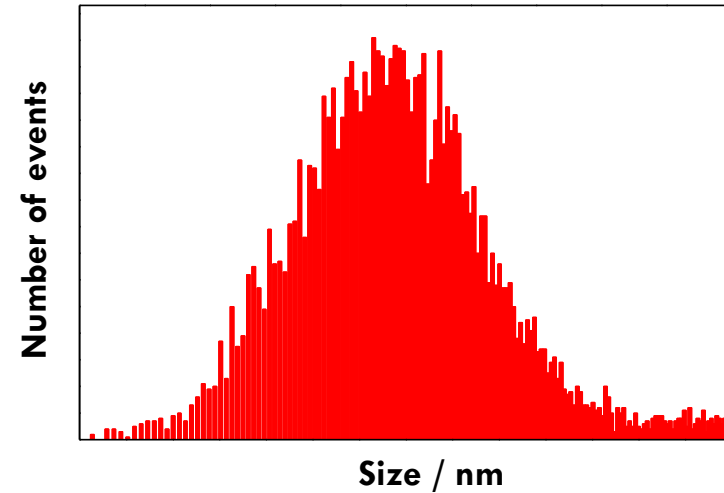
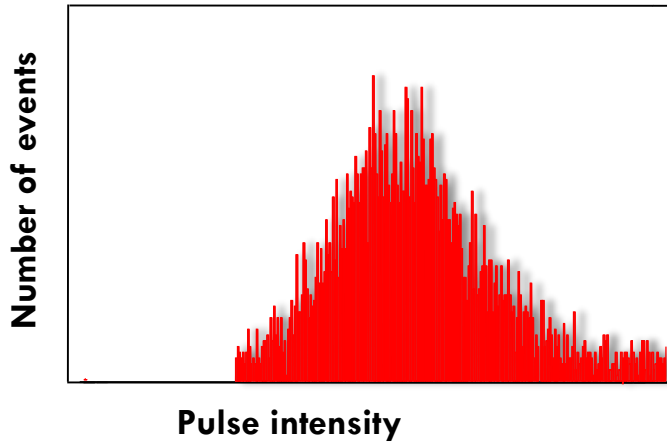
- Transport efficiency
- sample flow rate

**size??**

Particle information:

- Composition
- Density
- Shape

# Information obtained by Single Particle ICP-MS



dissolved  
standard

- Transport efficiency
- sample flow rate

$$d = \sqrt[3]{\frac{6m_{NP}}{\rho\pi}}$$

**size!!**

Particle information:

- Composition
- Density
- Shape

# Single Particle ICP-MS: applications

## Environmental Waters

### Occurrence of AgNPs and dissolved silver in influents and effluents of Waste Water Treatment Plant (WWTP)

- **Influents: 200 ng L<sup>-1</sup> Ag-bearing NPs + 520 ng L<sup>-1</sup> dissolved Ag**
- **Effluents: 100 ng L<sup>-1</sup> Ag-bearing NPs + 60 ng L<sup>-1</sup> dissolved Ag**

Mitrano et al. *Environ. Toxicol. Chem.* 2012

### Determination of anthropogenic nanoparticles in surface waters

- **Ti-bearing nanoparticles found in Old Danube Lake during a 12 months sampling period**
- **Highest concentration in summer (release of TiO<sub>2</sub>NPs from sunscreens)**

Gondikas et al. *Environ. Sci. Technol.* 2014

### Occurrence of silver-, titanium- and cerium-bearing nanoparticles in the Barcelona catchment area

- **The three studied metal containing nanoparticles were detected in the Besòs River Basin**
- **Ce-bearing nanoparticles observed in river waters were related to the natural occurrence of the mineral Monazite (by monitoring the Ce/La ratio)**

Sanchis et al. *Environ. Sci. Technol.* 2020



# Single Particle ICP-MS: applications

## Plants uptake

### Interaction of AuNPs with tomato plants

- **Uptake of intact 40 nm AuNPs**

Dan et al. *Environ. Sci. Technol.* 2015

### Uptake of PdNPs, CeO<sub>2</sub>NPs and TiO<sub>2</sub> NPs by edible plants

- **Preferential uptake of smaller NPs**

Kinska et al. *Sci. Total Environ.* 2018

Wojcieszek et al. *Sci. Total Environ.* 2019

Wojcieszek et al. *Front. Environ. Sci.* 2020

### Accumulation of CeO<sub>2</sub>NPs in cucumber, tomato, soybean, and pumpkin

- **Presence of dissolved Ce and particulate Ce in all plant tissues**
- **This transformation is thought to happen at the root surfaces**

Dan et al. *Anal. Bioanal. Chem.* 2016

Co-funded by the Horizon 2020 Framework Programme of the European Union under the grant N° 952306



# Single Particle ICP-MS: applications

## Exposed organisms

### Quantification of AgNPs and dissolved Ag in *Daphnia magna* hemolymph after exposure

- Concentrations of both silver forms in the hemolymph exceeded the initial AgNPs concentration
- Confirmation of accumulation during filter feeding

Scanlan et al. *ACS Nano* 2013

### Bioaccumulation of AuNPs and AgNPs exposed to zebrafish (*Danio rerio*)

- Larger amount of AgNPs in the liver compared to AuNPs

Kyung et al. *Chemosphere* 2018

# Single Particle ICP-MS: applications

## Food

### AgNPs in homogenized chicken meat

- **Previous separation of NPs by AF4**
- **Intact AgNPs in the meat**

Loeschner et al. *Anal. Bioanal. Chem.* 2013

### TiO<sub>2</sub> NPs in chewing gums

- **Detection of TiO<sub>2</sub> of sizes ranging 40 to 200 nm in chewing gums after water extraction**

Candas-Zapico et al. *Talanta* 2018

### Presence of PbNPs from ammunition in game meat

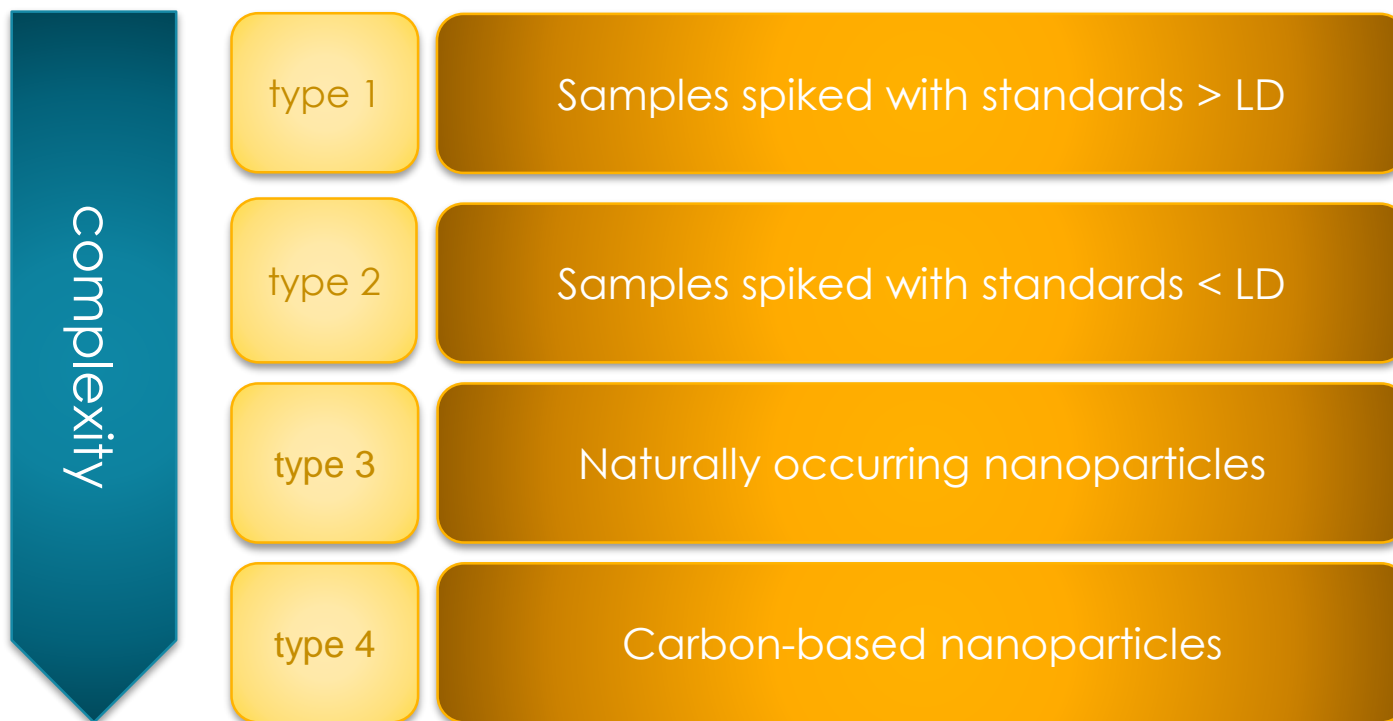
- **Pb-containing NPs with sizes from 75 to 750 nm were detected in game meat shot with lead containing bullets**

Kollander et al. *Anal. Bioanal. Chem.* 2017

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# Analysis of environmental samples: scenarios



# Practical case: PtNPs characterization in plants



JAAS

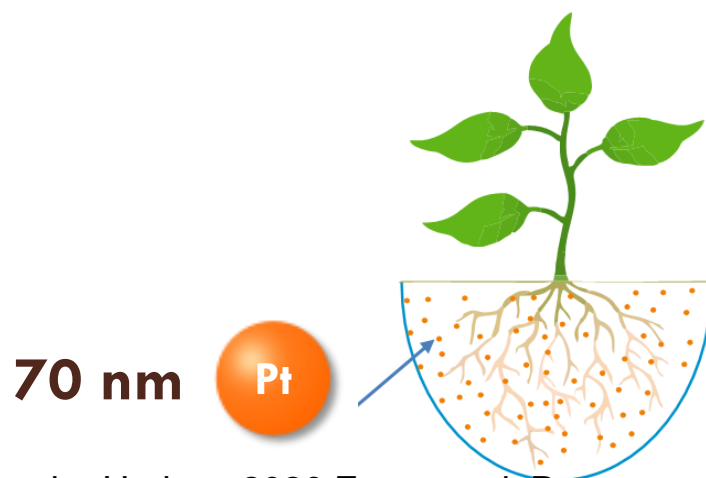
PAPER



Cite this: *J. Anal. At. Spectrom.*, 2016, 31, 2321

## Single particle ICP-MS characterization of platinum nanoparticles uptake and bioaccumulation by *Lepidium sativum* and *Sinapis alba* plants†

