AF4-MALS-ICPMS for the characterization of nanoparticles

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IPREM

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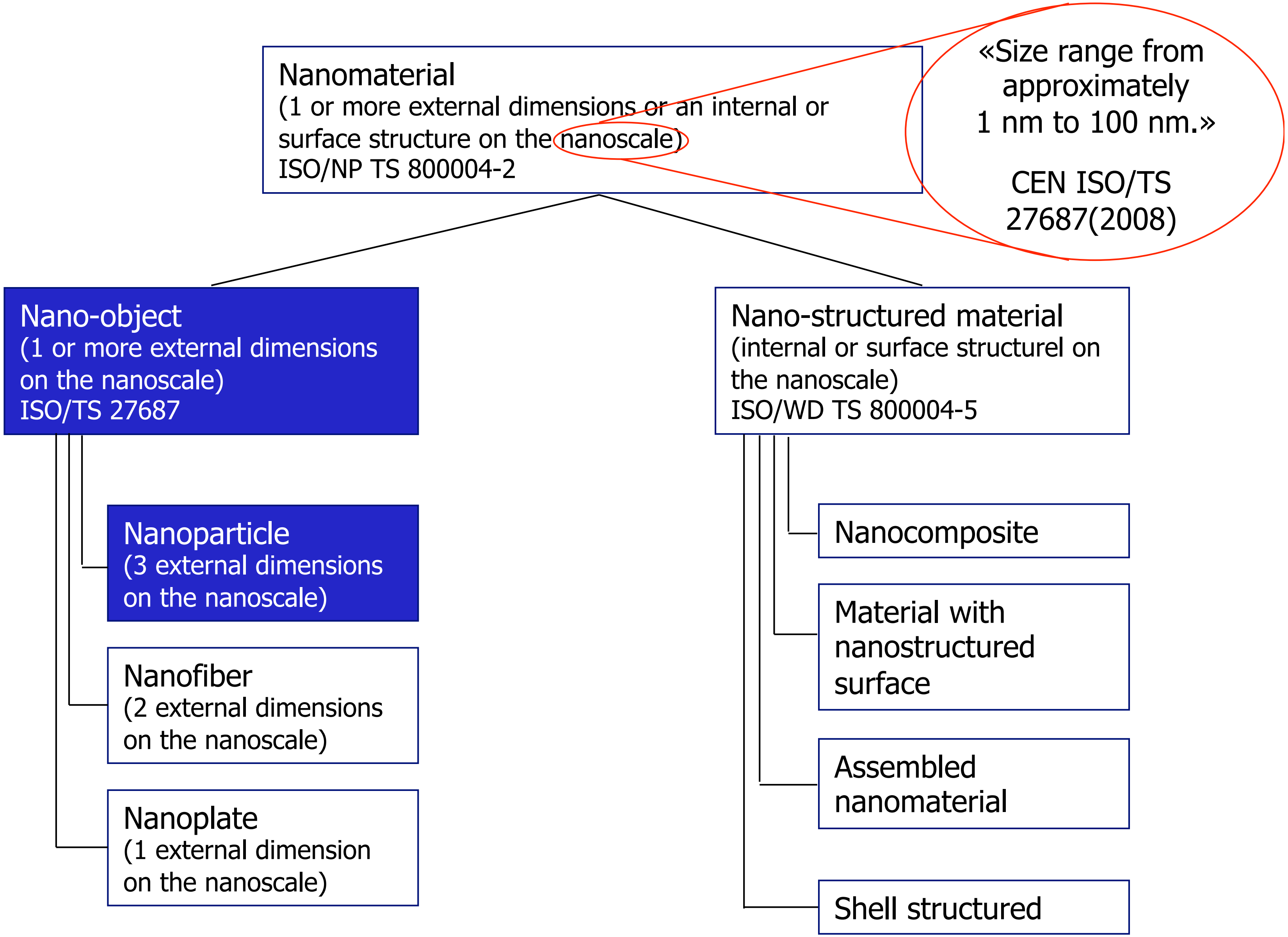
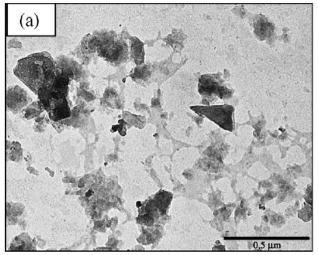
1. Nano-objects and nanoparticles



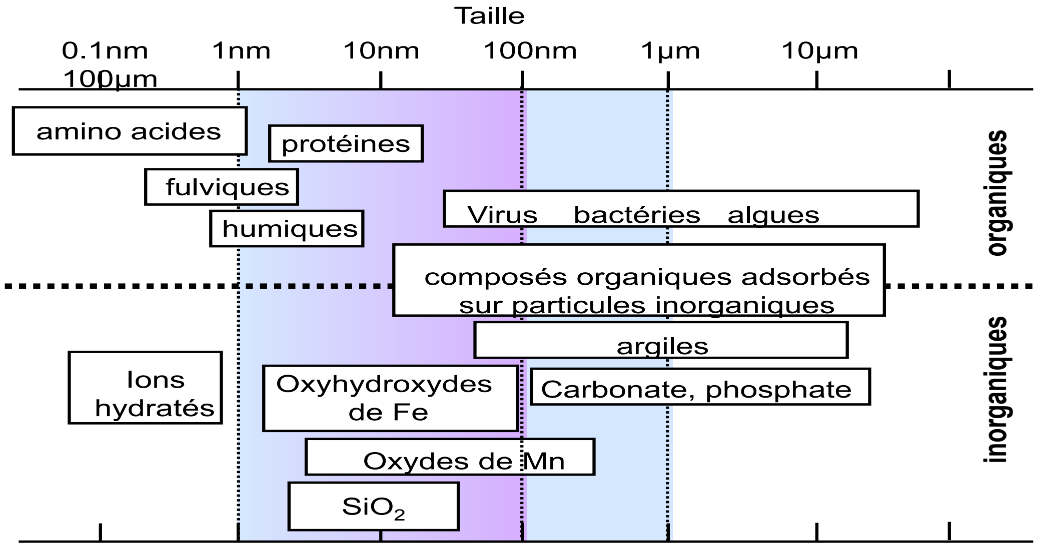
From JRC European Commission and Co-Nanomet, 2009

→ Differents types of nanoparticles :

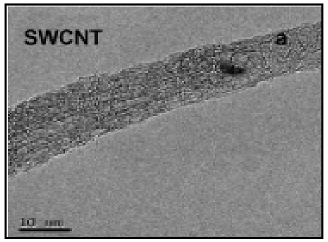
natural, in the environment :



Soil extract



manufactured :



Carbon nanotubes

	Examples	Applications
Carbon Based	nanotubes (CNT) simples or fonctionnalized	automobile, aeronautics, sport, electronics, textiles, plastics...
	fullerenes simples or fonctionnalizd	improving the optical or electrical properties of polymers, medicine & pharmaceutical appl.
	nanoglobules, nanosphères	pharmaceutical products
Inorganic	nanopowders of metal oxides	TiO_2 , ZnO : UV absorbants in sum creams, polymers & textiles; Fe_2O_3 : medical imaging NMR ; SiO_2 : abrasive ; CuO : bactericide
	metal nanopowders	Au : therapy, biology, catalysis... Ag : bactéeicide Fe : magnetic materials
	alumino-silicates	zeolites: catalysis, filtration (air/water) ceramic: photocatalysis, biology clays : lubricants, improving the thermal prop. of polymers...

