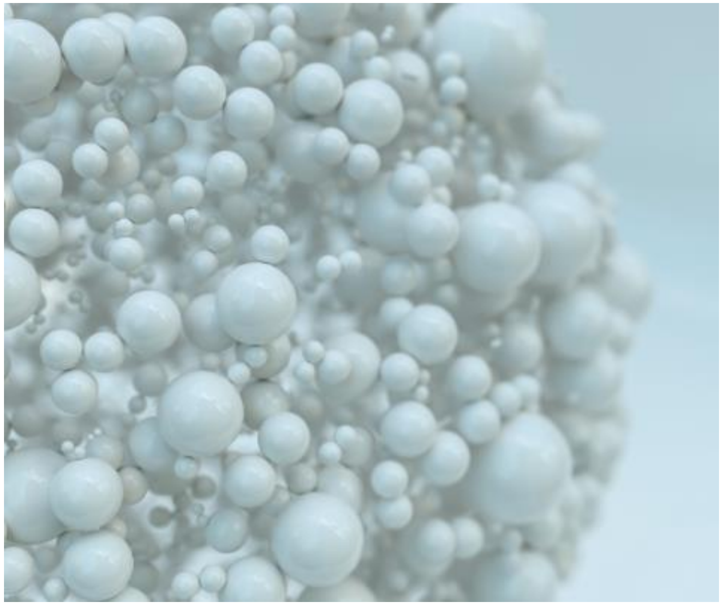
Ultra Traces Analyses Aquitaine

Adera

Nanoparticules: general introduction



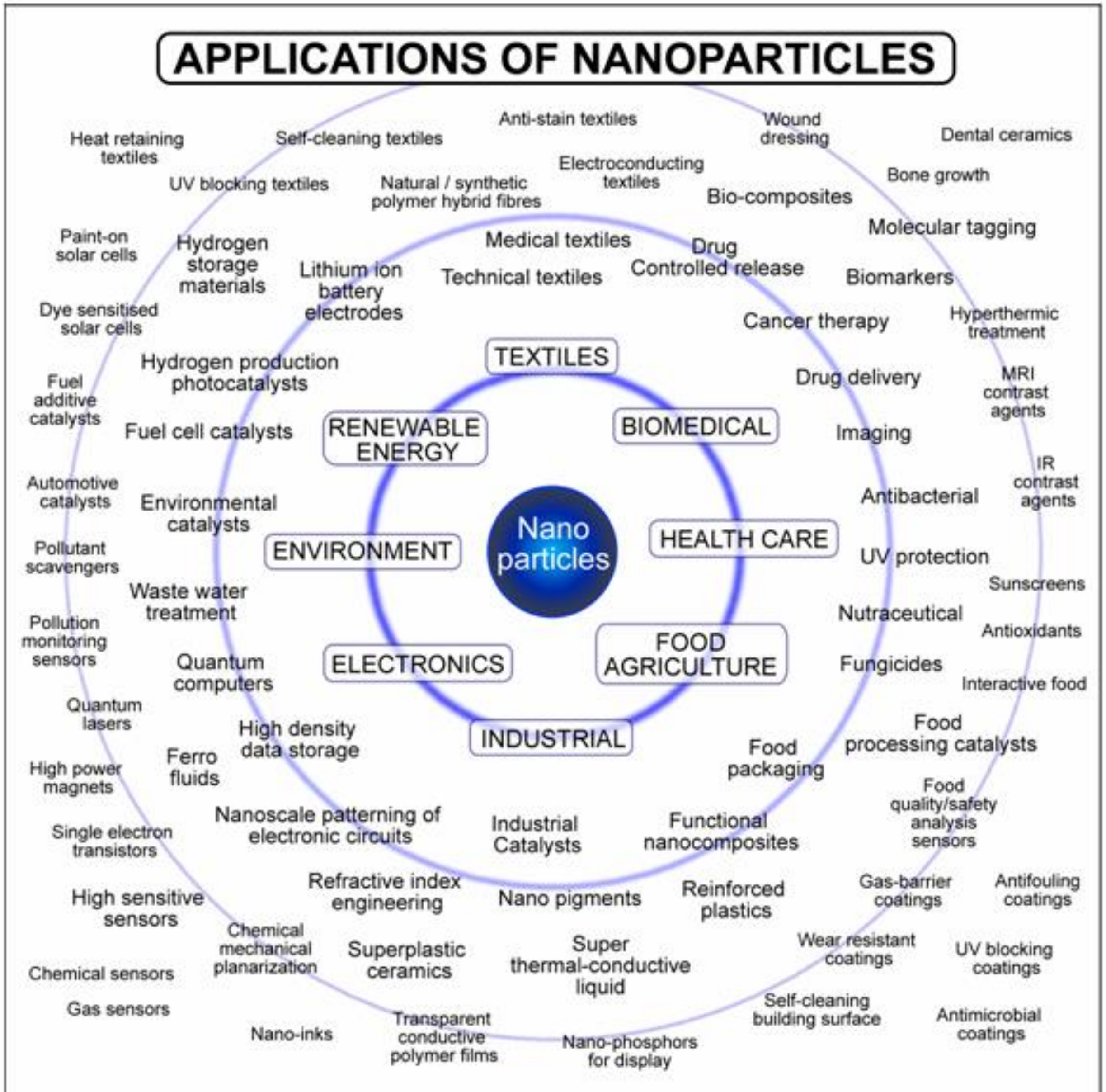
Fabienne Séby

Commission européenne

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

TUNTWIN

Use of nanoparticles



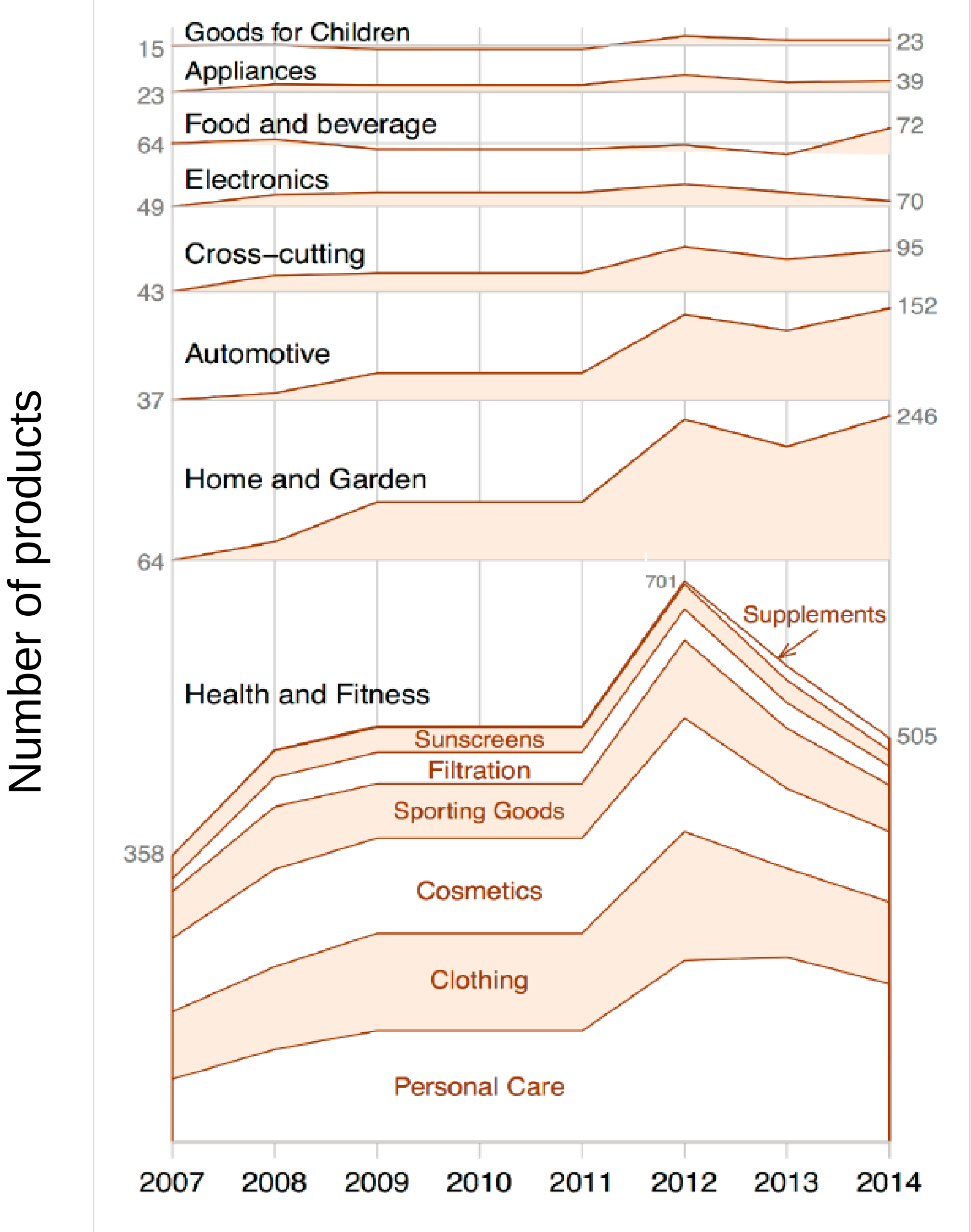
http://www.nanotechproject.org/cpi/

INVENTORY OF NANOTECHNOLOGY-BASED CONSUMER PRODUCTS

> 1600 products

TUNTWIN

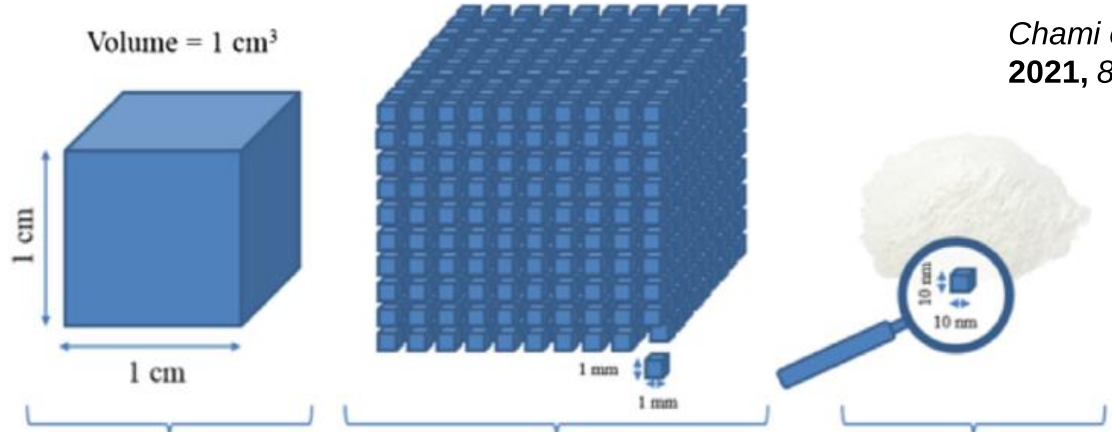
Use of NPs over time in daily products



Vance et al., Beilstein J. Nanotechnol., **2015,** *6,* 1769–1780.