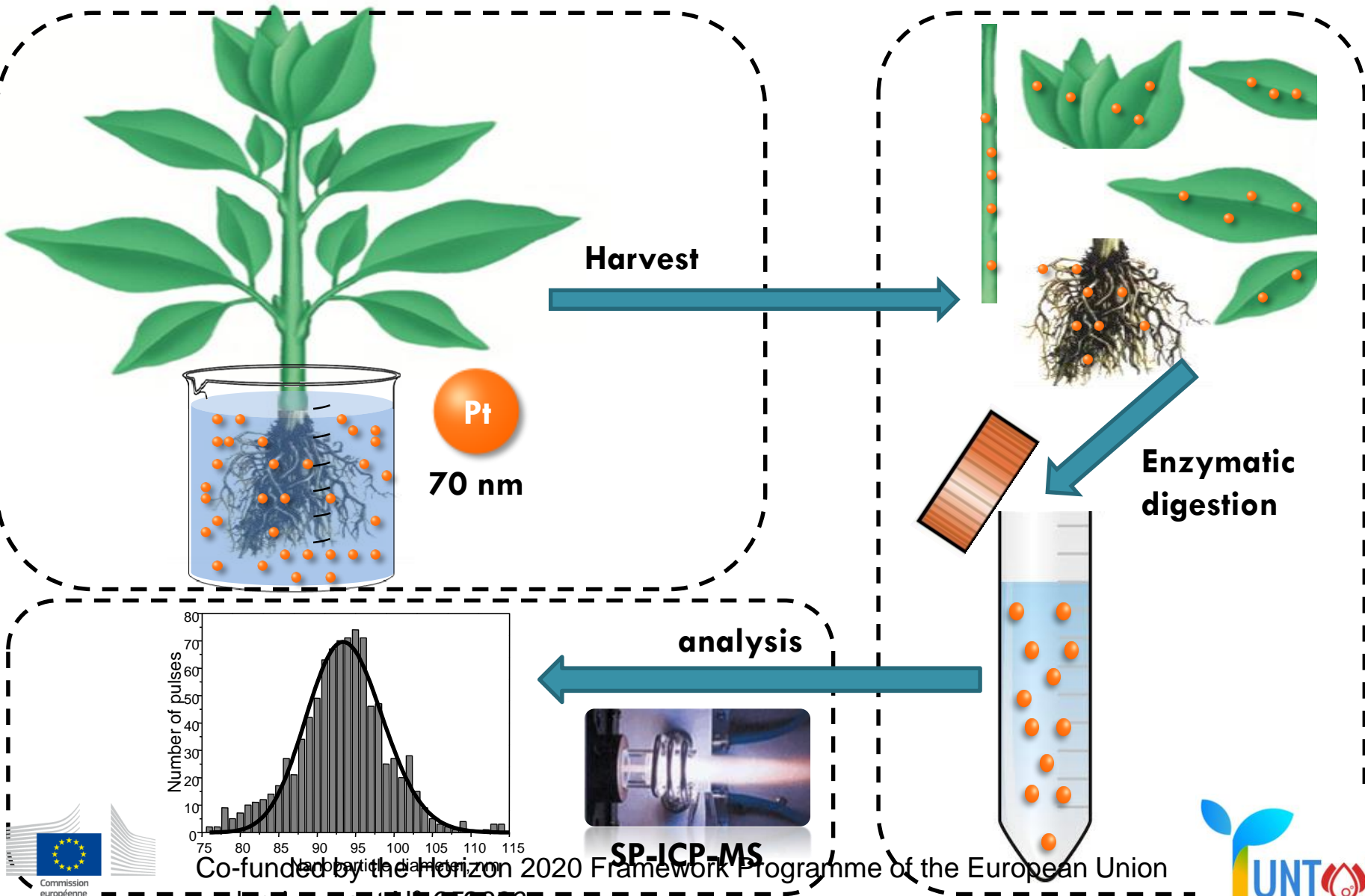
Javier Jiménez-Lamana,<sup>‡\*a</sup> Justyna Wojcieszek,<sup>‡b</sup> Matgorzata Jakubiak,<sup>c</sup> Monika Asztemborska<sup>c</sup> and Joanna Szpunar<sup>a</sup>



Co-funded by the Horizon 2020 Framework Programme of the European Union under the grant N° 952306

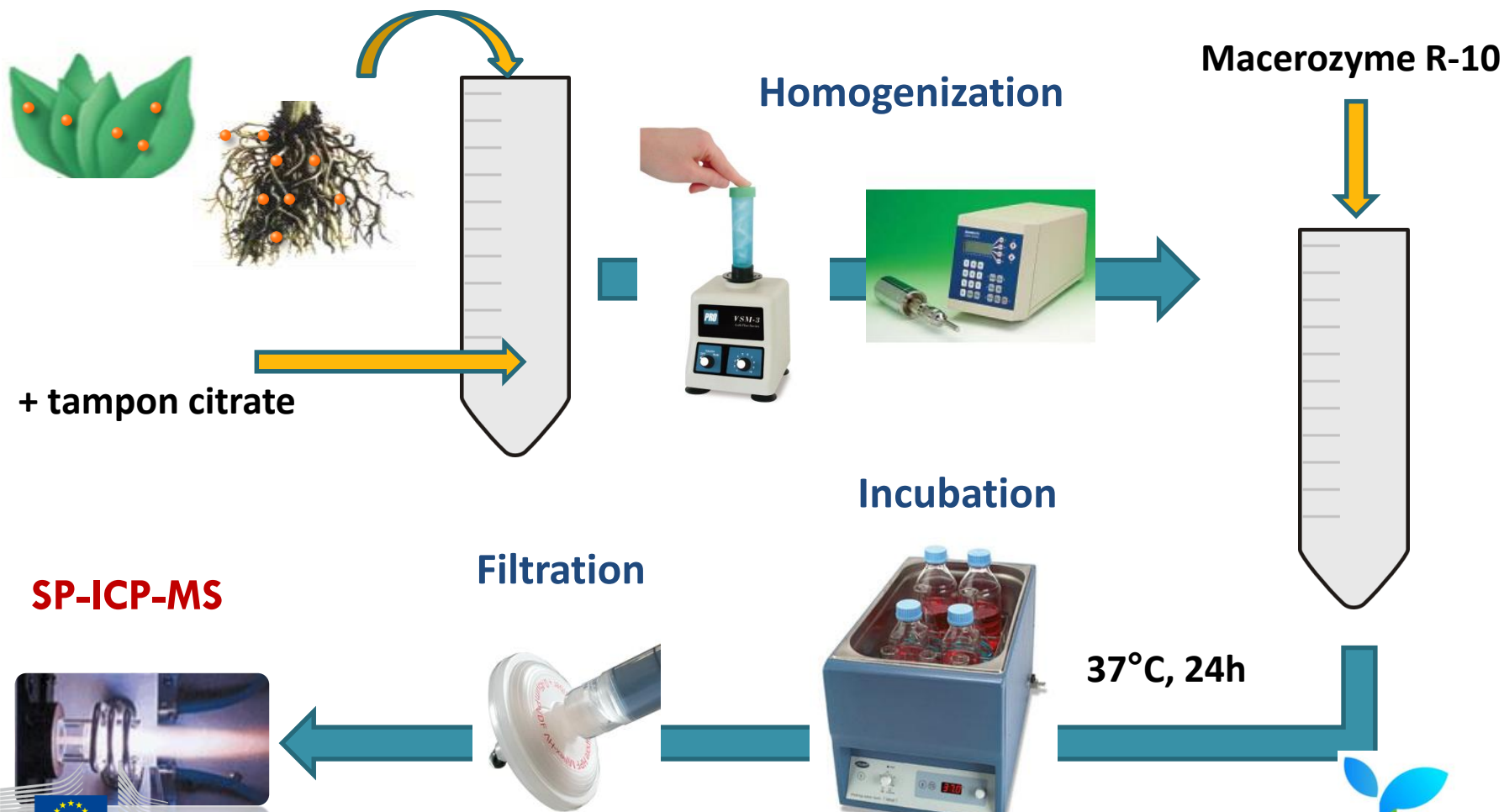


# Practical case: PtNPs characterization in plants



# Practical case: PtNPs characterization in plants

## Sample preparation: enzymatic digestion



Co-funded by the Horizon 2020 Framework Programme of the European Union under the grant N° 952306



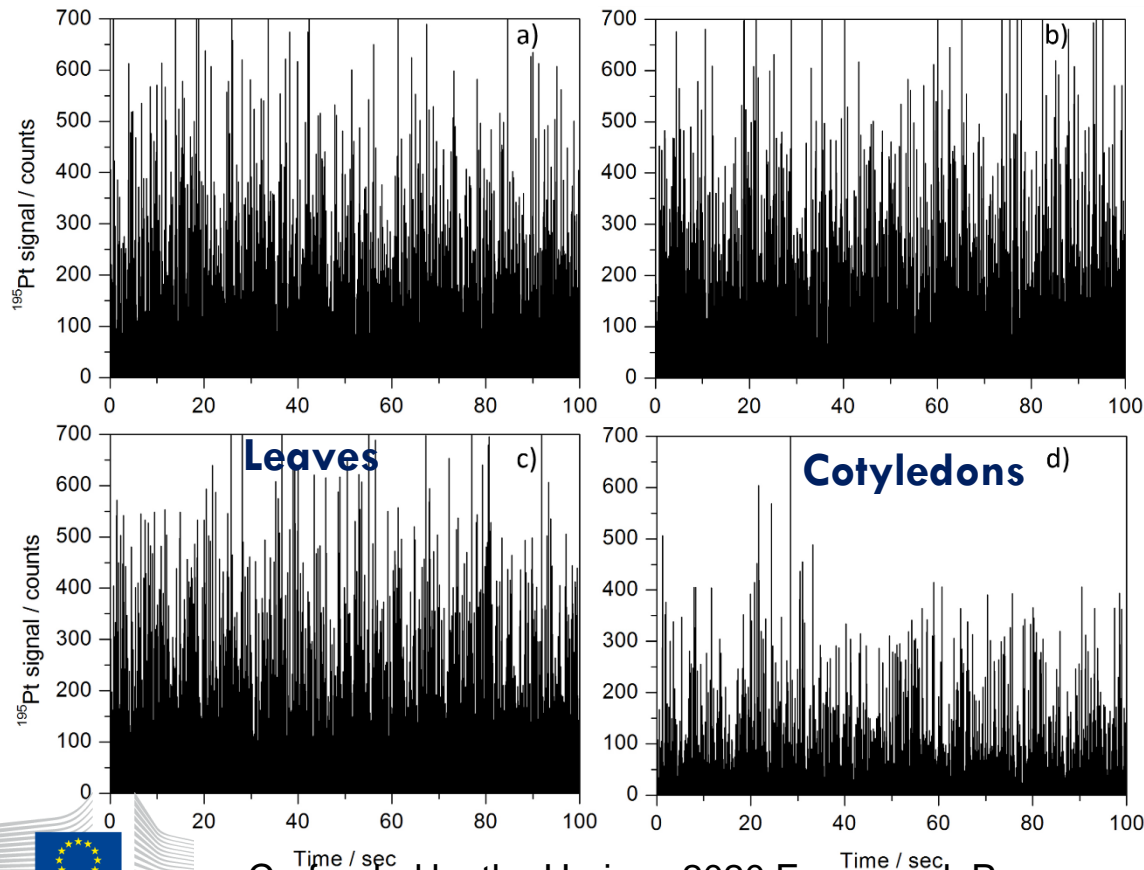
# Practical case: PtNPs characterization in plants

## SP-ICP-MS analysis

*Sinapis alba*

Roots

Stems



Sample	Number of NPs / NP L <sup>-1</sup>
Leaves	$5.30 \times 10^8$
Cotyledons	$2.85 \times 10^8$
Stems	$3.11 \times 10^{10}$
Roots	$6.18 \times 10^{11}$