Nanoparticles in environment and health effect, G. Lespes, Dans “Metallomics: Analytical techniques and speciation methods” Chap. 11 (2016) 319-337 (ISBN : 978-3-527-33969-3)

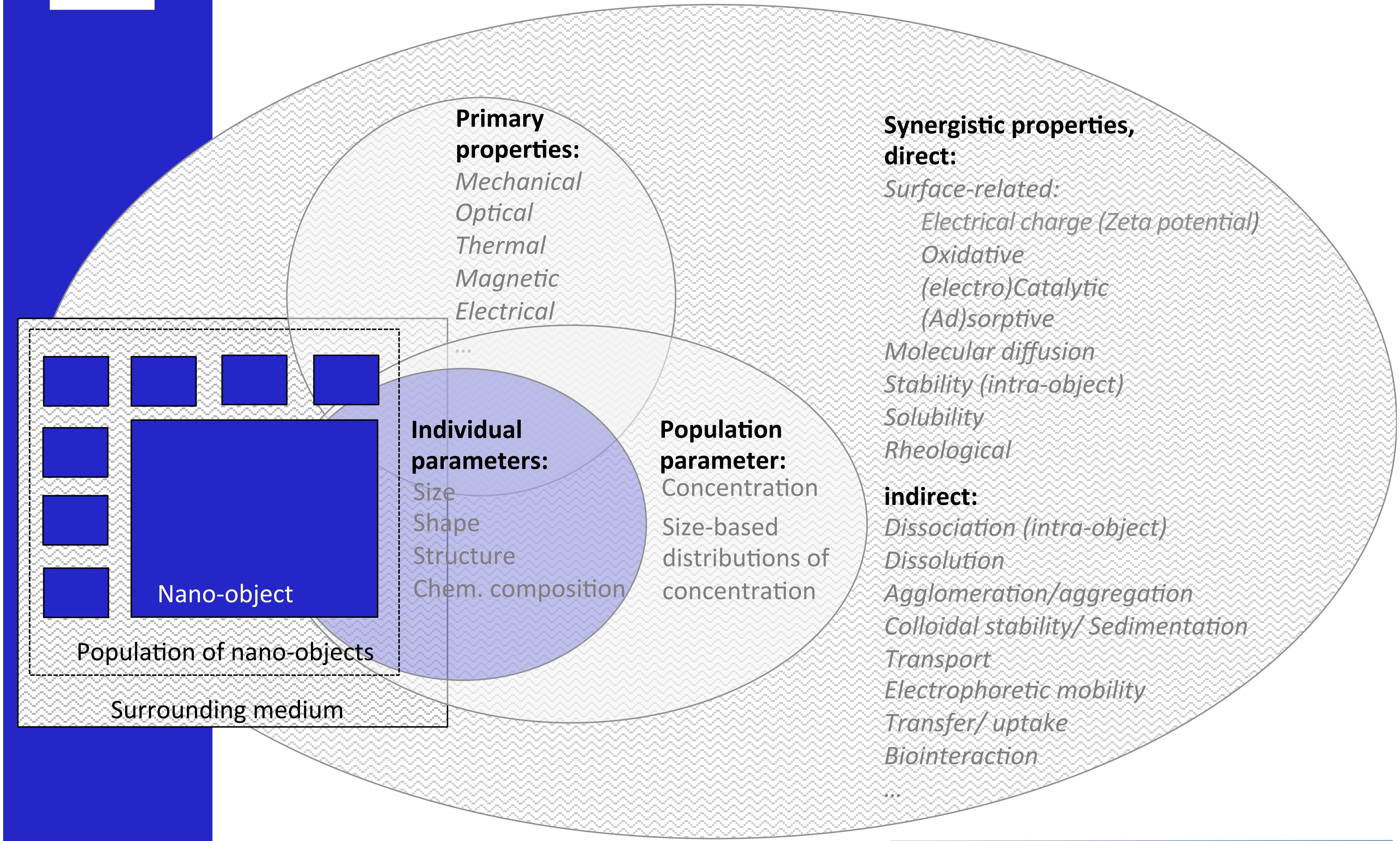
2. How to describe nanoparticle ?

→ Intrinsic parameters

Parameter	*Scale of observation*	Possible descriptor(s)
Size	*Nano-object*	Geometrical diameter or length or other typical dimensions, if shape is known
		Sphere-equivalent diameter
Shape	*Nano-object*	Geometrical shape (i.e. sphere, rod, polyhedron…) if relevant / possible
		Aspect ratio (*i.e. ratio between the respective longest and shortest dimensions of a nano-object, e.g. length-to-diameter ratio*) (ar)
		Shape factor (*i.e. ratio between gyration radius and hydrodynamic radius*) (ρ)
Structure	*Nano-object*	Chemical map *(Homogeneous or composite or structured, e.g. hollow, core-shell…)*
		Density
	Constitutive material	Porosity *(or specific surface area)*
		Crystalline state
Chemical composition	*Nano-object*	Elemental composition or ratio(s), in the whole and/or different structural components (*e.g. core-shell*)
	Surface	Surface functional group(s) and/ or elemental composition of the material at the surface of the nano-object

Nanoanalytics: History, concepts and specificities"
S. Faucher, P. Le Coustumer, G. Lespes, Environ. Sci. Pollut. Res (2018)

→ Compilation of intrinsic parameters and properties of nanoparticles, from the individual scale to the population scale



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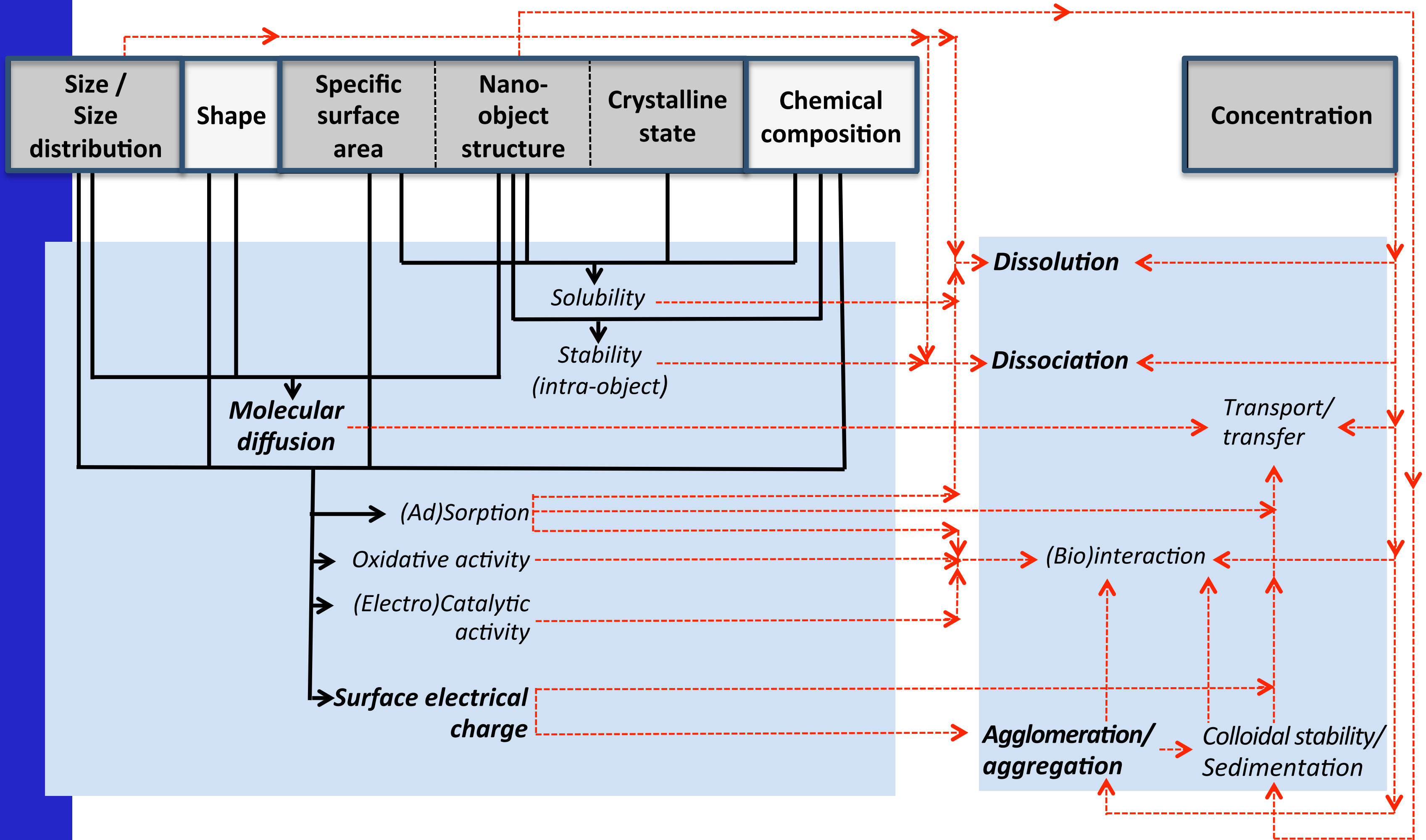
3. Nanoparticle characterization