Properties of nanomaterials due to size reduction

INCREASE OF THE SPECIFIC SURFACE WITH THE DECREASE IN SIZE **=**
INCREASE OF THE REACTIVITY OF THE MATERIAL

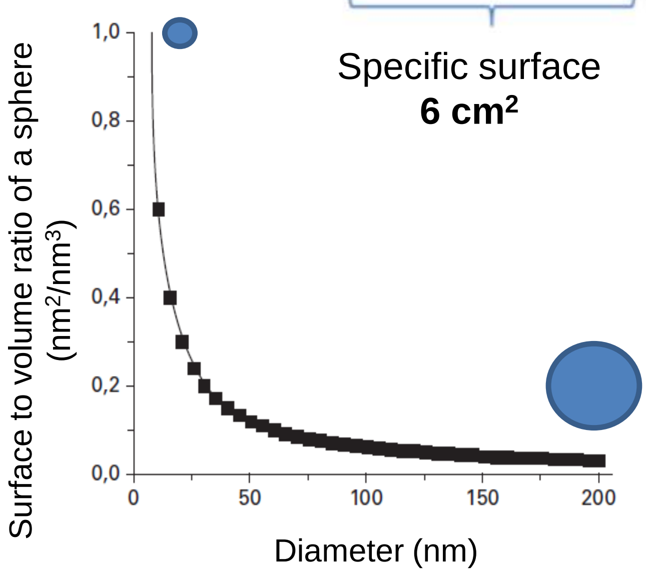


Chami et al., Arch. Mal. Prof. Env., **2021,** *82,* 51–68.

Specific surface
6 cm^2

Specific surface
1000 x 0,06 cm^2 = **60 cm^2**

Specific surface
10^{18} x 6.10^{-12} cm^2 = **6 000 000 cm^2**



Ropers, Techniques de l'ingénieur, **2020,** NM4500 v2.

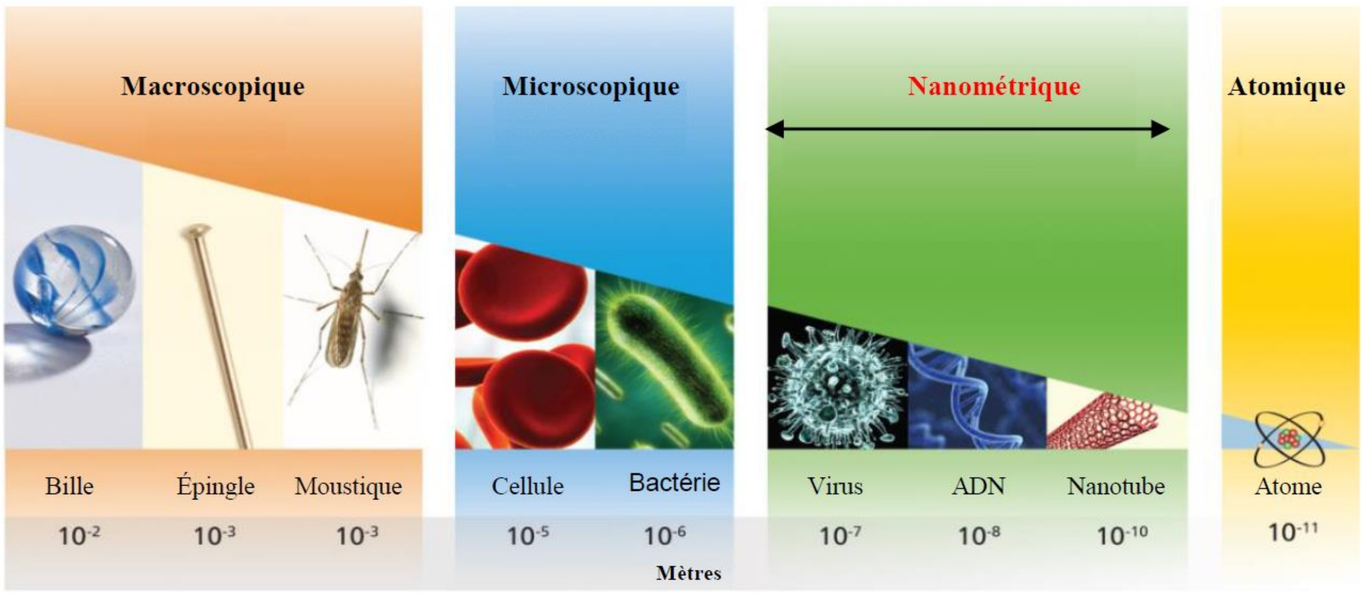
Increase of the mechanical, optical, chemical, electrical and magnetic properties of materials