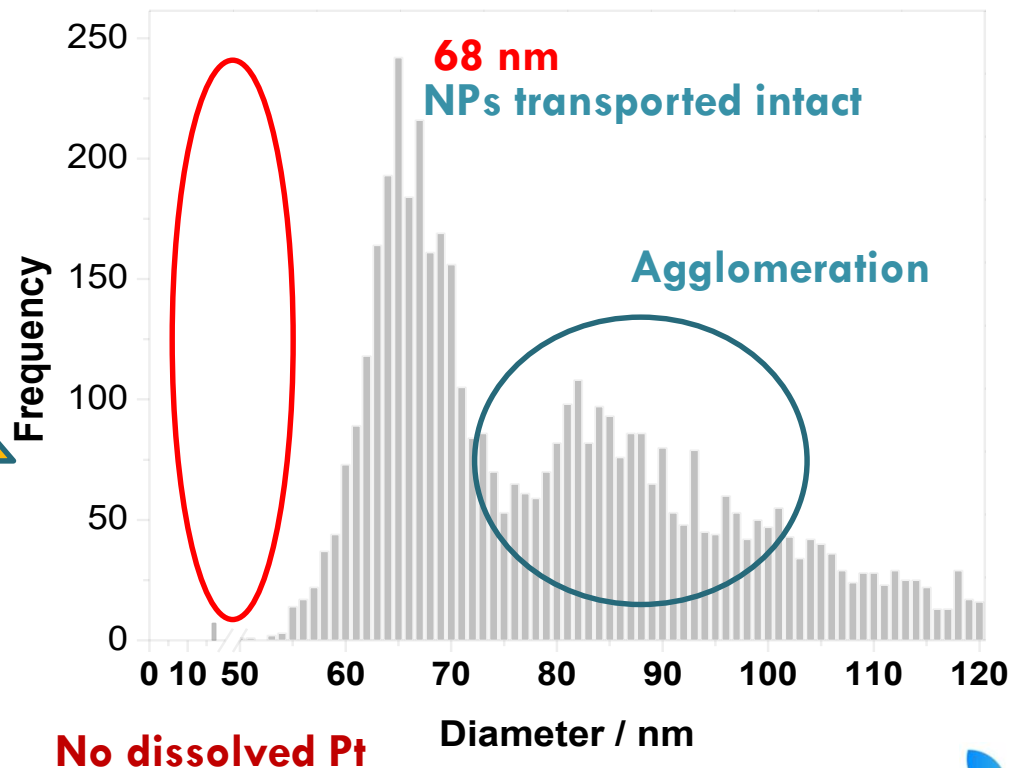
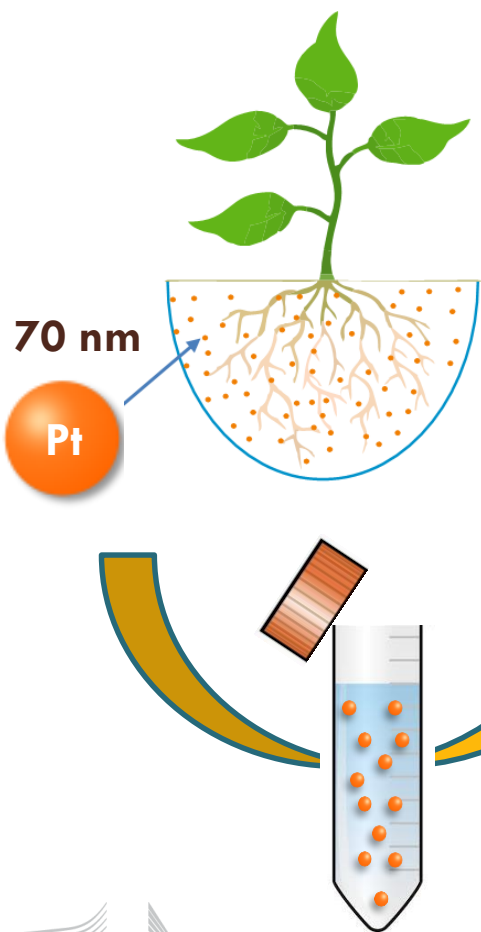
- Presence of NPs

- NPs transported to above ground organs

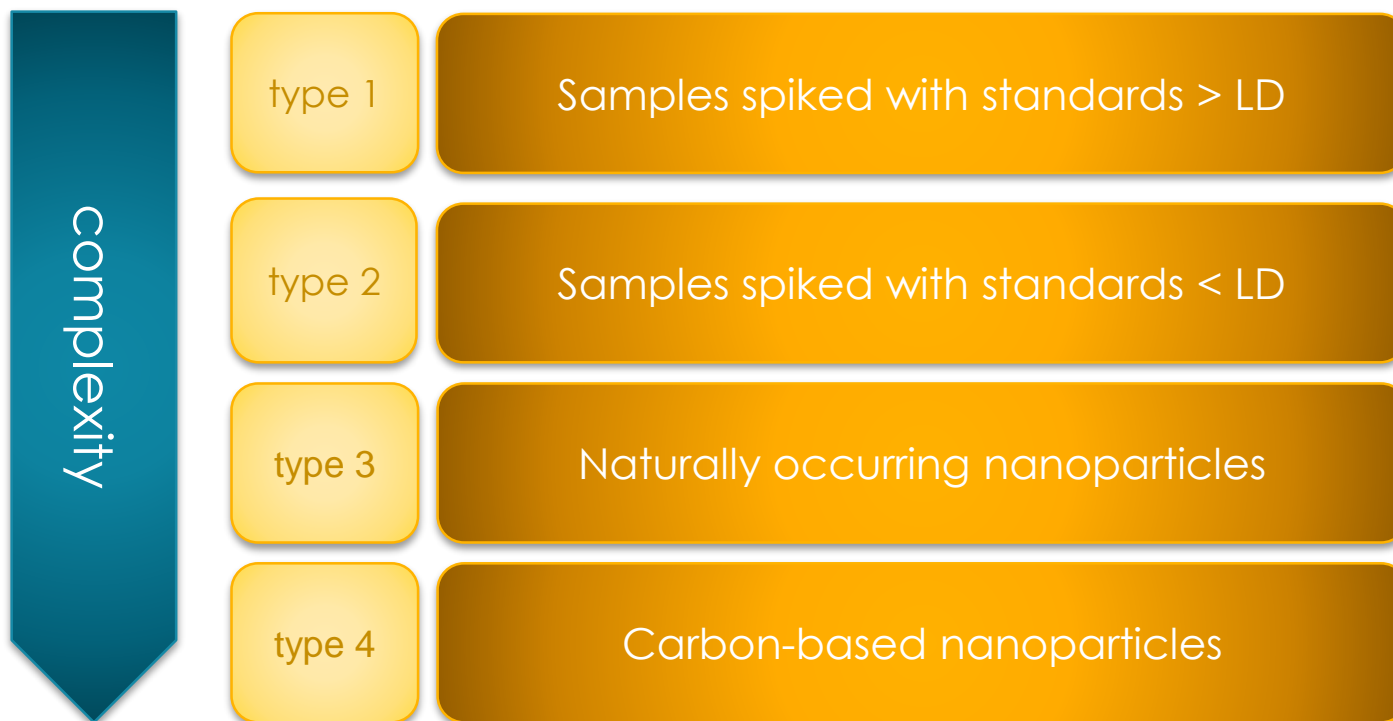


# Practical case: PtNPs characterization in plants

Known composition, shape and size > LD



# Analysis of environmental samples: scenarios



# Practical case: AgNPs in lake water



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journal homepage: [www.elsevier.com/locate/scitotenv](http://www.elsevier.com/locate/scitotenv)

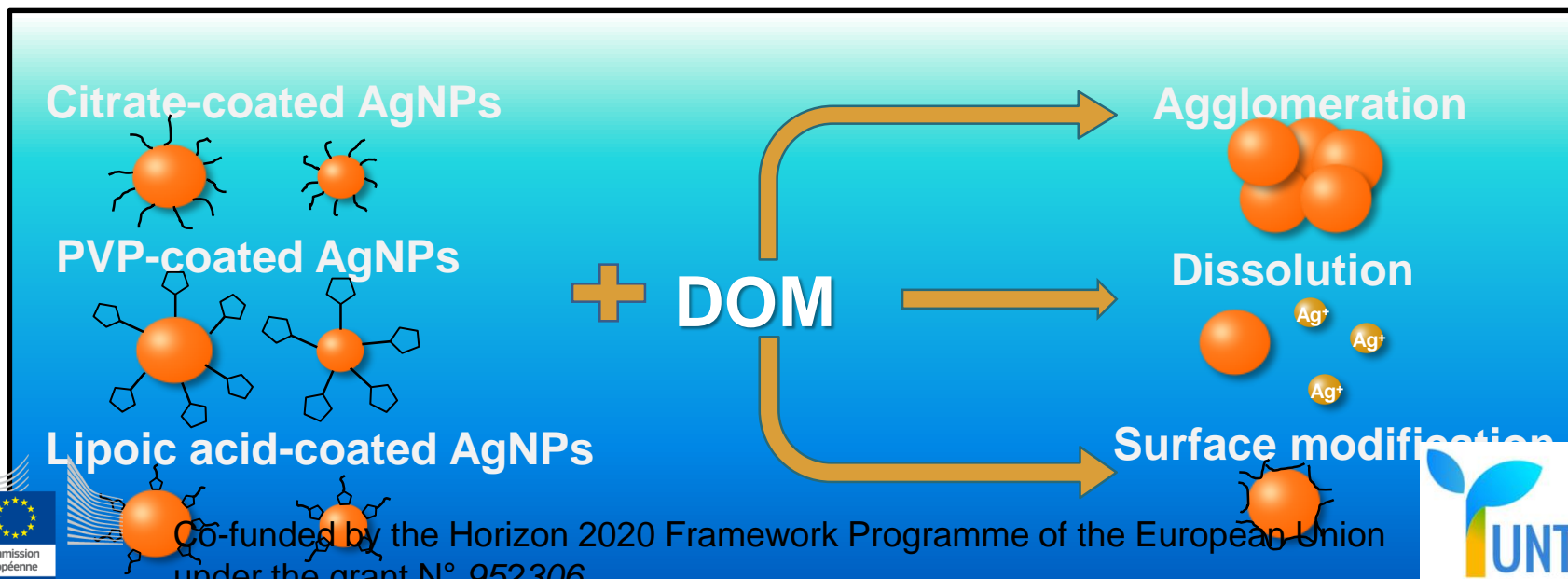


## Silver nanoparticle behaviour in lake water depends on their surface coating



Javier Jiménez-Lamana <sup>\*,1</sup>, Vera I. Slaveykova <sup>\*</sup>

*Environmental Biogeochemistry and Ecotoxicology, Institute F.-A. Forel, Faculty of Sciences, University of Geneva, Uni Carl Vogt, 66 Bvd. Carl Vogt, CH-1211 Geneva, Switzerland*



Co-funded by the Horizon 2020 Framework Programme of the European Union under the grant N° 952306