3.1. Objectives

The physico-chemical characterisitics to determined are selected by considering (1) all the intrinsic parameters and properties that can describe the nanoparticles, (2) the link between parameter and properties, (3) the parameters and properties that can be measured directly.



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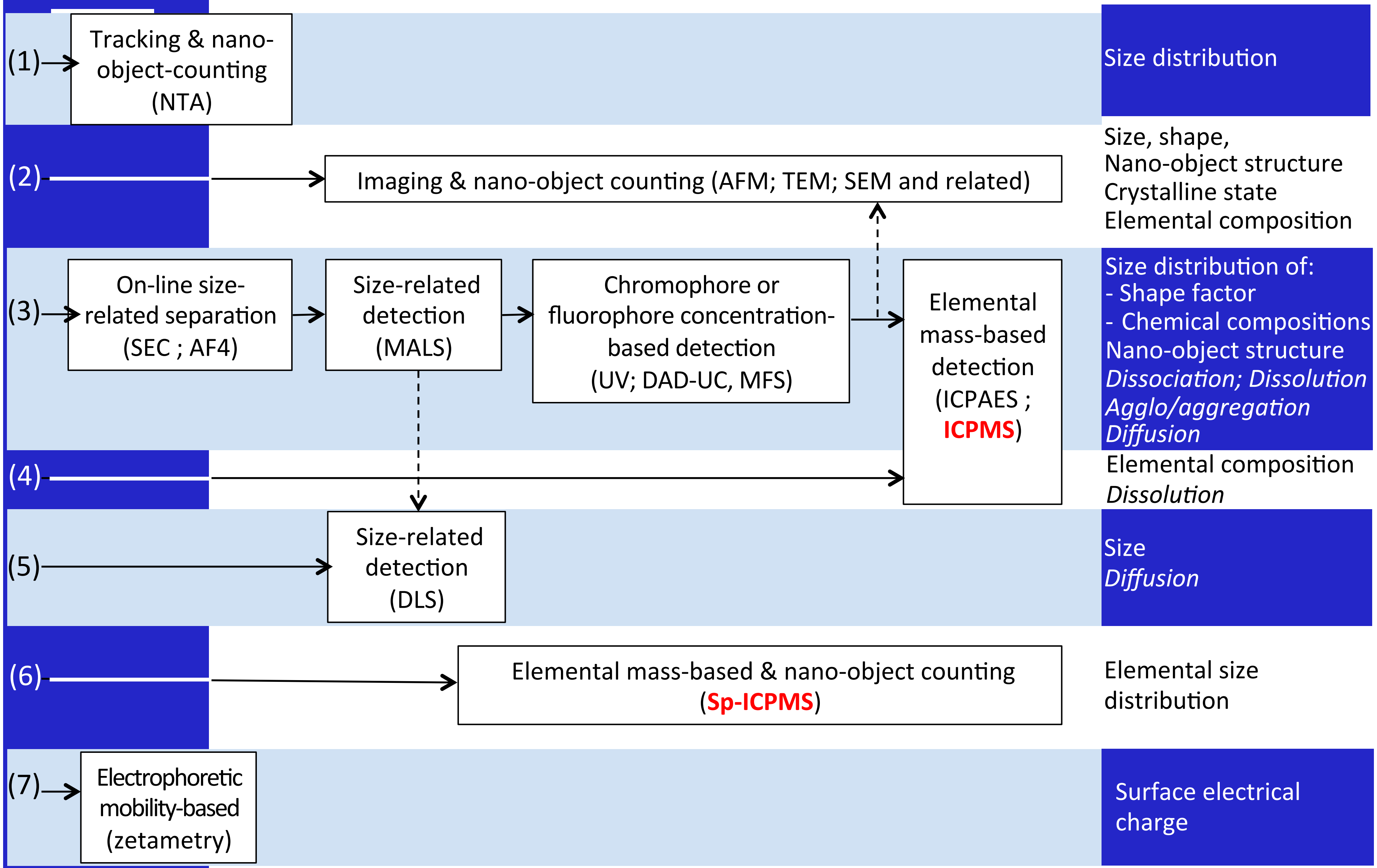
S. Faucher, P. Le Coustumer, G. Lespes, Environ. Sci. Pollut. Res (2018)