Definitions associated with nanomaterials

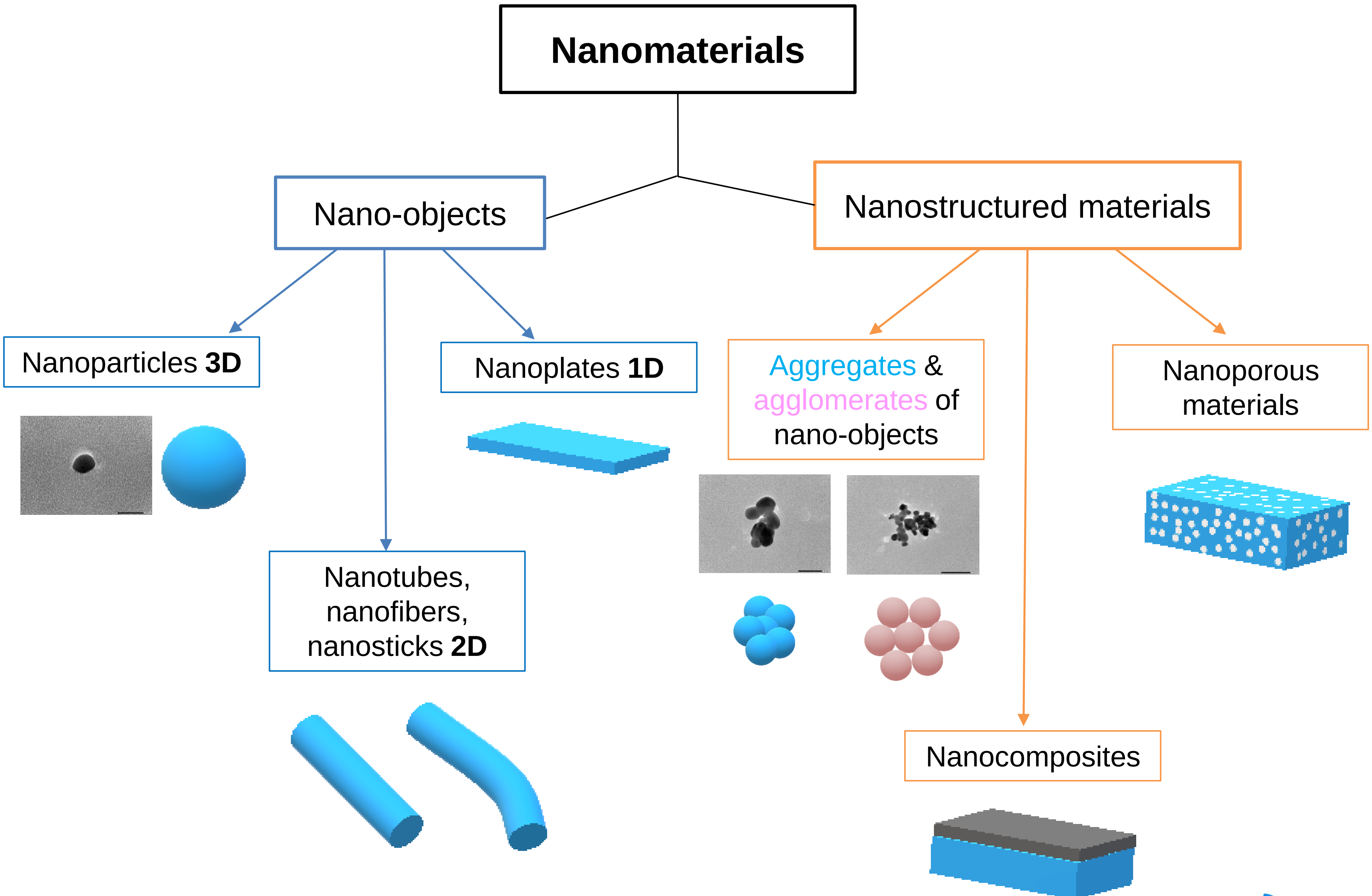
SEVERAL DEFINITIONS

- International Organization for Standardization — ISO/TS 80004-1:2005
- European Commission — 2011/696/EU (recommendation)
- Ministère de la transition écologique et solidaire — Décret n°2012-32

A natural, incidental or manufactured material containing particles, in an unbound state or as 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 - 100 nm

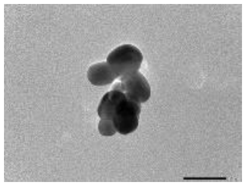


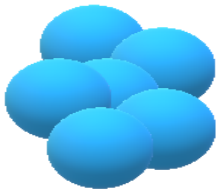
A wide variety of shapes and sizes



Aggregates and agglomerates

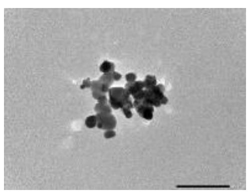
Aggregates of NPs

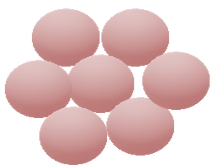




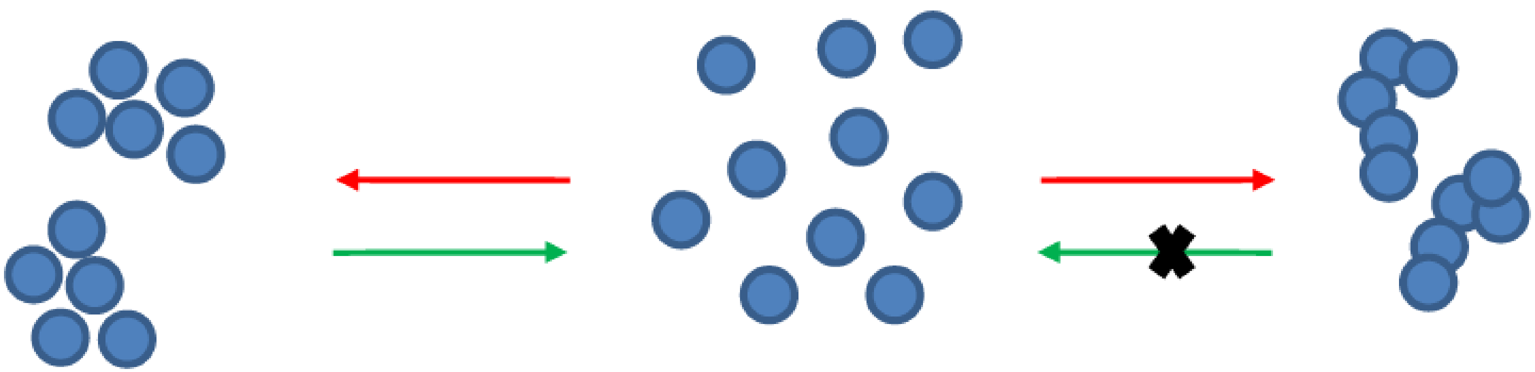
It is considered as a particle containing strongly bound or fused particles

Agglomerates of NPs





A collection of weakly bound particles or aggregates where the resulting external surface area is similar to the sum of the surface areas of the individual components



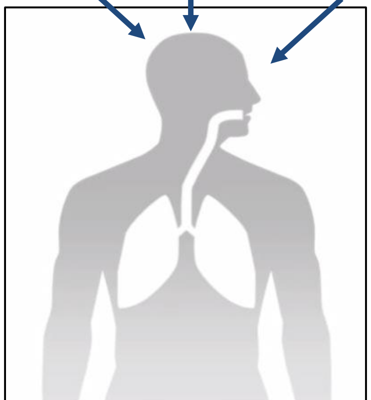
Agglomerates **Dispersed particles** **Aggregates**