# Practical case: AgNPs in lake water



50 nm



20 nm

- Citrate

- PVP

- Lipoic acid



- LW

- LW + SRHA

- LW + EPS

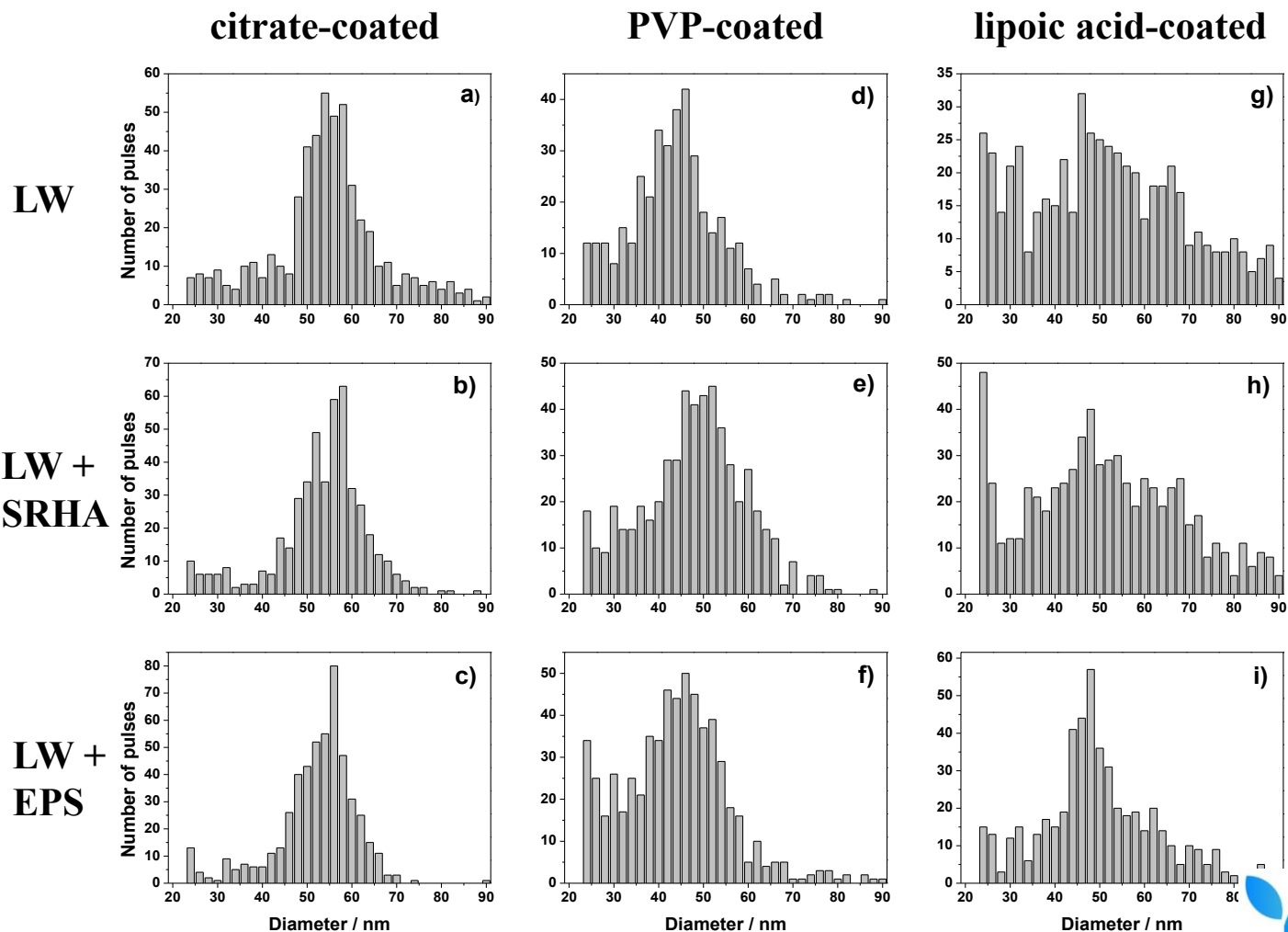


SP-ICP-MS



# Practical case: AgNPs in lake water

## 50 nm AgNPs



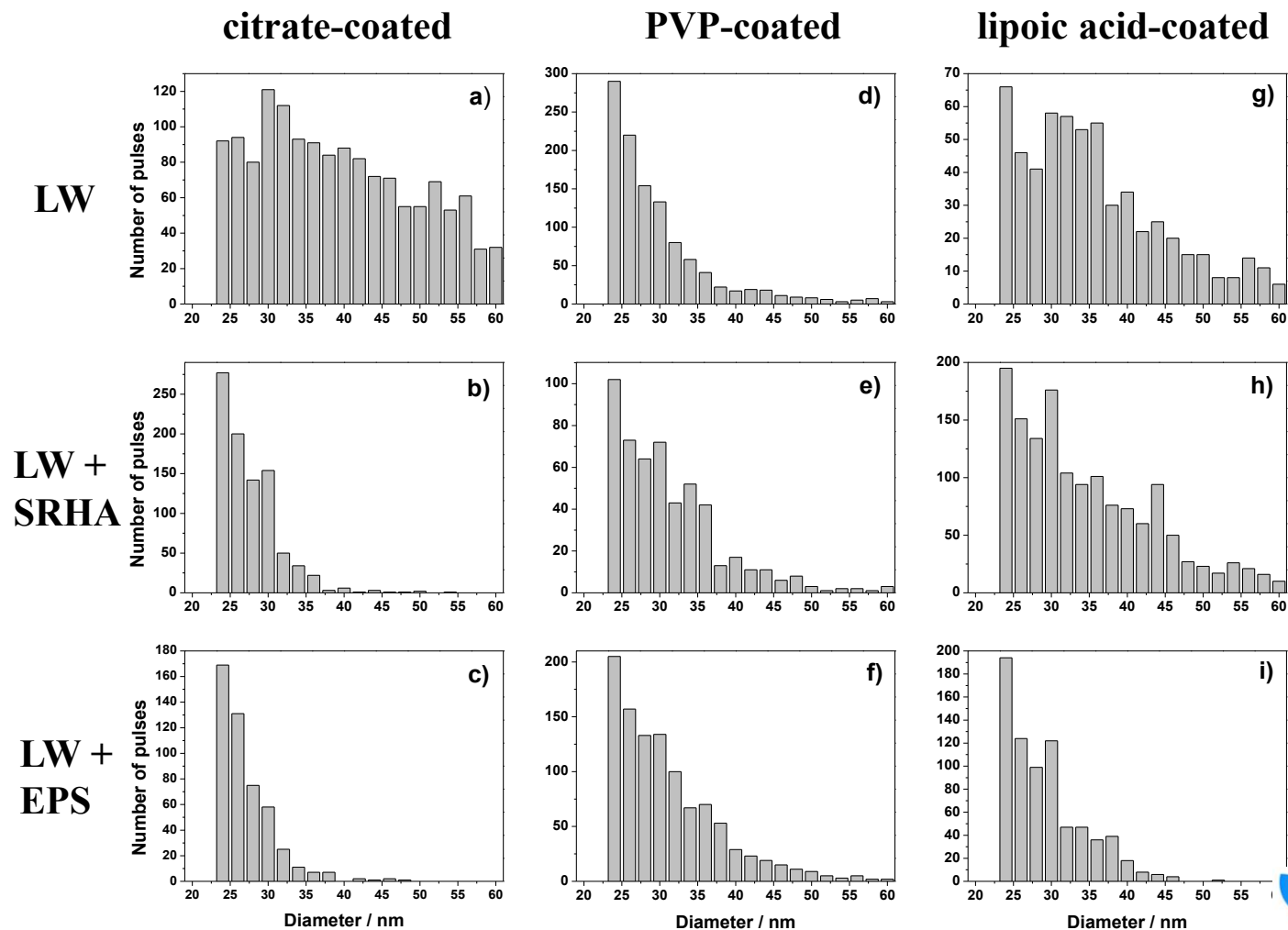
Co-funded by the Horizon 2020 Framework Programme of the European Union under the grant N° 952306



# Practical case: AgNPs in lake water

20 nm AgNPs

Known composition, shape and size < LD



Co-funded by the Horizon 2020 Framework Programme of the European Union under the grant N° 952306



# Practical case: AgNPs in lake water



50 nm



20 nm

- Citrate

- PVP

- Lipoic acid



- LW

- LW + SRHA

- LW + EPS



**AsFIFFF-UV-Vis**



**SP-ICP-MS**

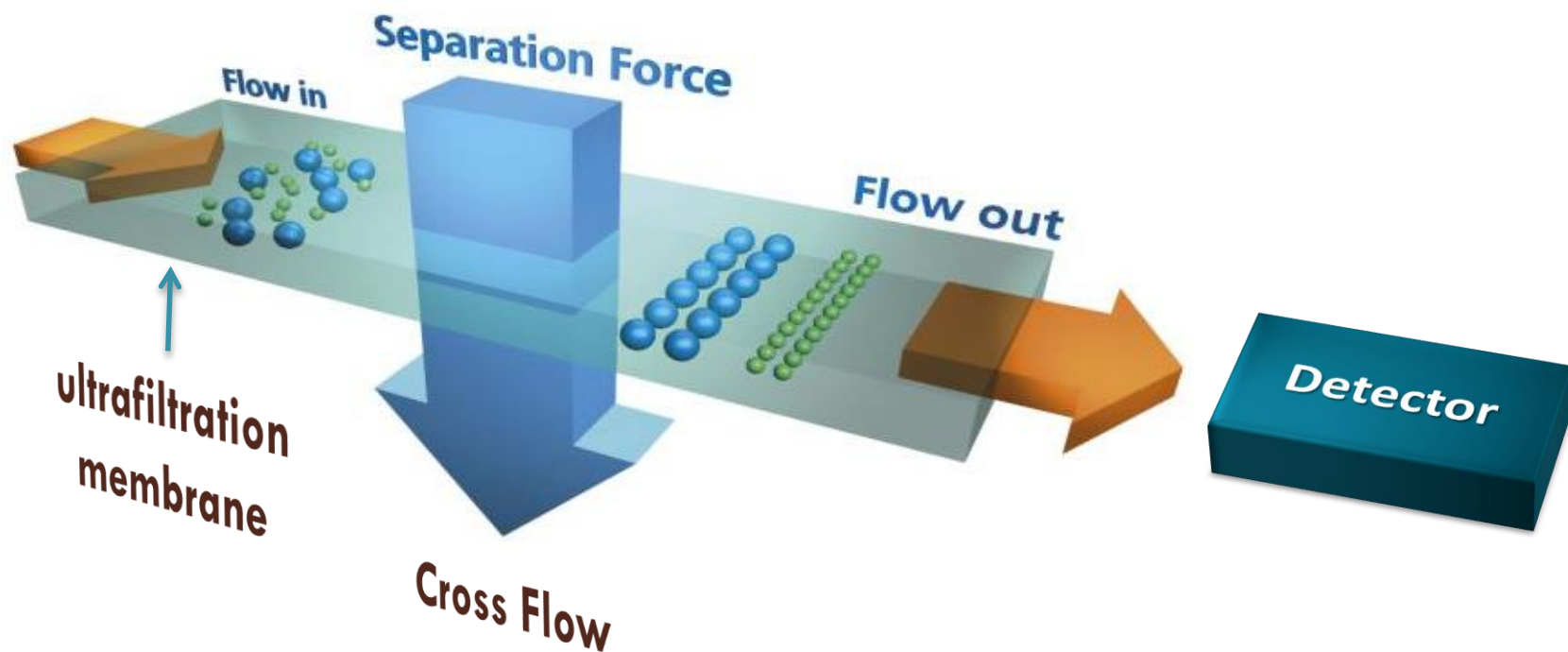


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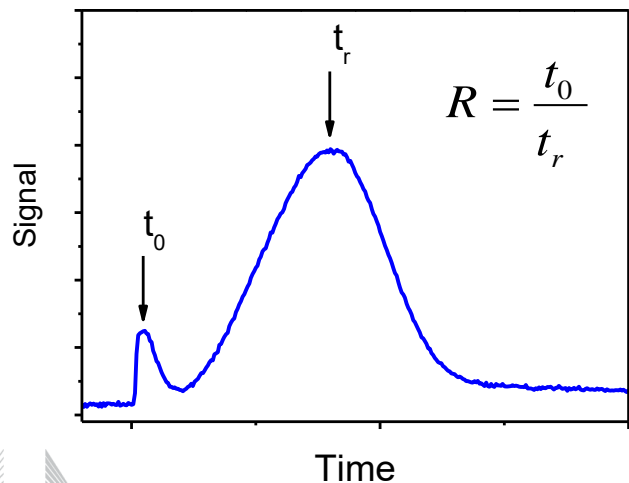
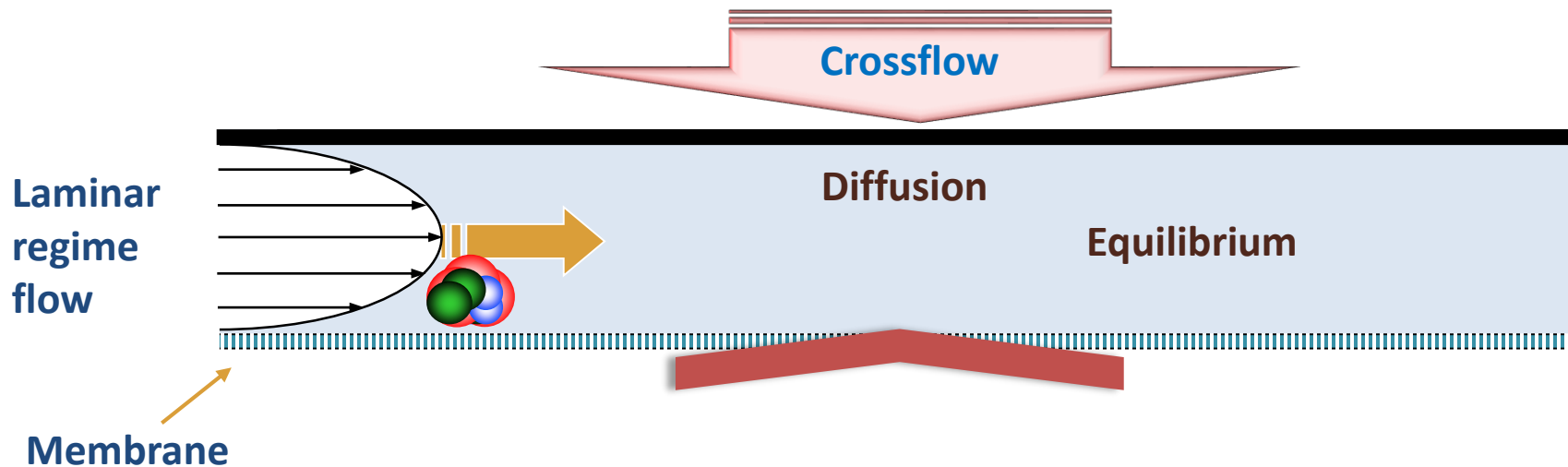
# Practical case: AgNPs in lake water