3.2. Main characterization methods



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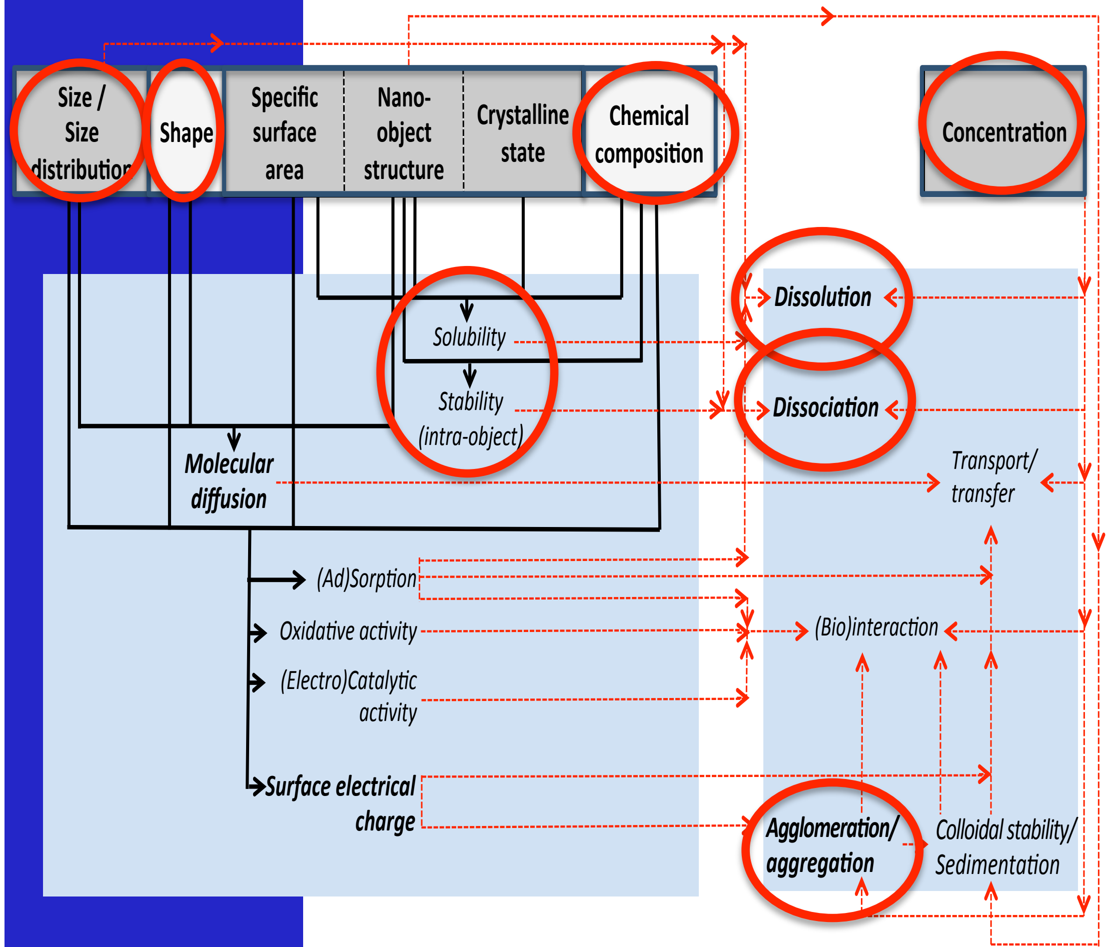
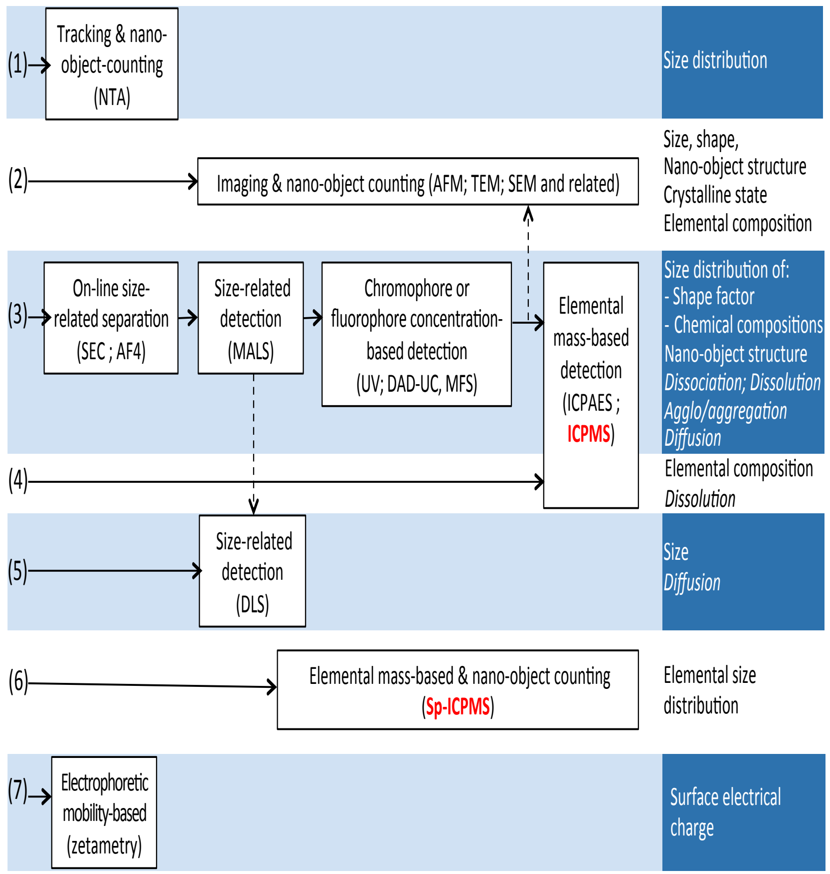
S. Faucher, P. Le Coustumer, G. Lespes, Environ. Sci. Pollut. Res (2018)

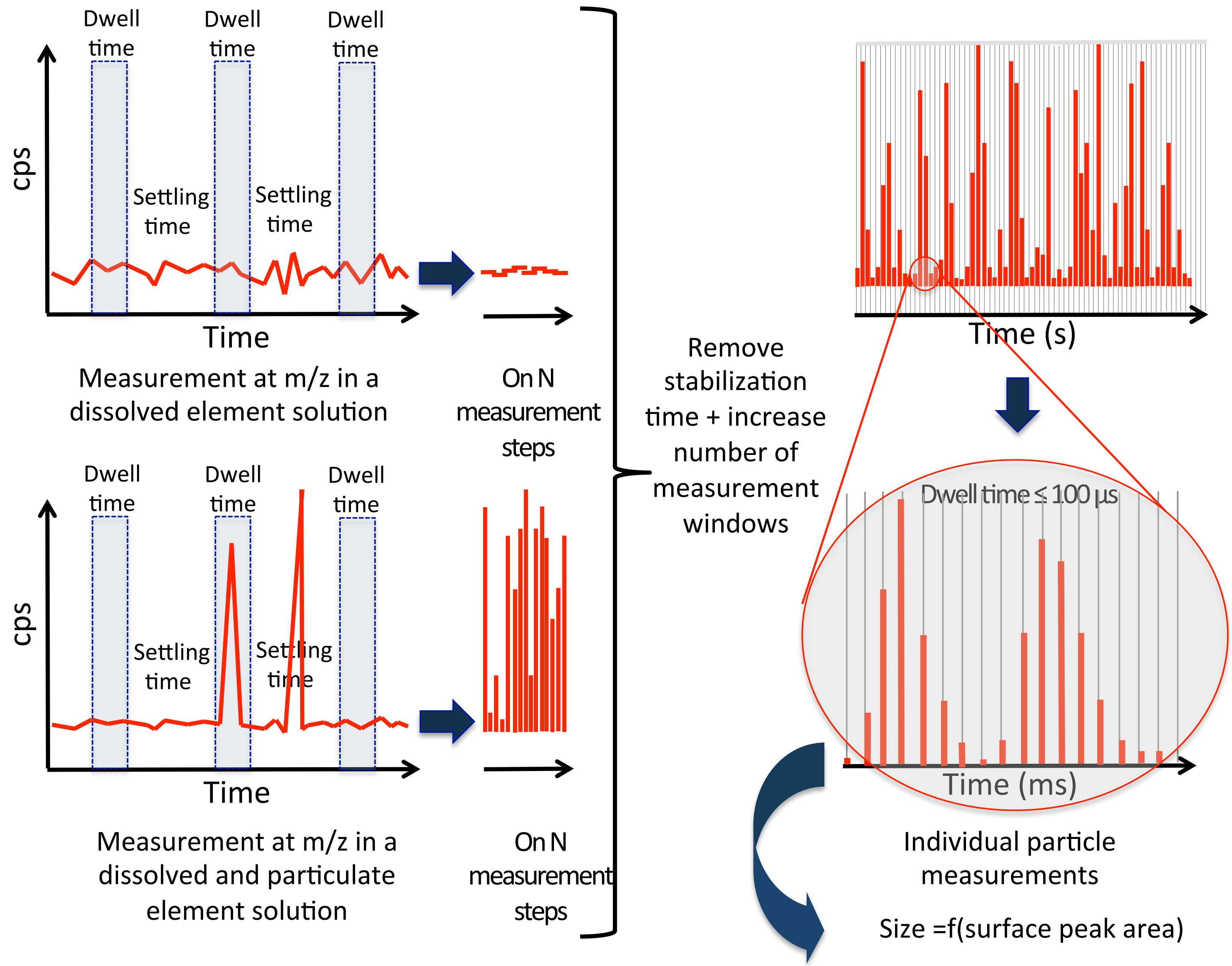
→ Focus on the IPC-MS: what does it allow to determine?