Exposure routes and risks associated with nanoparticles

Air contamination

Professional exposure

Spray



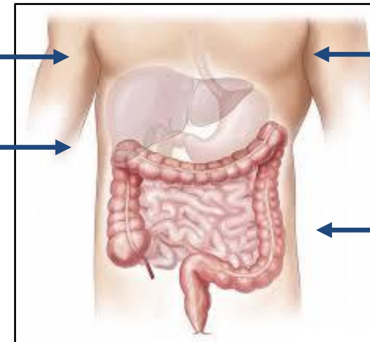
Inhalation route

Drugs

Food

Kitchen utensils

Hygiene products : toothpaste, lip balm & lipsticks …



Oral route

Clothes

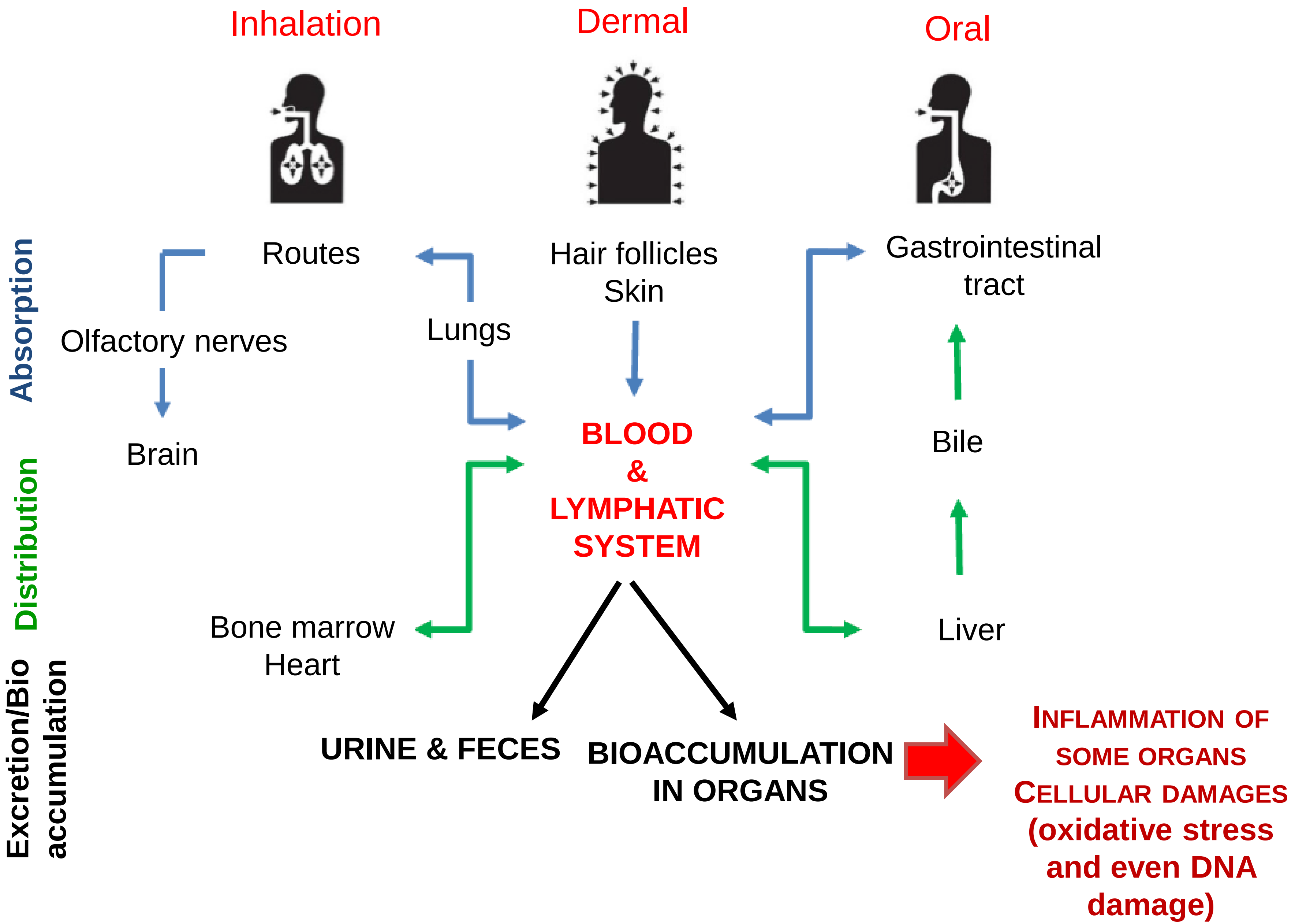
Tatoos

Cosmetics & skin care products

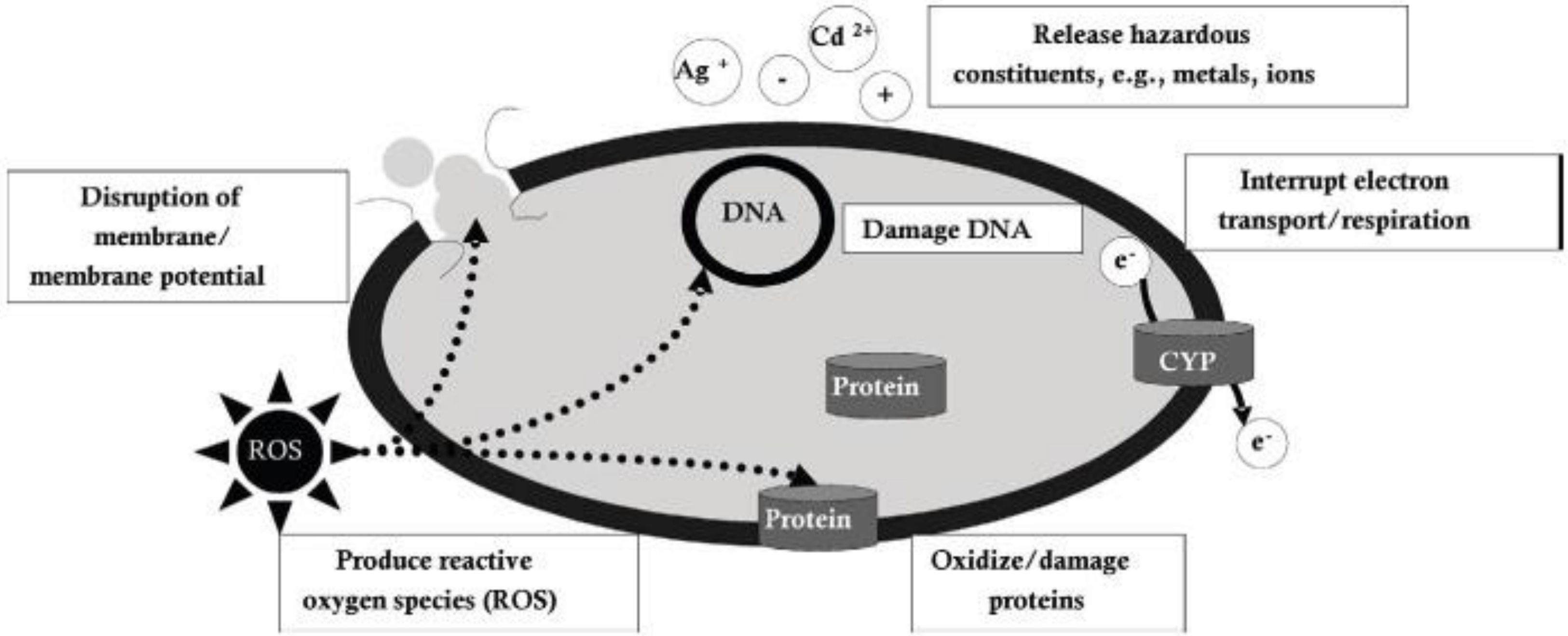
Dermal route

- Healthy skin: little penetration (*in vitro & in vivo studies*)
- Skin with lesions: possible penetration

NPs exposure, distribution and excretion routes in the body



Possible toxicity mechanisms of NMs on bacterial cells



Handy et al., Ecotoxicology., **2008,** 17, 287–314.

NPs physico-chemical properties affecting their toxicity

- **Size**: a decrease in size generally increases NPs penetration in cells and then their toxicity.

- **Surface**: A decrease in size increases the specific surface and then the chemical and biological reactivity.

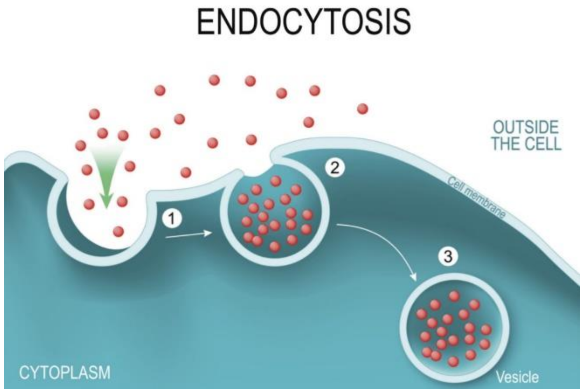
- **Number**: the increase of the number of NPs promotes their penetration and persistance in biological tissues. More easily bioaccumulated and distributed in the body.

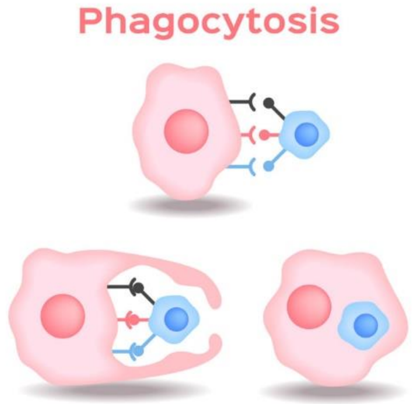
- **Shape**: nanotoxicity depends on the shape because of the cell envelopment process during endocytosis or phagocytosis. For exemple, endocytosis of a spherical form would be more easy than a nanotube.

- **Aggregation/agglomeration state**: modifies NPs deposition and penetration through cells and then their biological effects.