Separation technique where species are size-separated in a thin open channel with laminar flow under the influence of a perpendicular external field





# Practical case: AgNPs in lake water



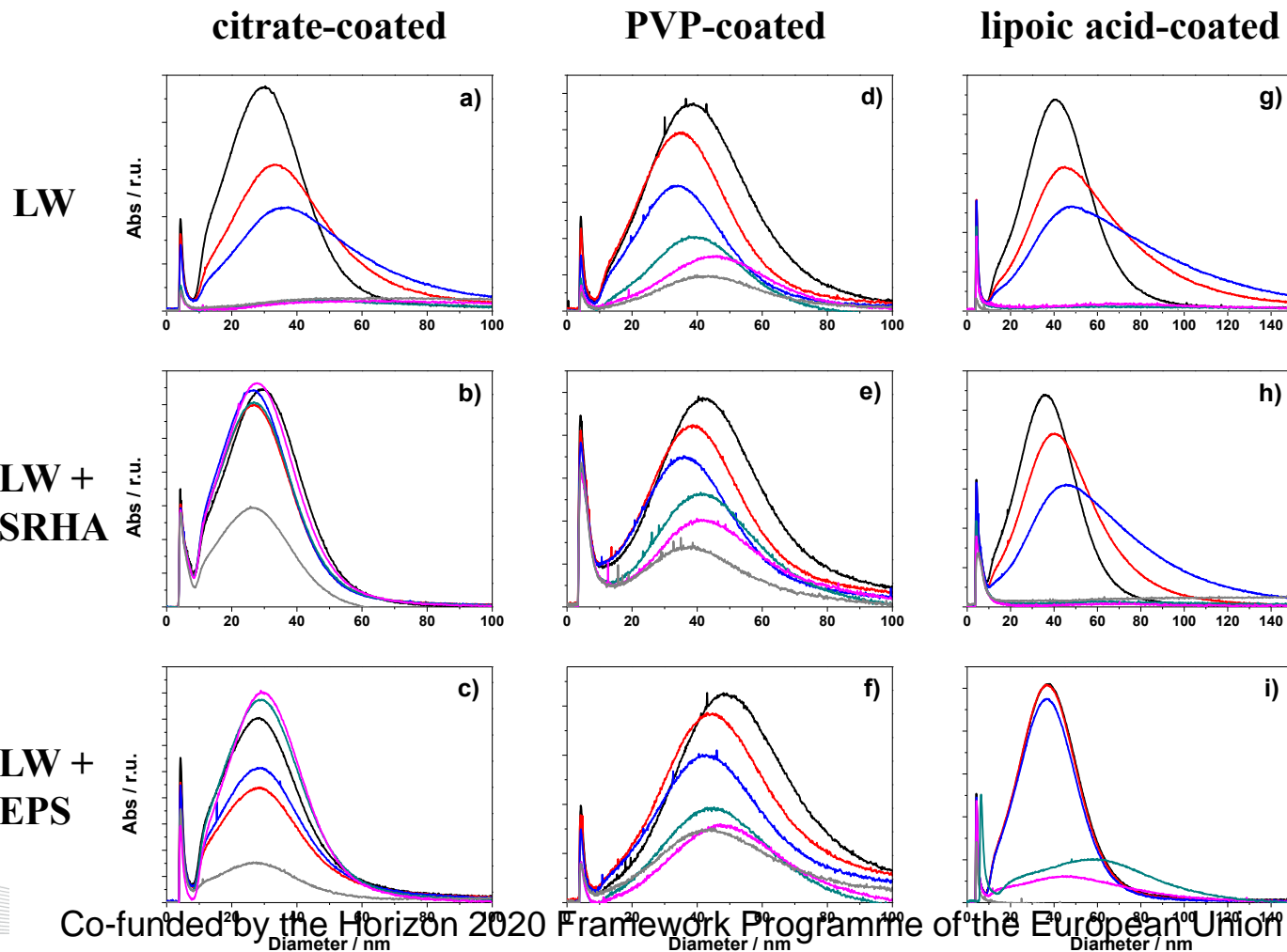
$$t_r \propto D \propto d$$

Hydrodynamic diameter

# Practical case: AgNPs in lake water

20 nm AgNPs

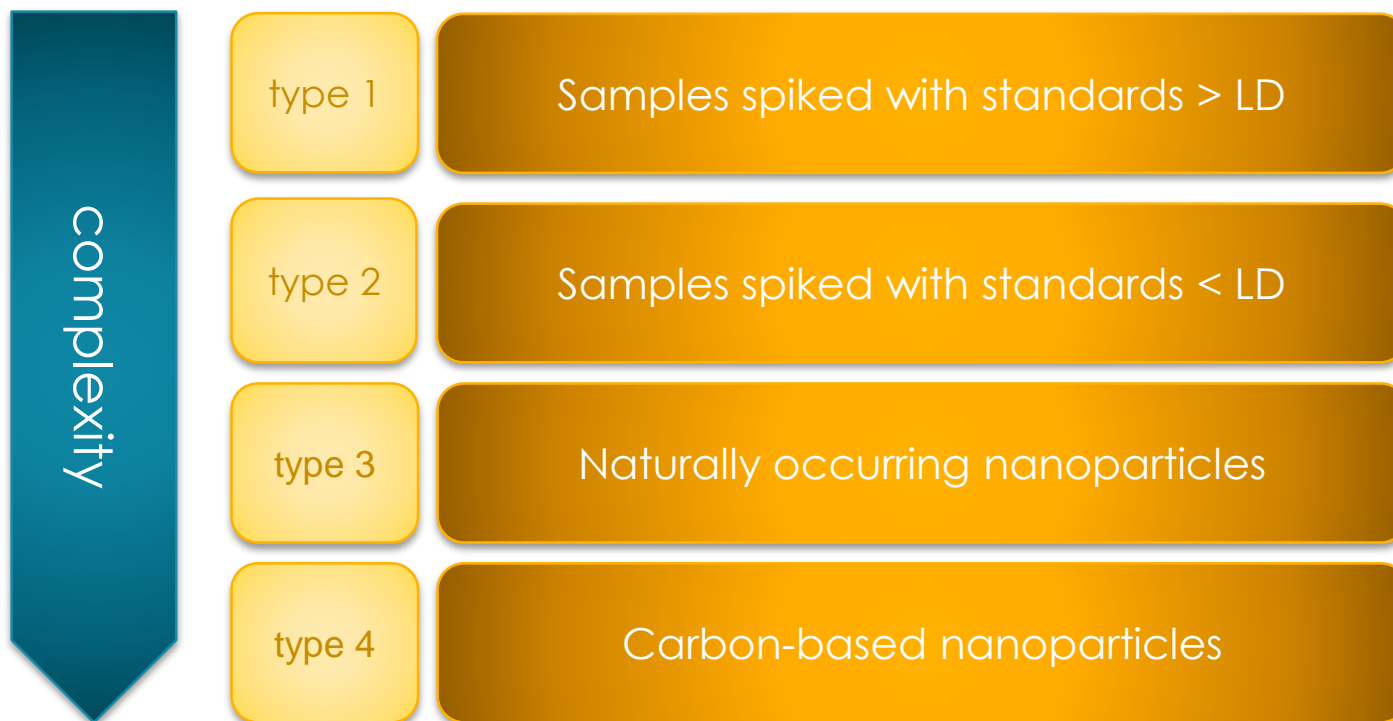
Asymmetric field-flow fractionation



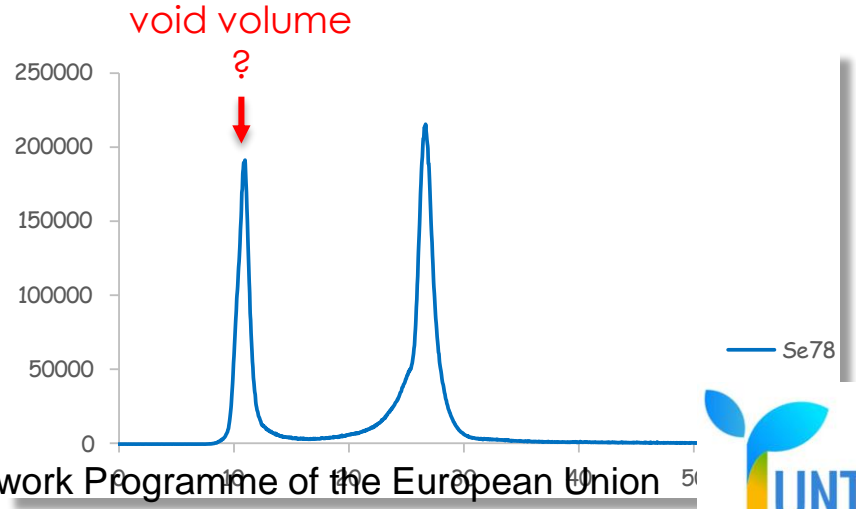
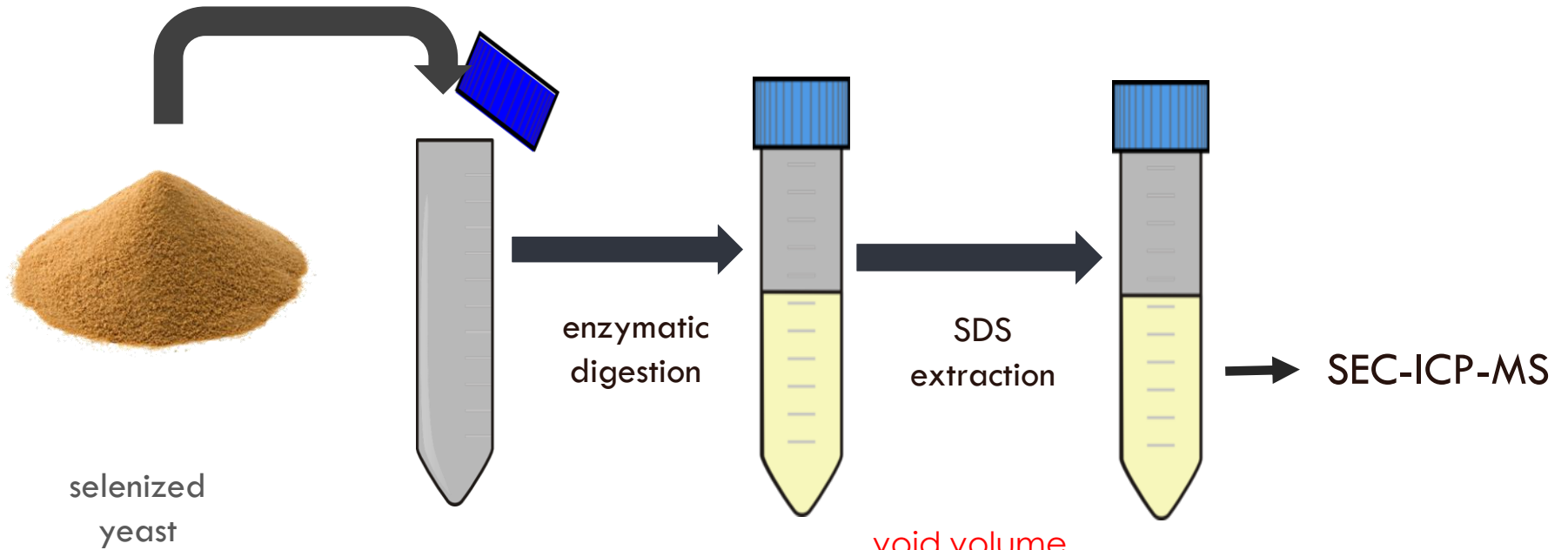
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# Analysis of environmental samples: scenarios