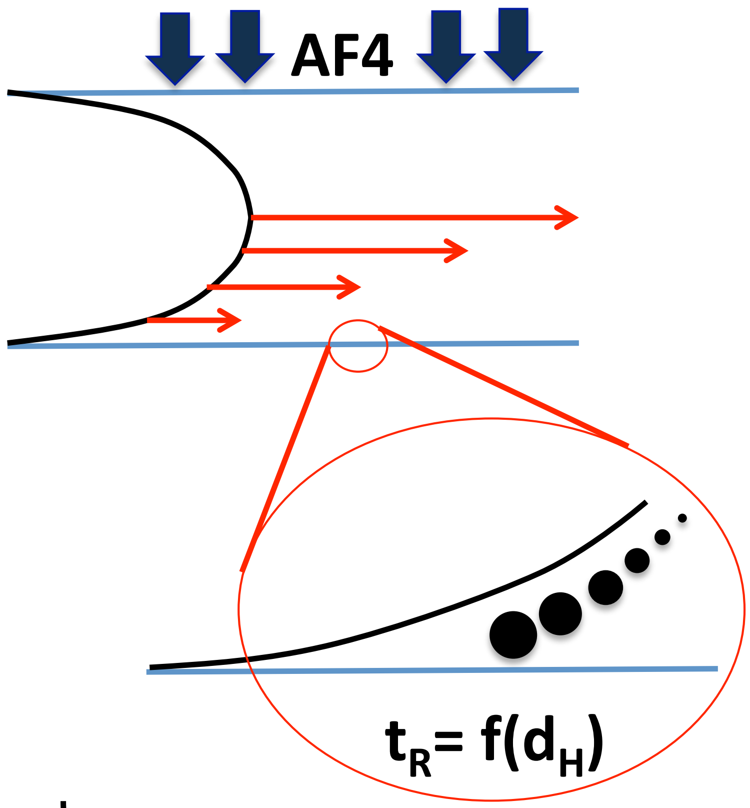


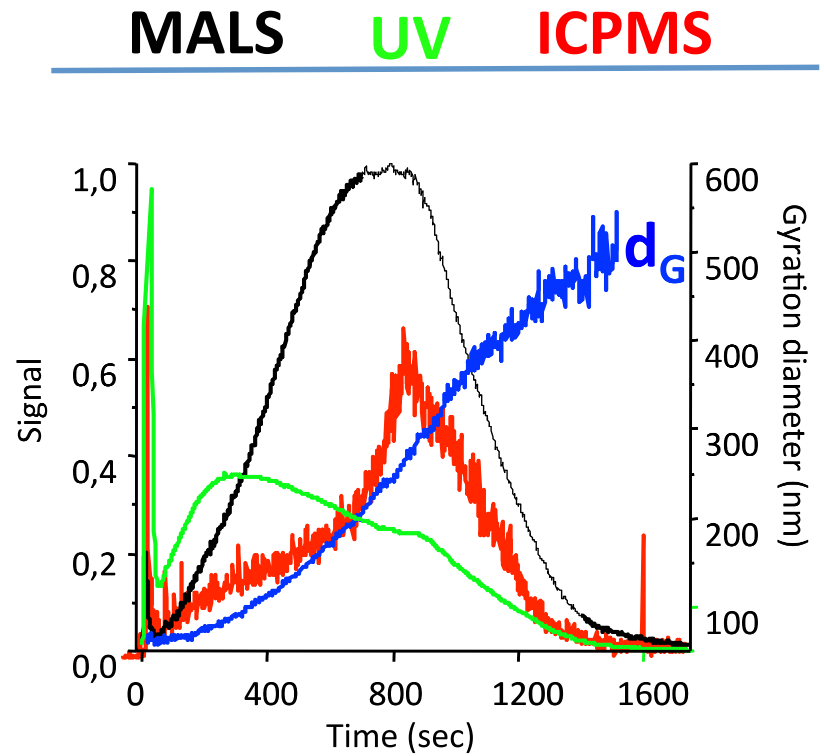
3.3. sp-ICP-MS *vs* AF4-MALS-ICP-MS

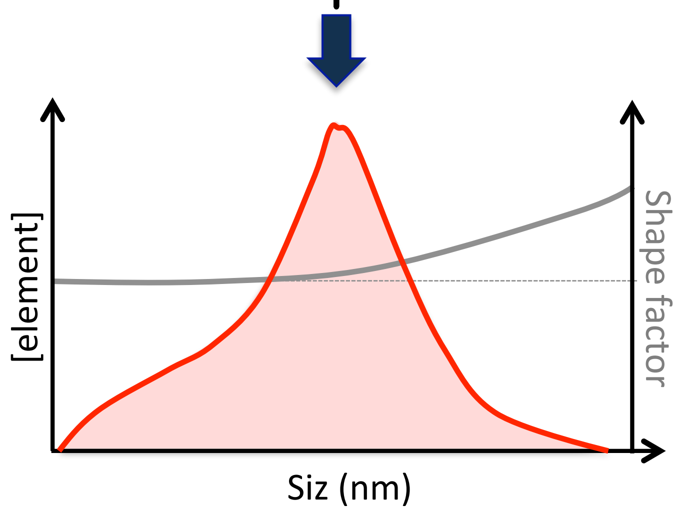
→ Sp-ICP-MS « Individual particle counting »