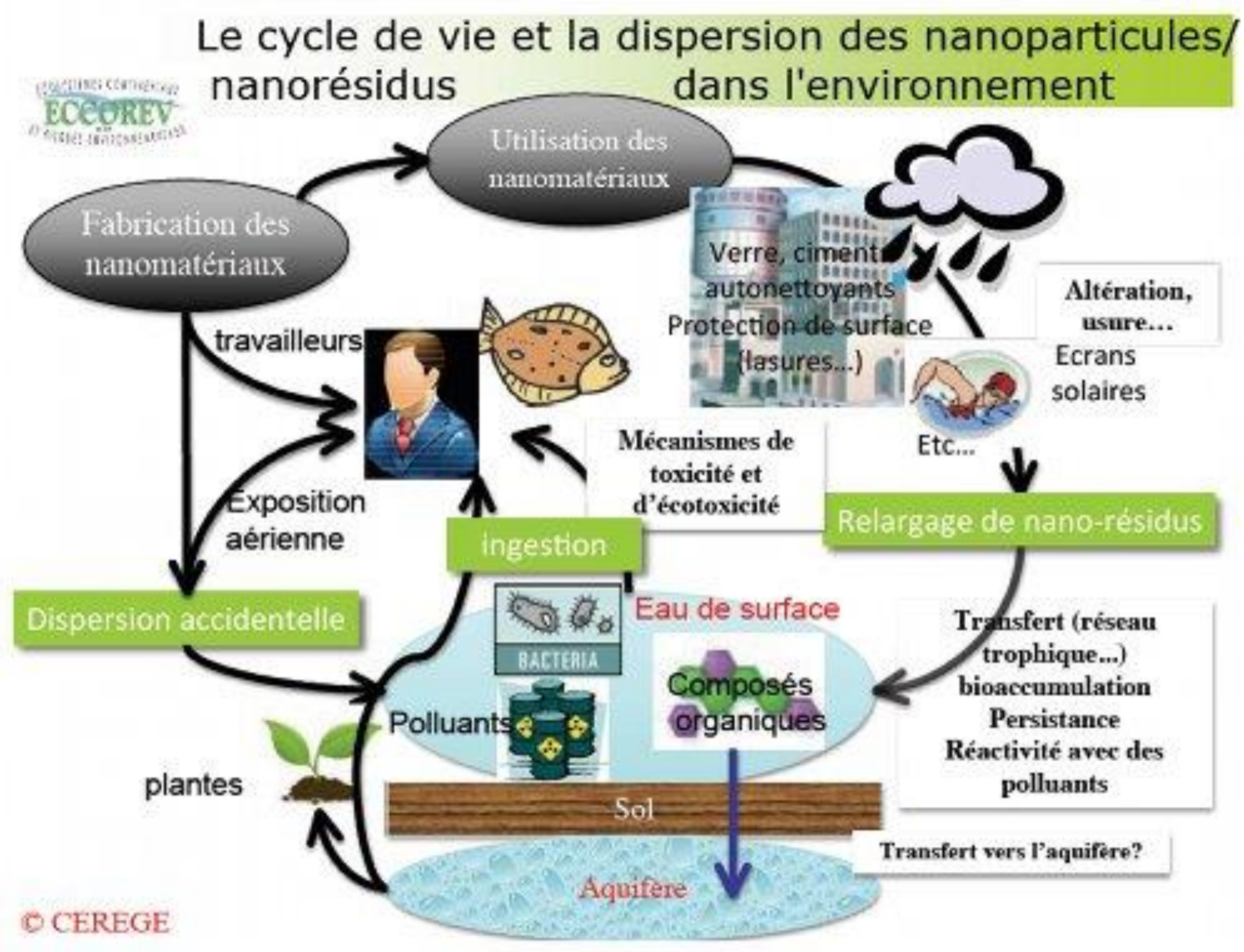
- **Crystalline structure**: plays a major role in cell absorption and the generation of reactive oxygen species (ROS). For example, toxicity of the two crystalline structures of TiO_2 is different for a similar size. Rutile would produce DNA oxidation contrary to anatase.

- **Chemical nature**: for a same size, shape or specific surface, the NPs chemical nature can influence their toxicity. For example, SiO_2 and ZnO NPs with a same size (20 nm) have different toxicity on mice, SiO_2 alters the DNA structure whereas ZnO induces an oxidative stress.