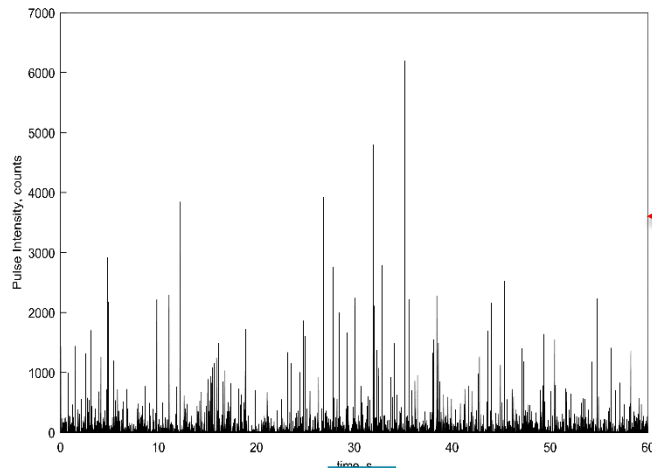


# Biogenic SeNPs in yeast

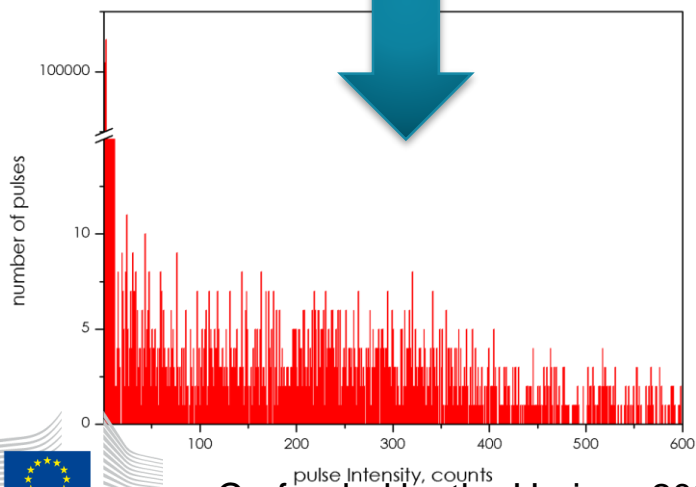
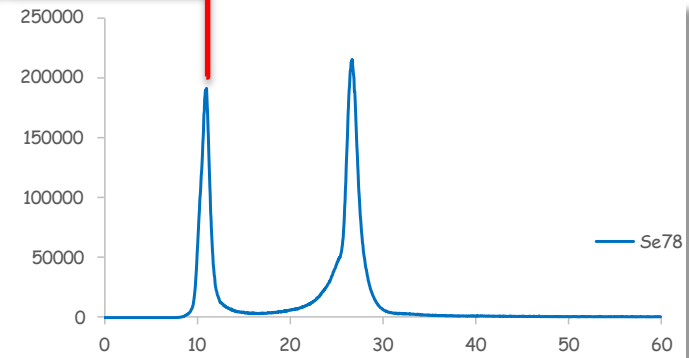


Co-funded by the Horizon 2020 Framework Programme of the European Union under the grant N° 952306

# Biogenic SeNPs in yeast

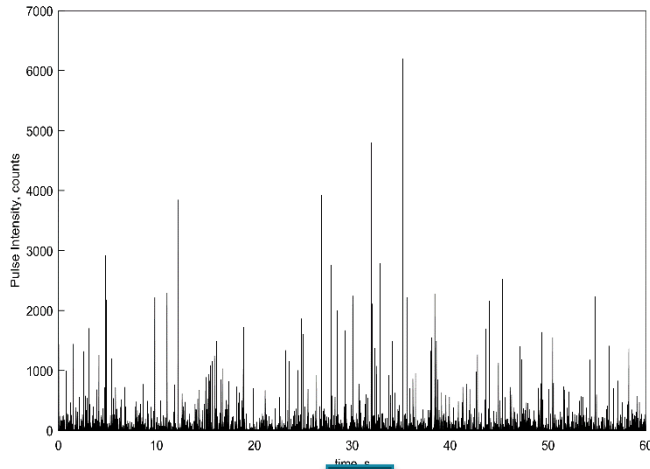


SP-ICP-MS

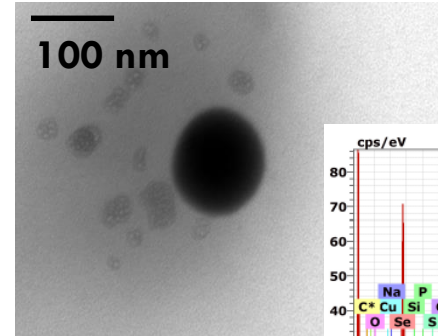


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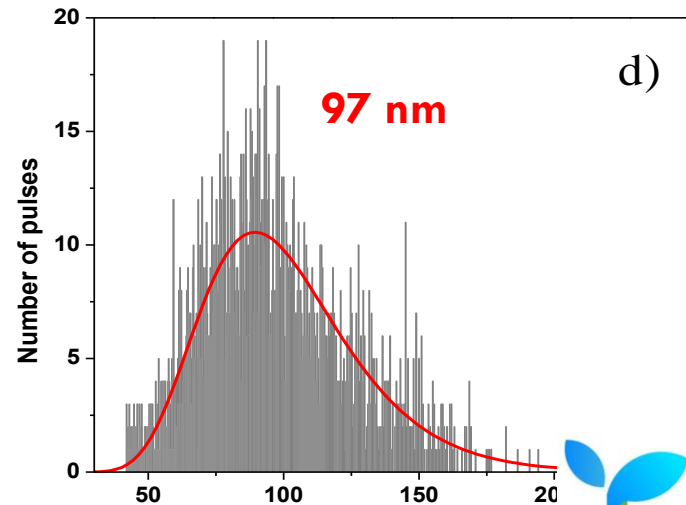
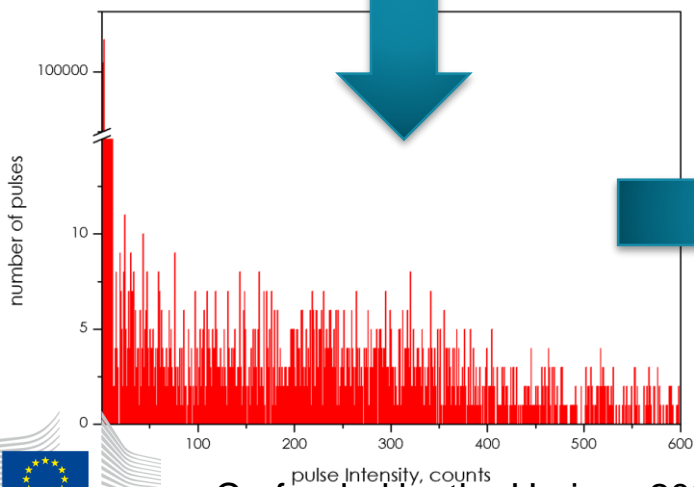
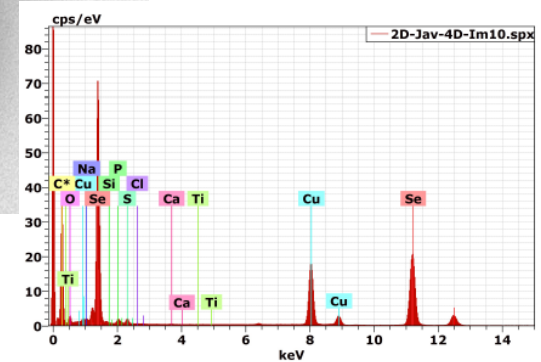
# Biogenic SeNPs in yeast



TEM-EDS  
analysis



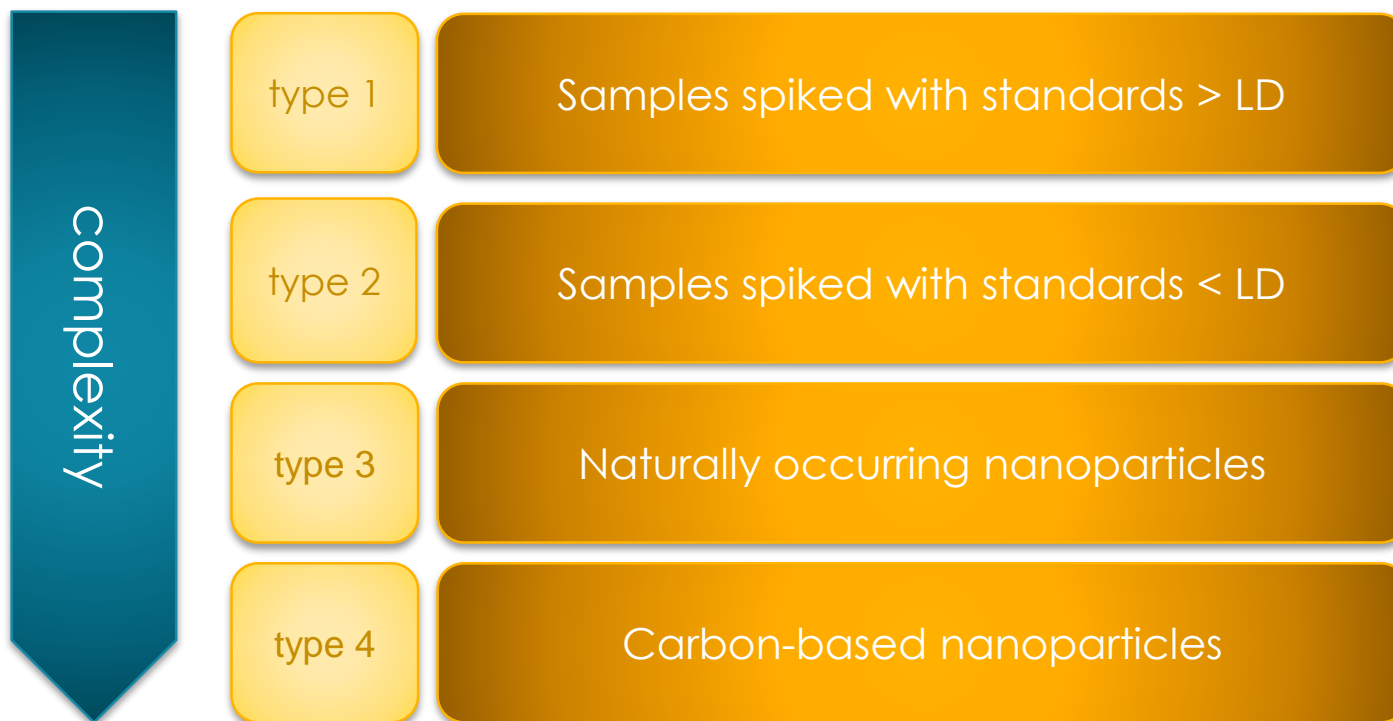
selenium  
density:  $4.81 \text{ g cm}^{-3}$   
spheres



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# Analysis of environmental samples: scenarios