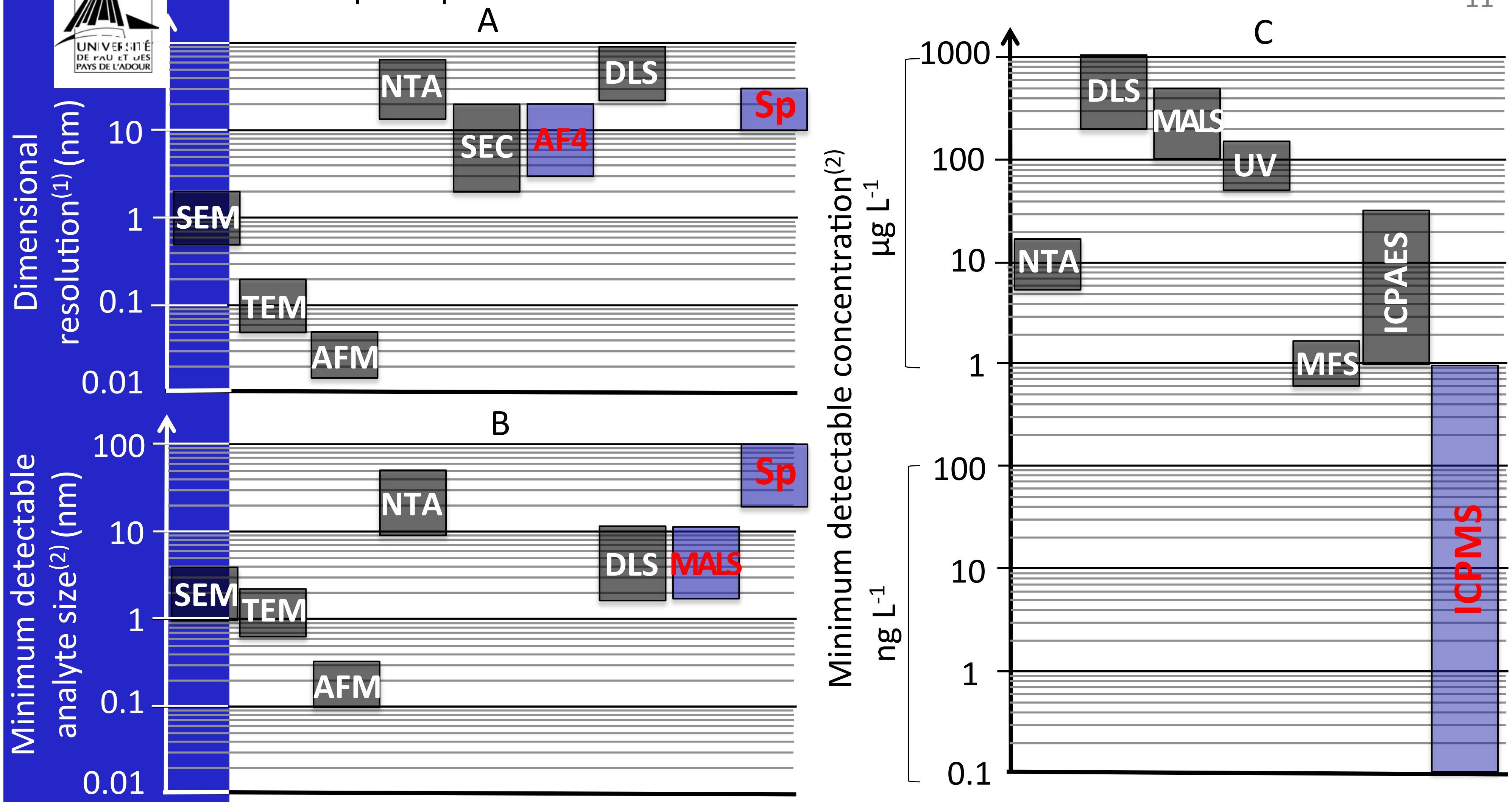
→ AF4-MALS-ICP-MS « Sorting of particles according to their size, then characterization »







→ Compared performances



(1) Spatial resolution for microscopu; Resolution estimated over 1-100 nm for DLS, SEC and AF4, from the minimum size difference btween 2 adjacent peaks that can be observed

(2) Depend on elements taken into account ICP-MS

→ **Sp-ICP-MS « simpler and direct » to instrumentally implement**

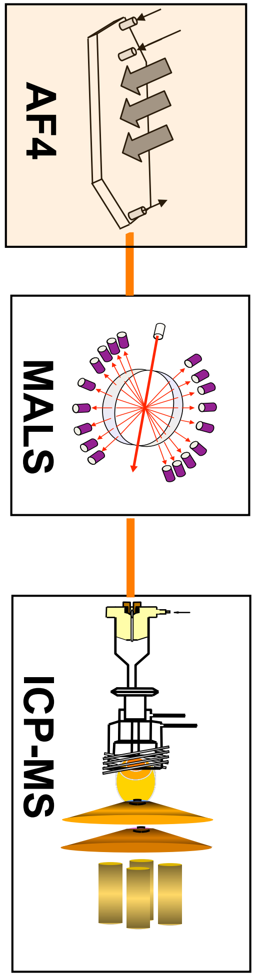
→ **AF4-MALS-ICPMS more complex, non based on hypotheses concerning shape or transfer rate, more resolved, better taking into account the nanorange, multielemental, with reduced sampe preparation**

3.3. Focus on AF4-MALS-ICPMS

Size range (nm)	≈(10 – 500)
Morphology information (nm)	*10- 500*
Size selectivity	0,8 – 1
Recovery (%)	> 90
Repeatability (%)	
peak top	2 - 3
half height	2 - 3

	Zn	Cd	Se
Relative detection limits (µg L^{-1})*	0,03	0,01	0,05
Repeatability (%)	3 à 10		
Size discrimination	*depends of the type of particles no observed in the following studies*		

*100 µL injected



Dimensional Fractionnation

Size /size distribution

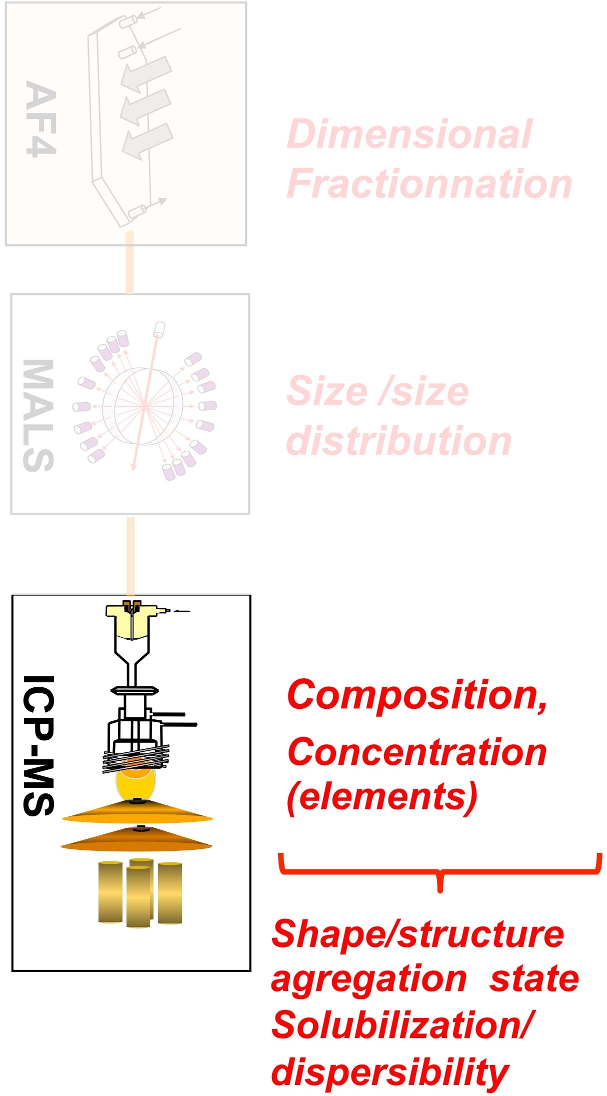
Composition, Concentration (elements)

Shape/structure agregation state Solubilization/ dispersibility

Other performances
TiO_2 nanoparticles & Gold- silver nanoshells (Au-Ag NS)

	^{46}Ti ^{49}Ti*	^{197}Au**	^{107}Ag ^{109}Ag**
Particle type	*TiO_2 NP (E 171)*	*Au NP, Au-Ag NS, Au-Ag NS@hybrid silica*	
Size range taille (nm)	*100- 300*	*20- 200*	
Relative detection limits	0,7 ($\mu g\ g^{-1}$)	5 ($ng\ L^{-1}$) <0,3 ($\mu g\ g^{-1}$)	8 2 ($ng\ L^{-1}$) <0,04 ($\mu g\ g^{-1}$)
Repeatability (%) Overall analytical process ICPMS analysis	 ≤ 6 ≤ 2	 ≤ 4 ≤ 2	 ≤ 4 ≤ 2
Mean recovery (%)	100	100	100