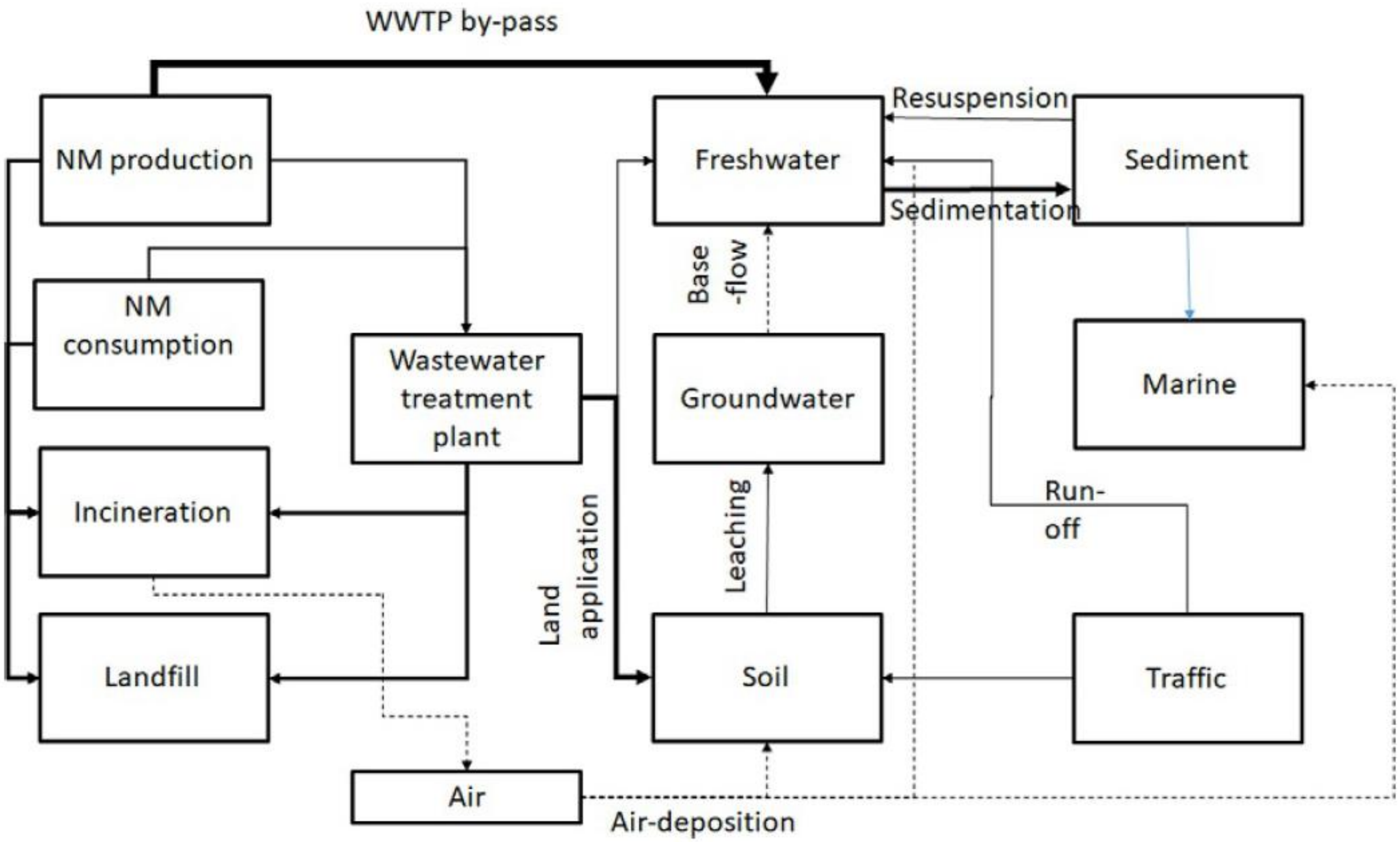




Life cycle of NPs in the environnement



Dominant fate pathways of NMs in the environment

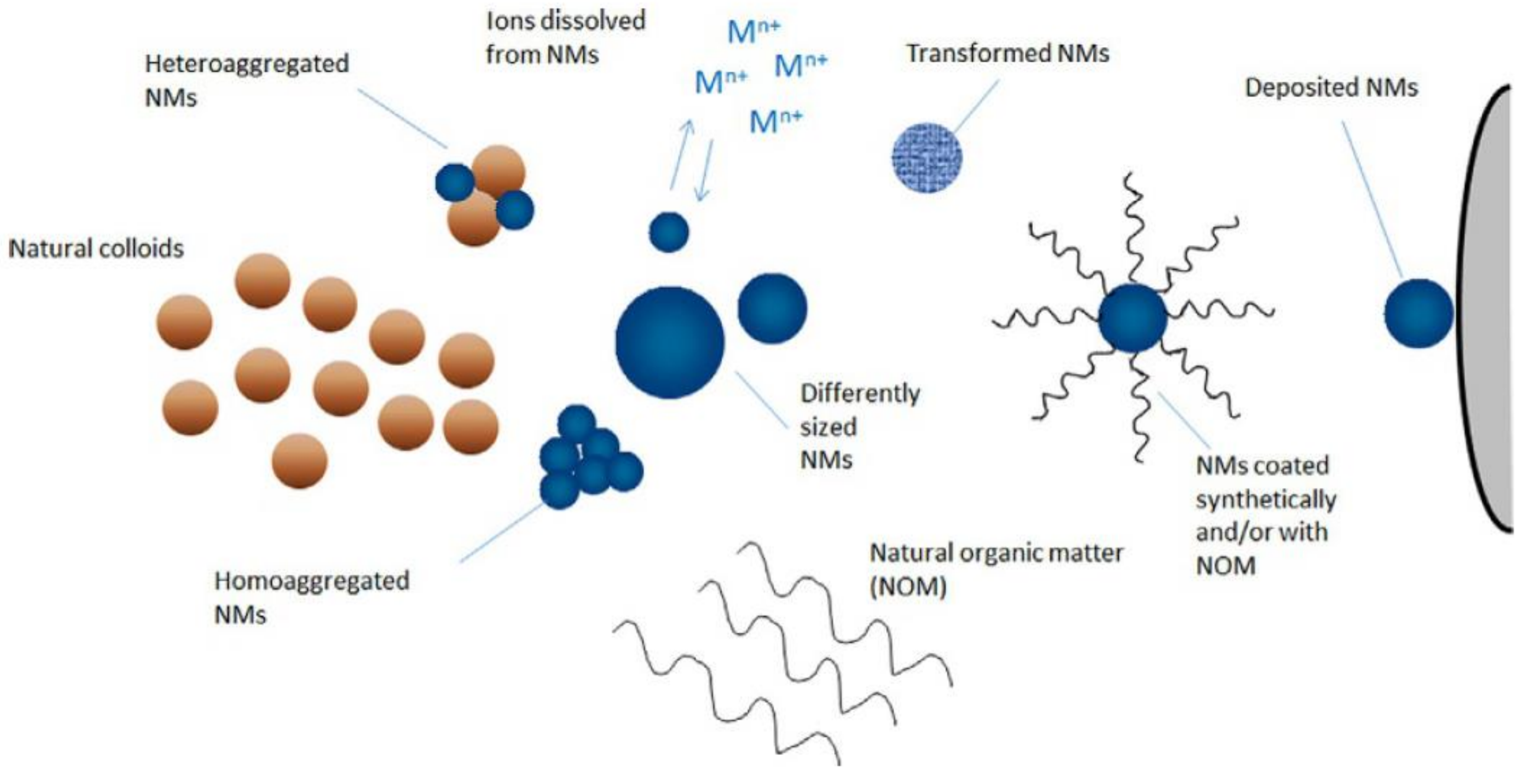


------- Poorly researched pathways

Cornelis et Lahive, Occurrence, behavior and effects of inorganic nanoparticles in the environment, In: Analysis and characterization of metal-based nanomaterials, **2021,** 93, 1–344.

Forms of occurrence of inorganic NMs in environmental compartments

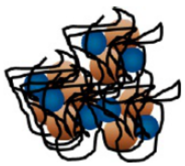
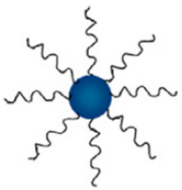
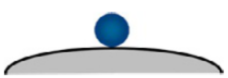
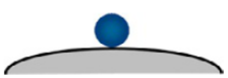
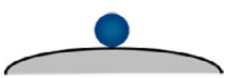
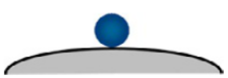
Dissolution: ZnO > Ag > Cu > CeO_2 > TiO_2 ~ Au



Soils and sediments

Cornelis et Lahive, Occurrence, behavior and effects of inorganic nanoparticles in the environment, In: Analysis and characterization of metal-based nanomaterials, **2021,** 93, 1–344.

Dominant form of NPs in the environmental compartments

Compartment	Dominant form of occurrence	Dominant process	Expected concentrations (mg/kg) TiO_2	Ag
Freshwater		Heteroaggregation and sedimentation	10^{-3}	10^{-6}
Marine		Coating	NA	NA
Agricultural soil[a]		Deposition	10^{4}	10^{0}
Other soil		Deposition	10^{3}	10^{1}
Sediment		Deposition	10^{3}	10^{1}
Landfill		Deposition	10^{3}	10^{1}
Air		Heteroaggregation	10^{-6}	10^{-10}

Cornelis et Lahive, Occurrence, behavior and effects of inorganic nanoparticles in the environment, In: Analysis and characterization of metal-based nanomaterials, **2021,** 93*,* 1–344.

Nanoparticles and consumers

Des traces de nanomatériaux détectées dans du lait maternisé

Par Lucile Morin — 29 mai 2016 à 21:11

Libération

Des nanoparticules cachées dans nos assiettes

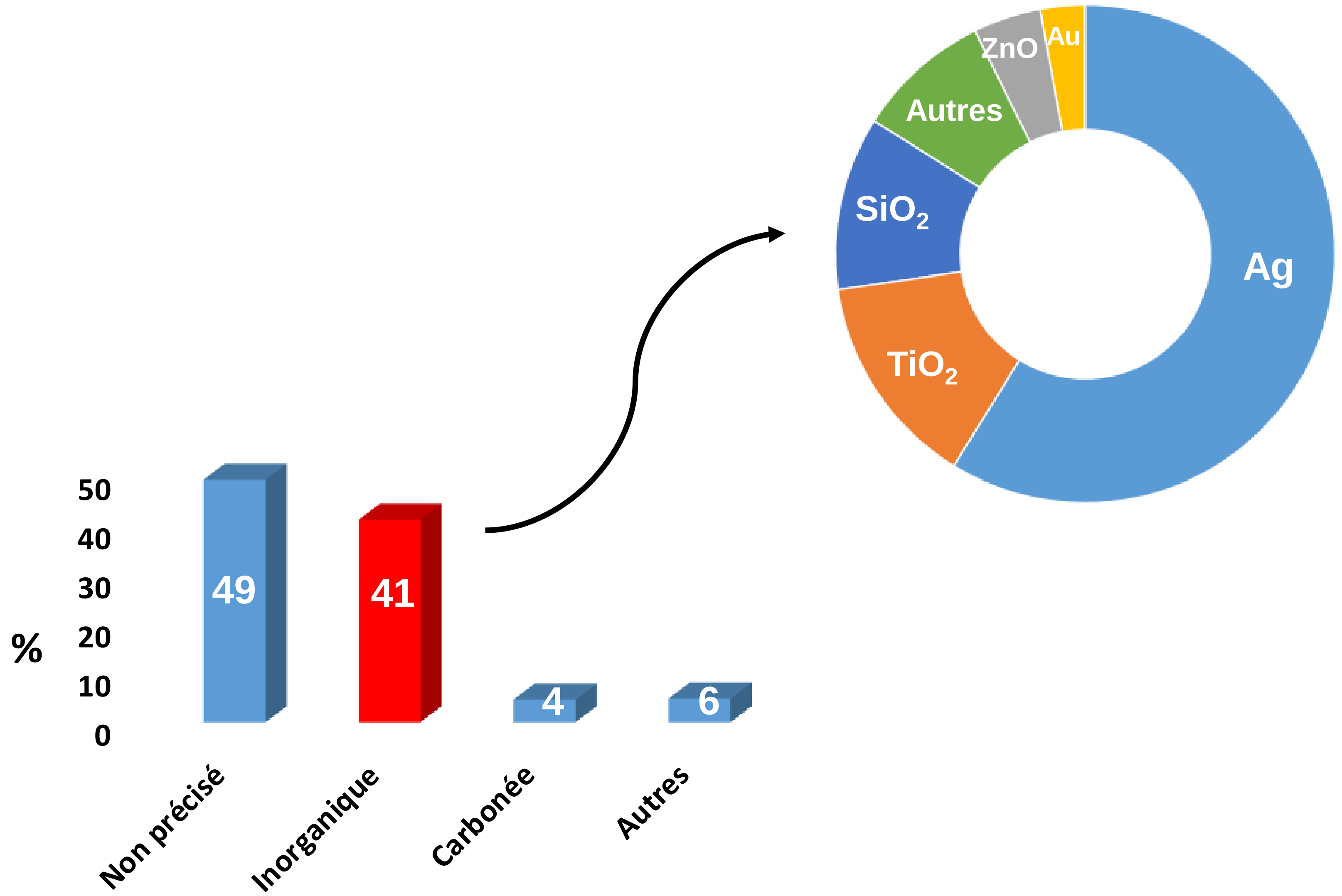
60 millions

Partager 630 Tweeter Envoyer Commentaires

100 % des bonbons et gâteaux que nous avons testés contiennent du dioxyde de titane sous forme « nano ». Contrairement aux dires des fabricants.