# SP-ICP-MS applied to plastic particles

## ✓ For inorganic nanoparticles

- **SP-ICP-MS is widely used for the analysis of metallic nanoparticles**
- **Its excellent sensitivity (detection at the attogram level) allows the characterization of nanoparticles with sizes down to 10 nm**

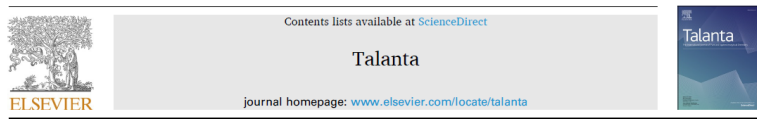
## ✗ For carbon based nanoparticles

- **C is not sensitive towards ICP-MS due to its low ionization efficiency (< 5 %) and high ionization potential (11.26 eV)**
- **The background of  $^{12}\text{C}$  is very high due the presence of carbon in water and air**
- **$^{13}\text{C}$  is not sensitive enough due to its low abundance (1.1 %)**



# SP-ICP-MS applied to plastic particles

## Detection and quantification of 1.2-5 $\mu\text{m}$ PS microplastics by monitoring $^{13}\text{C}$

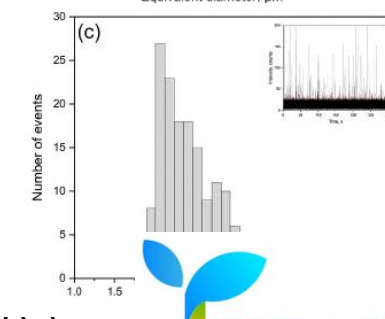
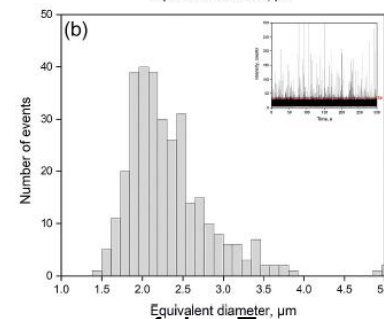
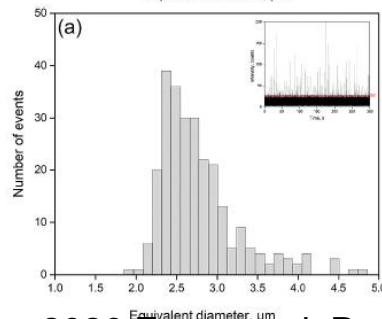
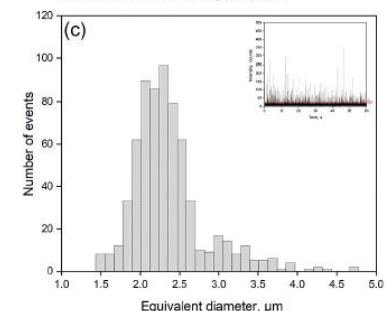
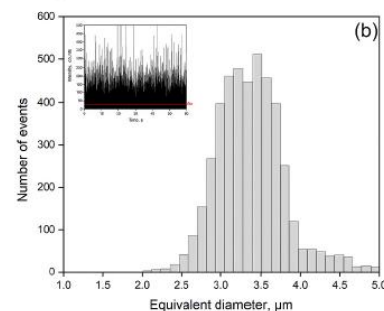
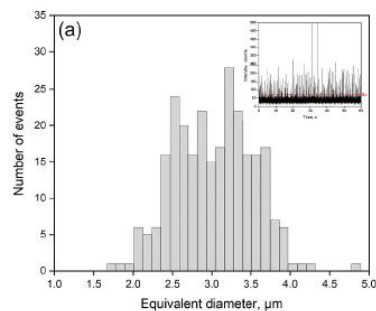
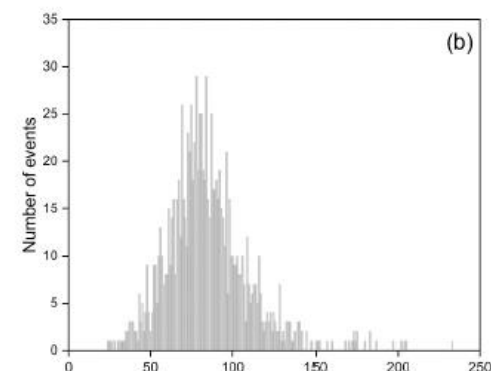
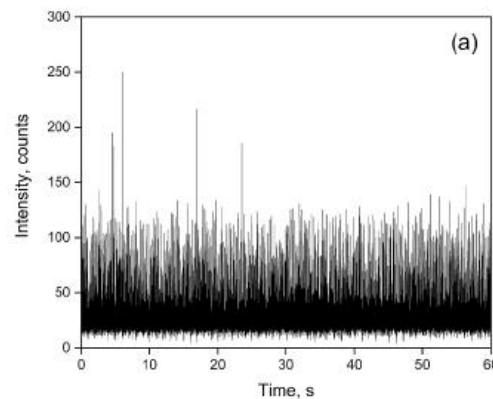


Analysis of microplastics in consumer products by single particle-inductively coupled plasma mass spectrometry using the carbon-13 isotope

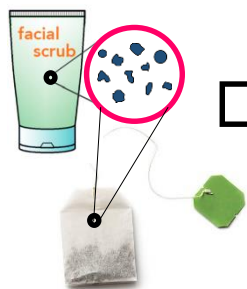
Francisco Laborda <sup>a,\*</sup>, Celia Trujillo <sup>a</sup>, Ryszard Lobinski <sup>b</sup>

<sup>a</sup> Group of Analytical Spectroscopy and Sensors (GEAS), Institute of Environmental Sciences (IIUCA), University of Zaragoza, Pedro Cerbuna 12, 50009, Zaragoza, Spain  
<sup>b</sup> Université de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM UMR 5254, Hélioparc, 64053, Pau, France

Laborda et al. *Talanta* 2021



### Applied to screening in food packaging and personal care products



Microplastics  
SP-ICP-MS

Co-funded by the Horizon 2020 Framework Programme of the European Union under the grant N° 952306



# SP-ICP-MS applied to plastic particles

Bolea-Fernandez et al. *RSC* 2020

JAAS



COMMUNICATION

View Article Online  
View Journal



Detection of microplastics using inductively coupled plasma-mass spectrometry (ICP-MS) operated in single-event mode

Cite this: DOI: 10.1039/c9ja00379g

Received 9th November 2019  
Accepted 4th December 2019

Eduardo Bolea-Fernandez,<sup>a</sup> Ana Rúa-Ibarz,<sup>a\*</sup> Milica Velimirovic,<sup>b</sup> Kristof Tirez<sup>b</sup> and Frank Vanhaecke<sup>b</sup>

- Determine size and number concentration of spherical polystyrene microspheres of 1 and 2.5  $\mu\text{m}$  by monitoring  $^{13}\text{C}$
- Number based concentrations were assessed by comparing  $^{13}\text{C}$ -related events with the events detected when monitoring the  $^{165}\text{Ho}$  signal for 2.5 mm lanthanide-doped polystyrene beads

Gonzalez de Vega et al. *Analytica Chimica Acta* 2021



Characterisation of microplastics and unicellular algae in seawater by targeting carbon via single particle and single cell ICP-MS

Raquel Gonzalez de Vega<sup>a</sup>, Samantha Goyen<sup>b</sup>, Thomas E. Lockwood<sup>a</sup>, Philip A. Doble<sup>a</sup>, Emma F. Camp<sup>b</sup>, David Clases<sup>a,\*</sup>

<sup>a</sup> The Atomic Medicine Initiative, University of Technology Sydney, 15 Broadway, Ultimo NSW, 2007, Australia  
<sup>b</sup> Faculty of Science, Climate Change Cluster, University of Technology Sydney, Sydney, NSW, Australia

- Development of an SP/SC ICP-MS method for the analysis of C-based microstructures in a particle-by-particle basis
- Achieved a size detection limit of 0.6  $\mu\text{m}$  for PS-based microplastics by monitoring  $^{12}\text{C}$

Co-funded by the Horizon 2020 Framework Programme of the European Union under the grant N° 952306



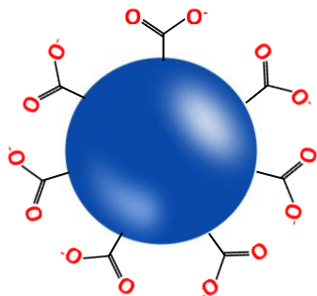
# SP-ICP-MS applied to plastic particles

## How to make the invisible nanoplastics visible to ICP-MS?



Nanoplastics labelled with specific metal probes

PS nanoparticles  
functionalized with  
carboxyl groups



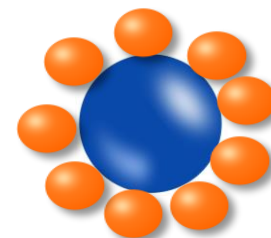
Positively  
charged gelatin-  
coated AuNPs



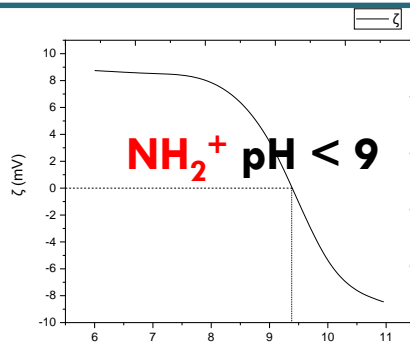
+



Labelled NPT  
 $\text{COO}^- \text{NH}_2 \text{AuNPs}$



$\text{COO}^-$  pH > 5



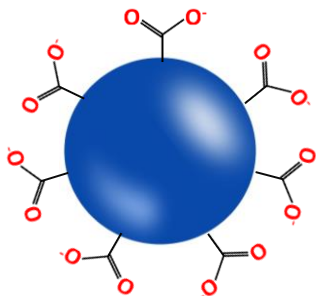
At working pH (6-8):  
labelling through  
electrostatic interactions  
 $\text{COO}^-$  (NPTs surface)

$\text{NH}_2^+$  (AuNPs)

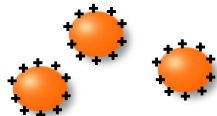
# SP-ICP-MS applied to plastic particles

## Labelling of nanoplastics with AuNPs as specific metal probes

PS nanoparticles  
420 nm

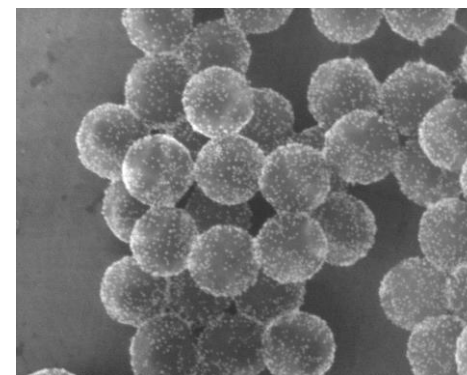
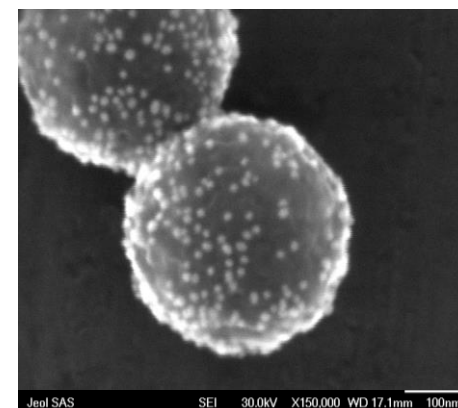