* Biological tissue
** Cell samples and suspensions



F. Faucher, G. Lespes "Quantification of titanium from TiO2 particles in biological tissue", J. Trace Elements in Medicine and Biology, 2015, 32:40-44
F. Faucher, S. Soulé, A-L. Bulteau, J. Allouche, G. Lespes " Gold and silver quantification from gold-silver nanoshells in HaCaT cells ", J. Trace Elements in Medicine and Biology, 2018, 47:70-78

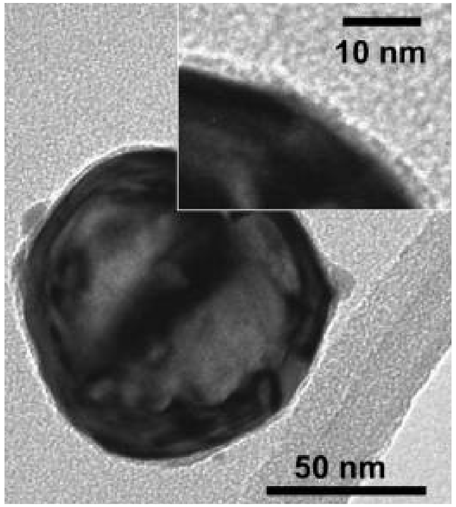
4. Examples of characterization

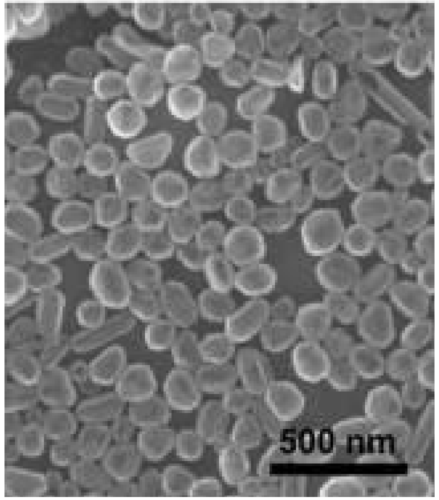
4.1. Au-Ag NS

Main characteristics

Particle type	Au NP	Au-Ag NS	Au-Ag NS@PLL	Au-Ag NS@PLL-SiO_2
Size range (nm)	25-200	70-150	70-150	80-160
Coating thickness (nm)	-	-	10	15
Atomic ratio (Ag/Au)	-	1,82 ±0,07* // 1,71 ±0,05**		
(*Mass ratio (Ag/Au)*)	-	*1,00 ±0,04* // 0,93±0,04***		

* XPS ** ICPMS





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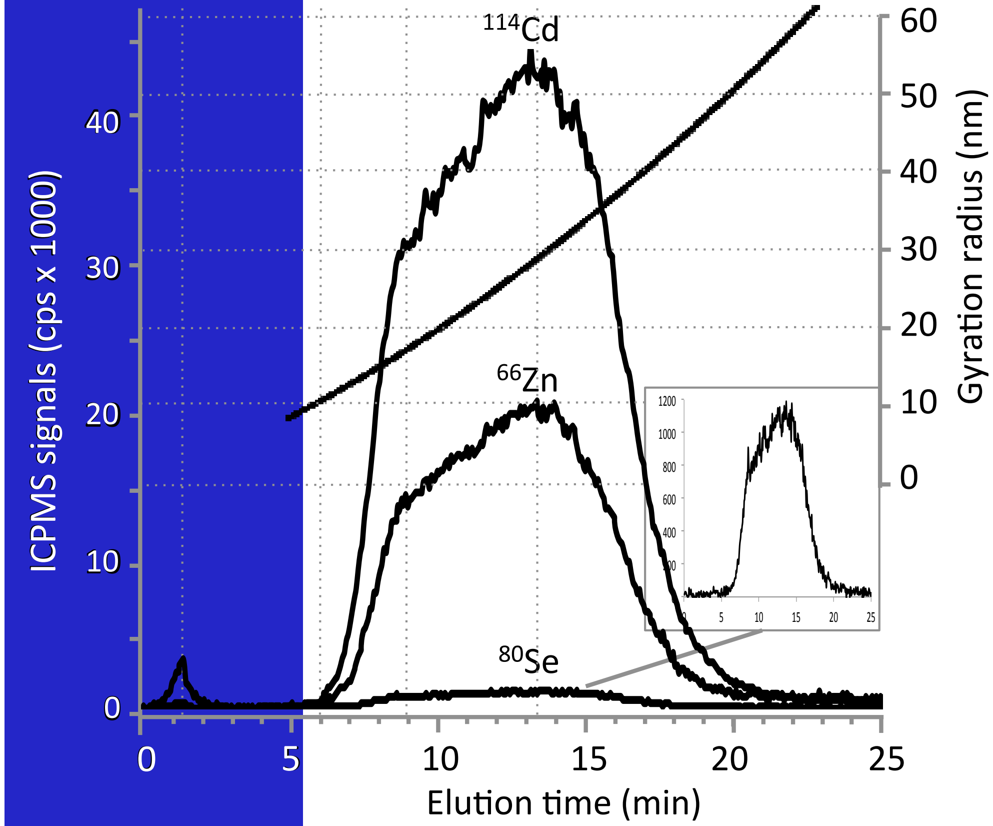
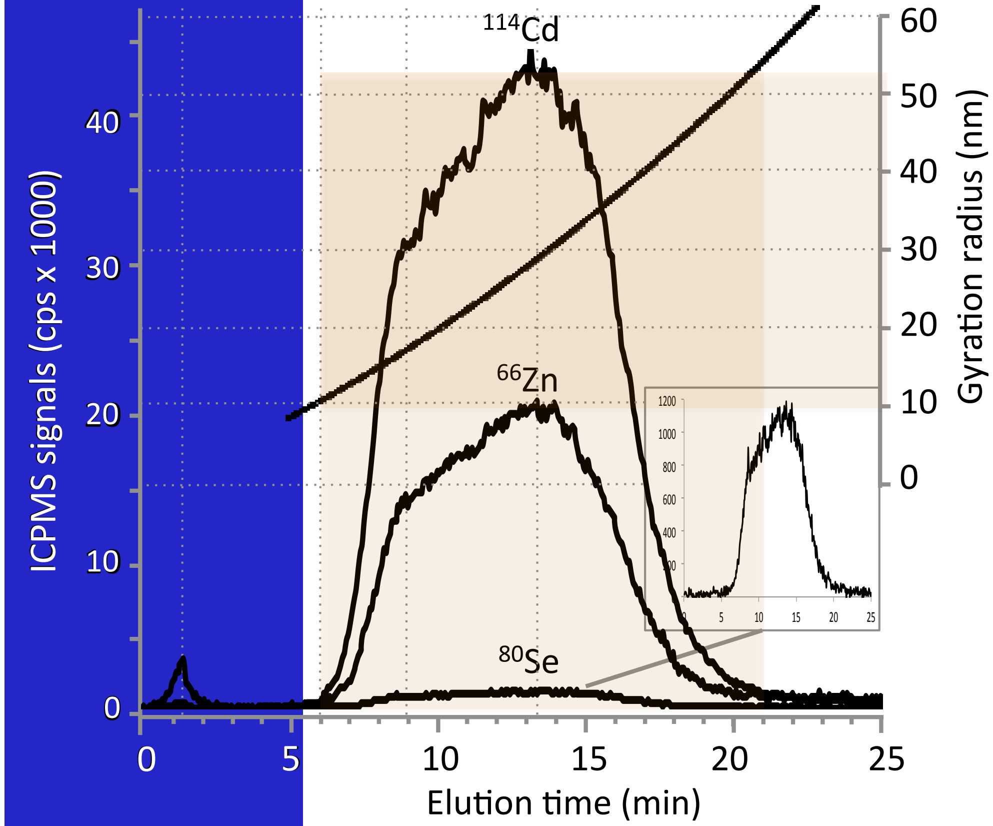
S. Soulé, A.L. Bulteau, S. Faucher, et al., "Design and cellular fate of bioinspired Au-Ag nanoshells@hybrid silica particles", Langmuir, 2016, 32:10073-10082