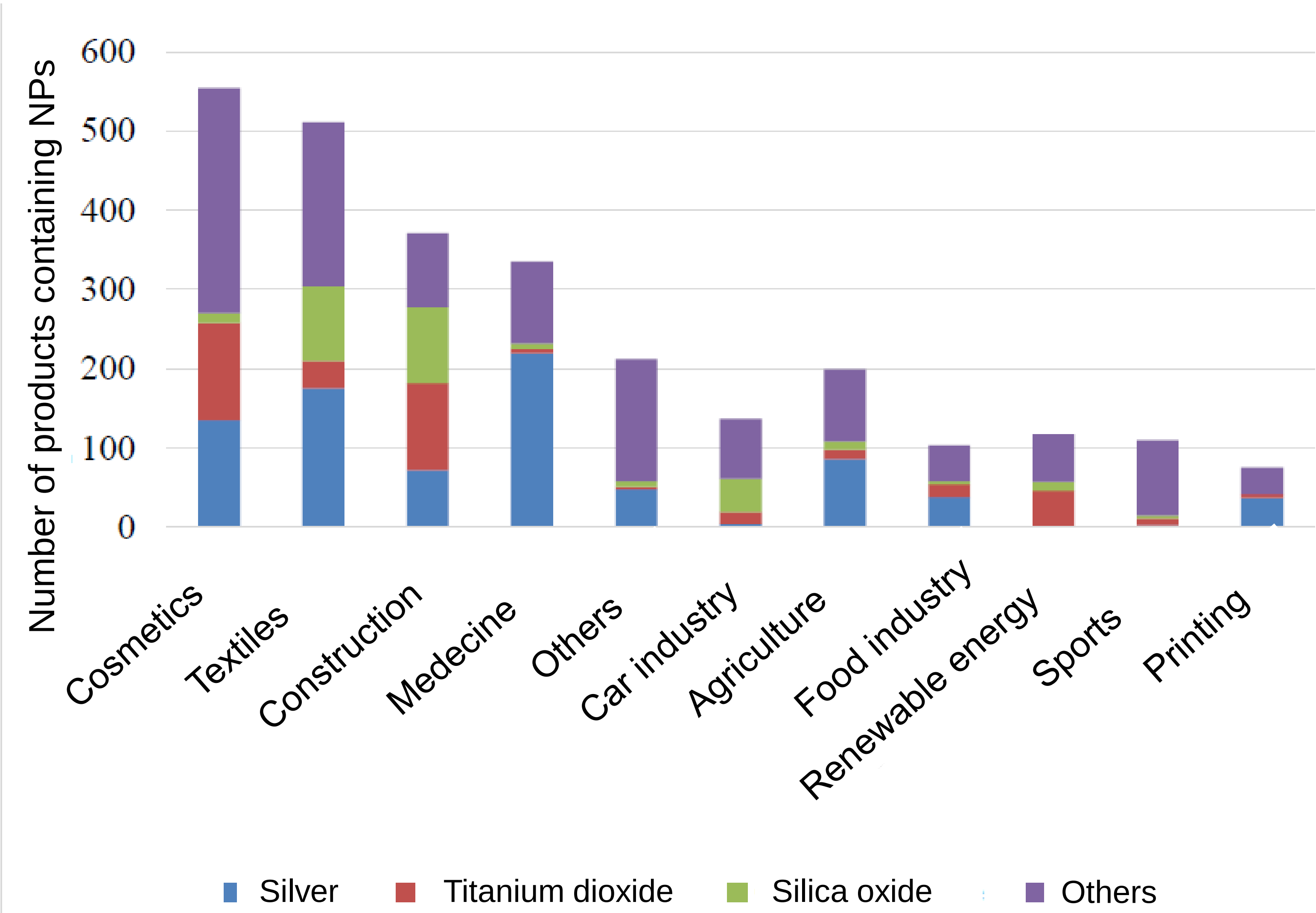
iStock

Nanoparticles used in consumer products



Adapted from Vance et al., Beilstein J. Nanotechnol., **2015,** *6,* 1769–1780.

Nanoparticles used in consumer products



Salou S., PhD thesis, **2021**.

TUNTWIN Inorganic NPs used in consumer products





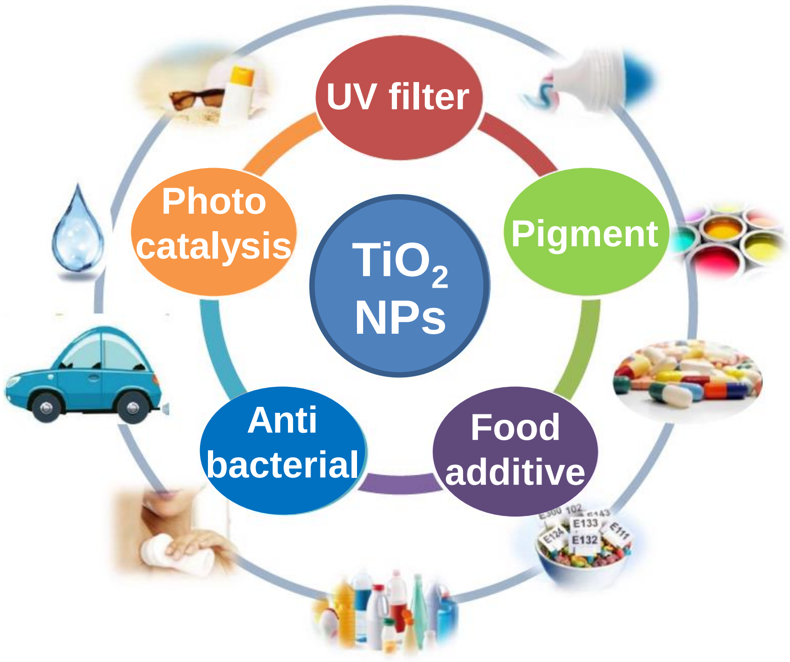




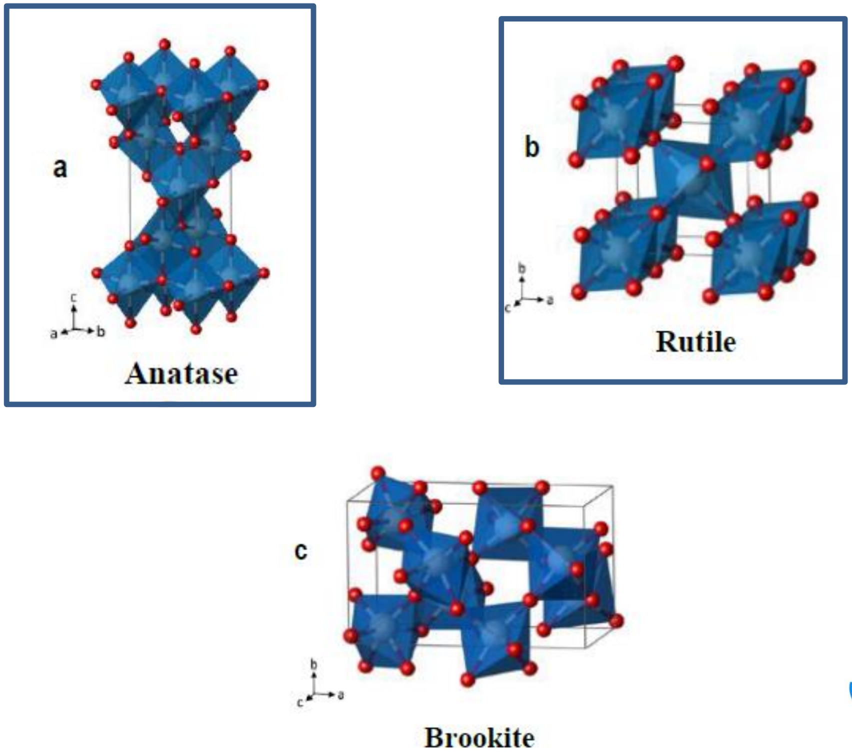
Particles	Products	Main use	Food Additive
TiO_2	Food (sweets & sauces), paints, textiles, hygiene products, food packaging, cosmetics, drugs, …	✓White pigment ✓UV filter (in combination with ZnO) ✓Flavour enhancer (dry fruits, soups, mustard …) ✓Self cleaning,	*E171*
Ag	Food packaging, textiles, food, food supplements, hygiene products, medical devices, textiles	✓Antimicrobial agent ✓Decorative agent for patisserie …	*E174*
SiO_2	Food, powder soups, coffee, hygiene products, mayonnaise …	✓Anti-caking agent ✓Improvement of texture and smoothness …	*E551*
Iron oxide	Food	✓Colour agent ✓Increase of bioavailability	*E172*