AuNPs@gel  
17 nm



+

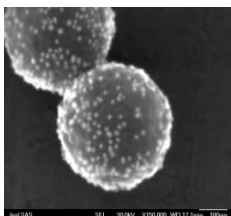
SEM



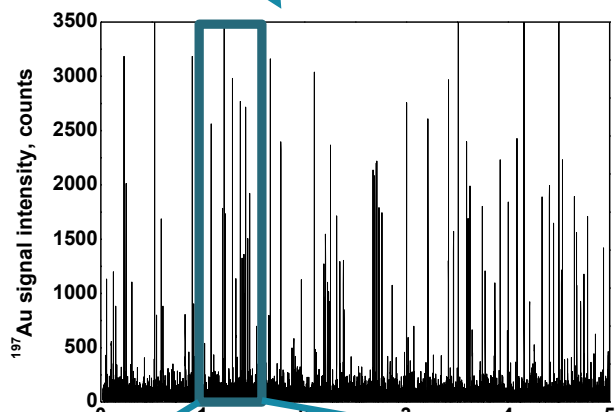
- Successful labelling of NPTs
- Homogeneous Au coverage
- Significant number of AuNPs and hence enough Au mass for ICP

Co-funded by the Horizon 2020 Framework Programme of the European Union under the grant N° 952306

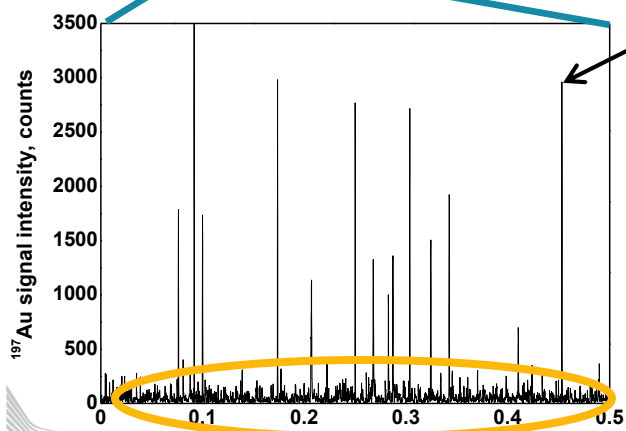
# SP-ICP-MS applied to plastic particles



Suspension of conjugates  
NPTs-AuNPs@gel

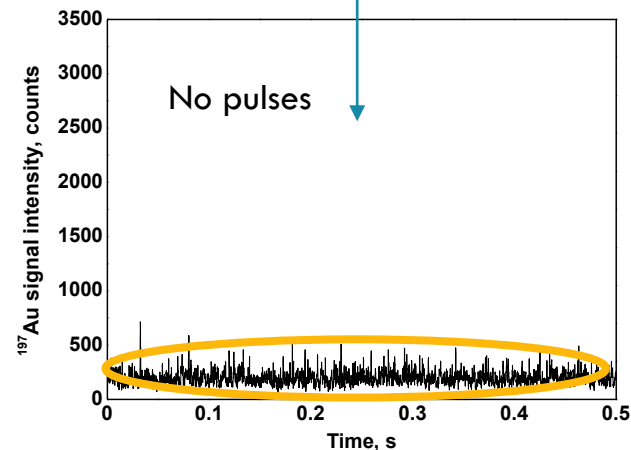
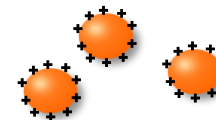


Each NPTs-AuNPs conjugate produces a cloud of Au ions that produces a discrete signal pulse due to AuNPs in surface.



"Background"  
Due to free AuNPs

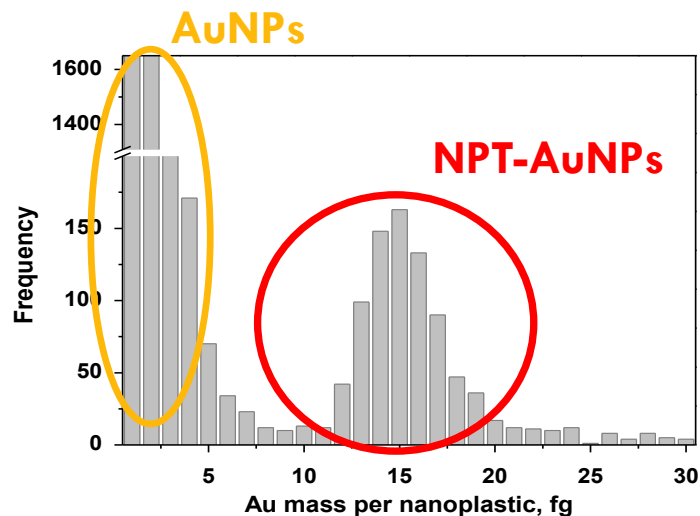
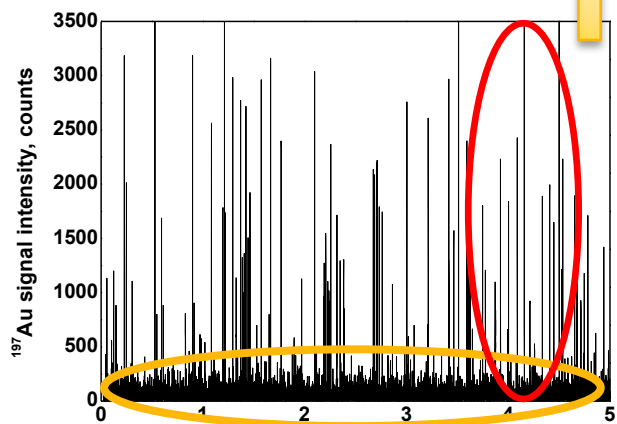
AuNPs@gel  
17 nm



# SP-ICP-MS applied to plastic particles

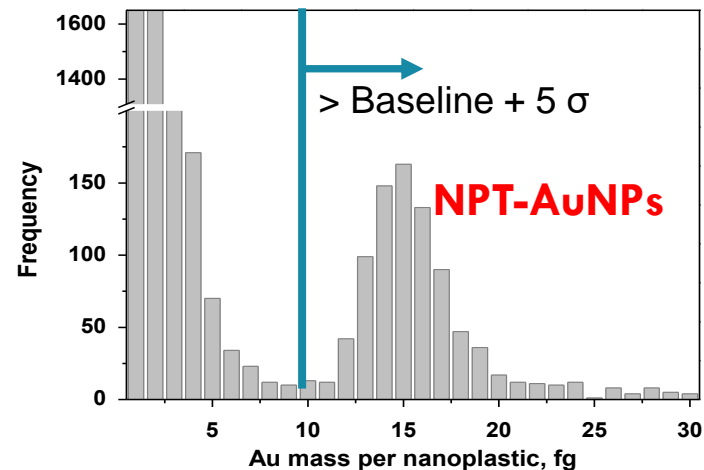
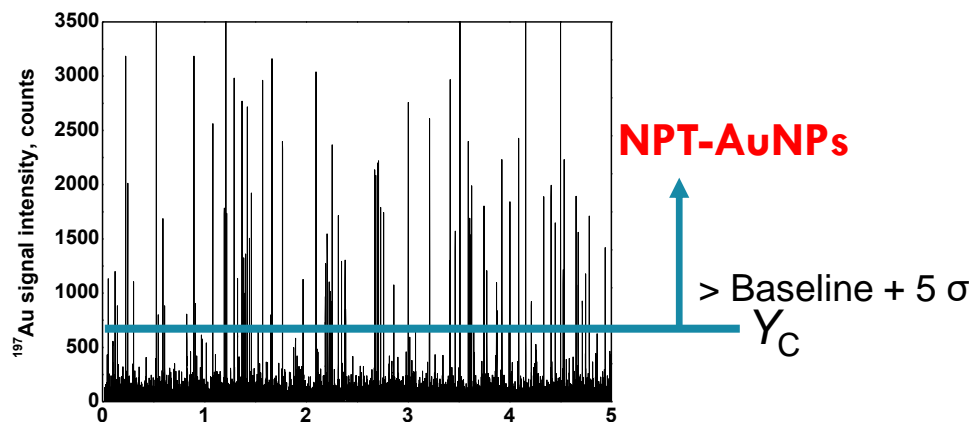
Each intensity can be converted into mass sorbed on each NPT for the evaluation of the mass distribution

$$m_{sorb}(ag) = \frac{Ip}{s} * q * t_d * \eta * 10^6$$



We observe 2 types of signal: the first one due to presence of **free AuNPs** and the second one due to the **NPTs labelled**

# SP-ICP-MS applied to plastic particles



Nanoplastic	Size, nm	Theoretical concentration, NPTs L <sup>-1</sup>	Experimental concentration, NPTs L <sup>-1</sup>	Average Au mass per NPT, fg	Average number of AuNPs per NPT
PS22	420 ± 20	6.42 × 10 <sup>7</sup>	6.25 ± 0.36 × 10 <sup>7</sup>	14.4 ± 1.4	290 ± 28



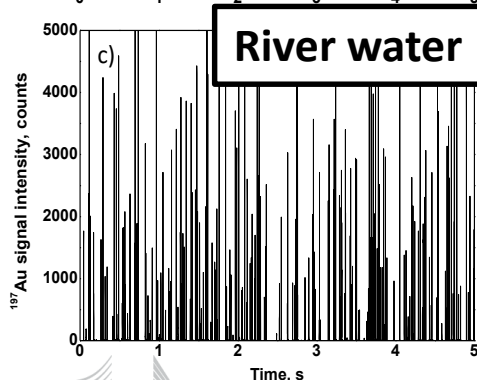
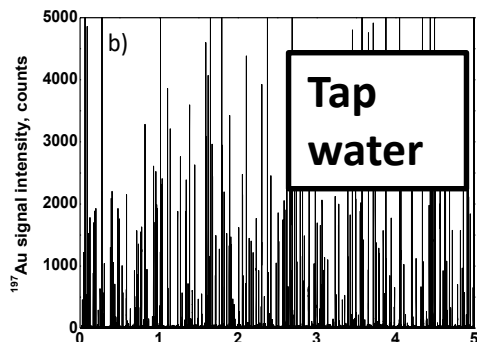
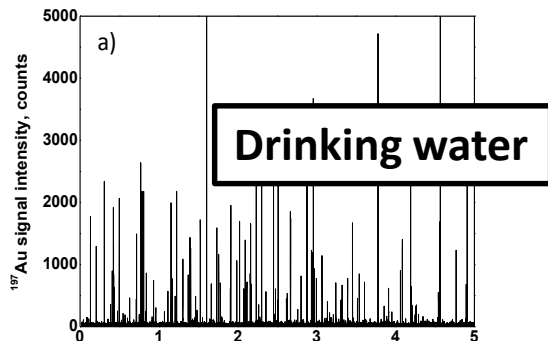
**good agreement between theoretical and experimental values**

Co-funded by the Horizon 2020 Framework Programme of the European Union under the grant N° 952306



# SP-ICP-MS applied to plastic particles

## Detection and quantification on water samples



Water sample	Theoretical concentration, NPTs L <sup>-1</sup>	Experimental concentration, NPTs L <sup>-1</sup>	Average Au mass per NPT, fg
Drinking water	$5.46 \times 10^7$	$5.74 \pm 0.19 \times 10^7$	$7.4 \pm 0.1$
Tap water	$2.23 \times 10^8$	$2.00 \pm 0.07 \times 10^8$	$13.1 \pm 0.4$
River water	$2.15 \times 10^8$	$2.12 \pm 0.07 \times 10^8$	$13.2 \pm 0.2$
Ultra pure water	$6.42 \times 10^7$	$6.25 \pm 0.36 \times 10^7$	$14.4 \pm 1.4$

- ✓ Nanoplastics well detected in all the matrix
- ✓ Au mass per NPT for drinking water and tap water close to the value obtained with ultra pure water

Hypothesis: higher conductivity of drinking water may influence the electrostatic interaction between negative and positive charges



# Take-home message

- Single particle ICP-MS is a powerful technique.
- SP-ICP-MS can detect particulate forms of elements at very low concentrations.
- SP-ICP-MS cannot size unknown particles by itself.
- Additional techniques are needed to know the nature of the particles.
- SP-ICP-MS must be used in combination with other characterization techniques to analyze real-world samples.

# References

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