4.2. CdSe/ZnS quantum dots (QD)



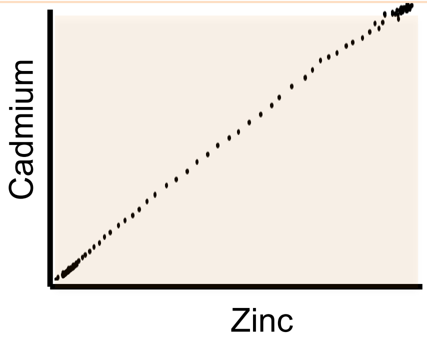
QD test suspension prepared from the synthesis batch (1:200 v:v)

F. Faucher, G. Charon, E. Lützen, P. Le Coustumer, Y. Sivry, G. Lespes " Characterization of polymer-coated CdSe/ZnS quantum dots and investigation of their behaviour in soil solution at relevant concentration by asymmetric flow field-flow fractionation- multi angle light scattering- inductively coupled plasma- mass spectrometry" Anal Chim Acta, 2018, 1028:104-112



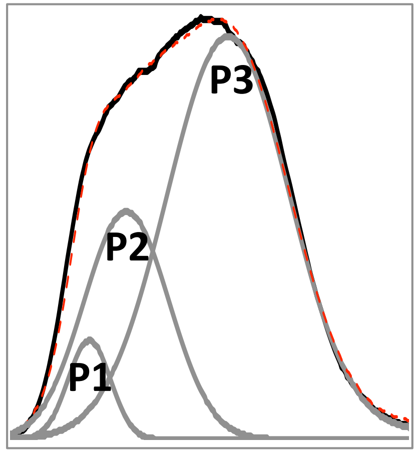
$[Zn] = (450 \pm 10)\ \mu g.L^{-1}$
$[Cd] = (144 \pm 4)\ \mu g.L^{-1}$
$[Se] = (77 \pm 3)\ \mu g.L^{-1}$

Size range (P-QDs) : ≈ 20- 100 nm ≥ *15*



Nucleus metal composition, homogeneous over the size range

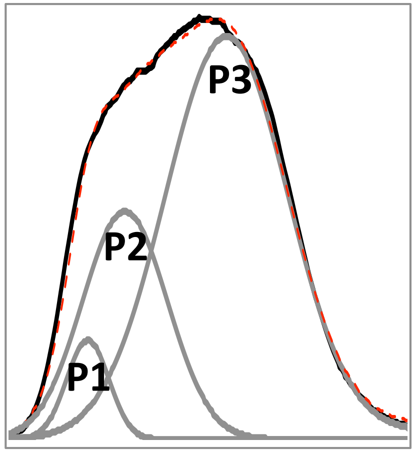
DLS : 30-100 nm ; 2 populations



	Diameter (P-QDs)	Relative concentration
P3:	(68 ± 8) nm	(68,7±0,8)%
P2:	(44 ± 5) nm	(26,3±0,5)%
P1:	(36 ±2) nm	(5,0±0,3)%

Metal nucleus diameter : (6,0 ± 0,1) nm	*6,8*	*Mean values*
Core diameter : (3,20 ± 0,05) nm	*3,2*	
Shell thickness : (1,36 ± 0,05) nm	*1,8*	

Size range (P-QDs) : ≈ 20- 100 nm *≥ 15*



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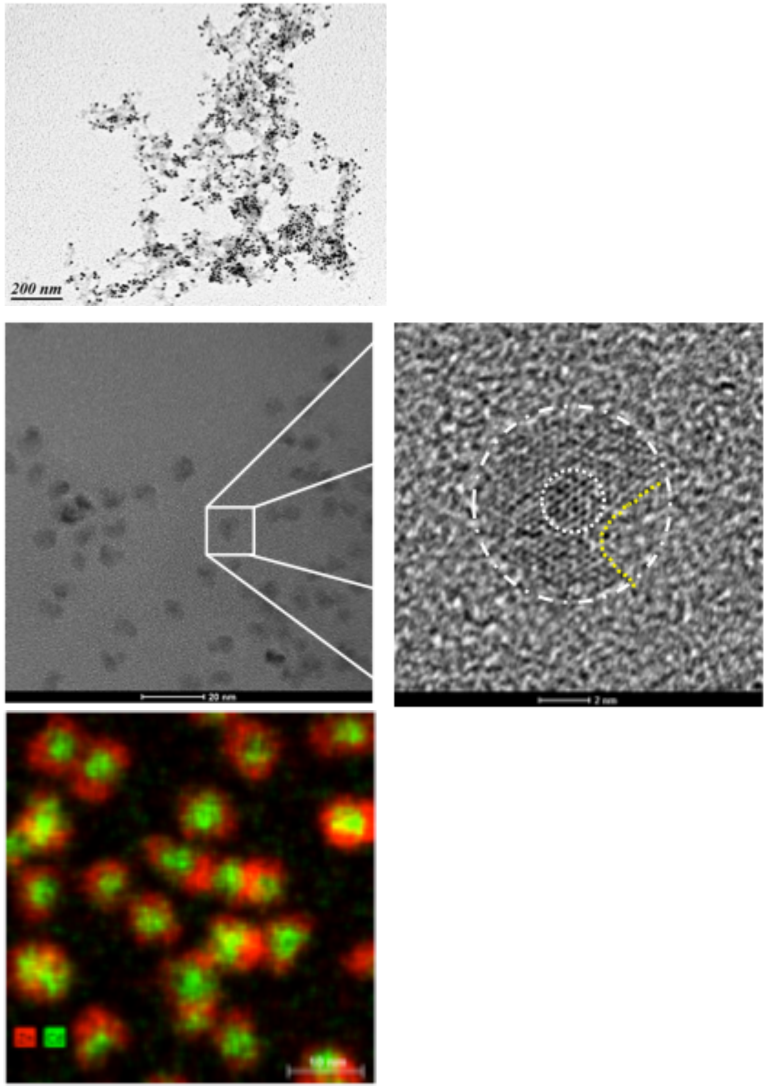
Core diameter : (3,20 ± 0,05) nm *3,2*
Shell thickness : (1,36 ± 0,05) nm *1,8*

(mean values)

A nucleus with inhomogeneous shell
A polymer coating of variable thickness

Metal nucleus diameter : between 5 and 8 nm



Bibliography

G. Lespes, “Nanoparticles in environment and health effect”, Metallomics: Analytical techniques and speciation methods, 2016, 11:319-337 (ISBN : 978-3-527-33969-3)

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