TUNTWIN

TiO_2 NPs



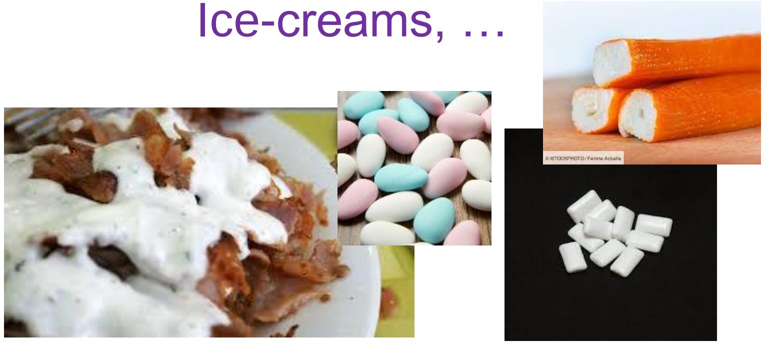
Crystalline structures



TiO_2 NPs in food

Mainly used white pigment, mostly as anatase or as a mixture of anatase/rutile

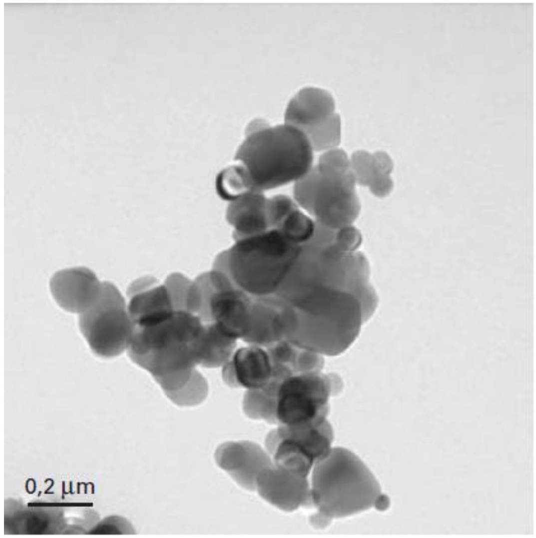
Candies
Chewing-gum
Processed fishery products
Sauces
Ice-creams, …



E171

- Powder used since a long time at the non-nanometric scale
- But 15 to 55 % present as nanoparticules
- Size distribution between 30 and 400 nm

Food packaging as a UV barrier or as an antibacterial agent



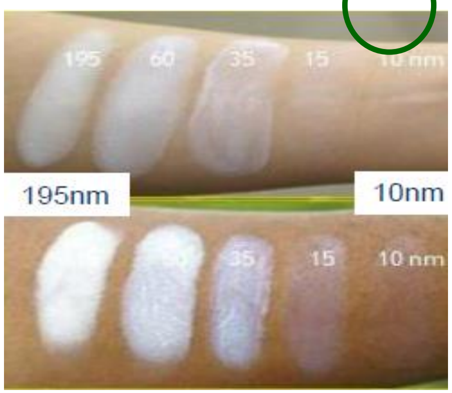
TiO_2 NPs in cosmetics

Used as white pigment

Not allowed in cosmetics (EU)

Personal care products ??

Used as anti-UV filter



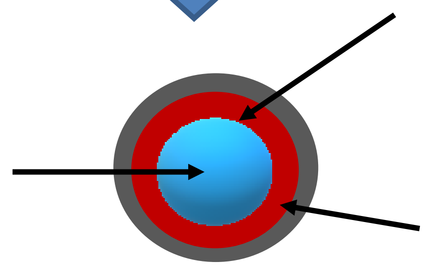
Allowed (EU, FDA)

TiO_2 very photoreactive

↓

Production of ROS giving cell damage

↓



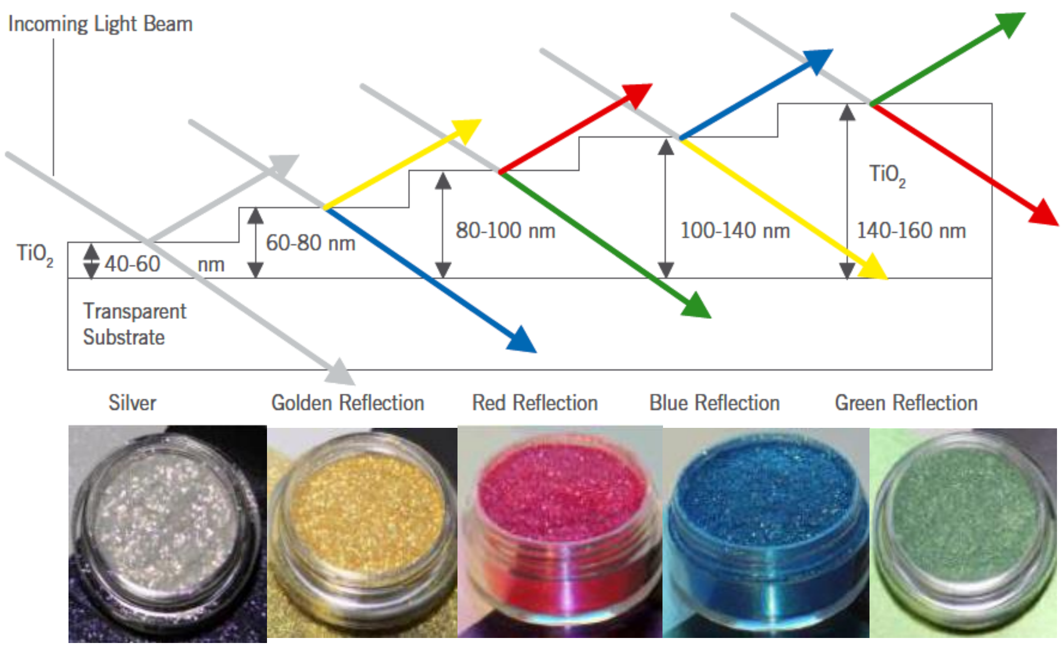
- Often used in association with ZnO NPs
  - TiO_2: against UVA
  - ZnO: against UVB (200 nm or smaller, 25% max, as wurtzite)
- Mainly as rutile or as rutile/anatatase combination

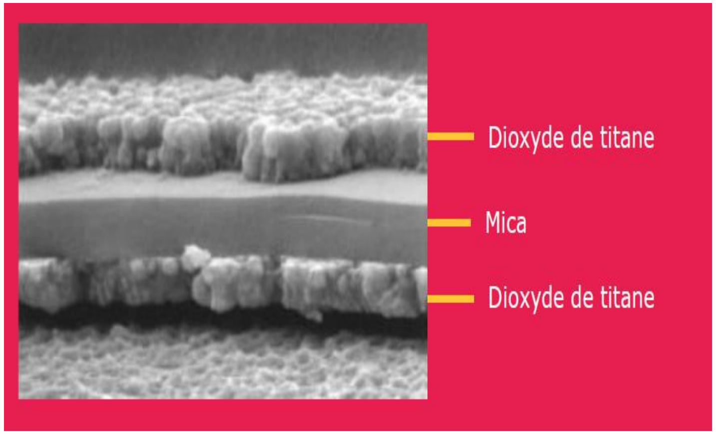
TUNTWIN Other type of TiO_2 NPs in food and cosmetics

Always new products based on nanoparticles for "new properties":

Glitter effect in make-up, confectionery, spices, gastronomic cook

Goden pepper





TUNTWIN TiO_2 NPs in consumer products: health effects

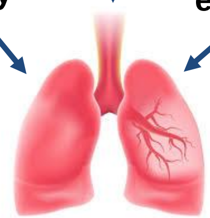
○ Inhalation

Possible carcinogen (group 2B) *(from IARC)*

Air contamination

Spray

Professional exposure



○ Dermal

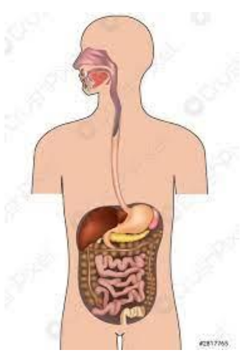
Cosmetics & skin care products

Tatoos, clothes, …

Dermal route

- Healthy skin: little penetration (*in vitro* & *in vivo studies*)
- Skin with lesions: possible penetration ?

○ Ingestion



Daily intake :

- **0.03** mg per kg body weight (adult)
- until **13** mg per kg body weight (children < 10 years)

Possible carcinogen by ingestion ?
Possibility to cross the placental barrier ?

Increasing TiO_2 NPs concentrations in all the compartments

Environnement	Concentration en TiO_2 prédite
Air	0.001 µg m^{-3}
Eaux de surface	0.53 µg L^{-1}
Sédiments	1.9 mg kg^{-1} par an
Boues de station d'épuration	170 mg kg^{-1}
Sol naturel et urbain	0.13 µg kg^{-1} par an
Sol traité avec boues de station d'épuration	1.2 mg kg^{-1} par an

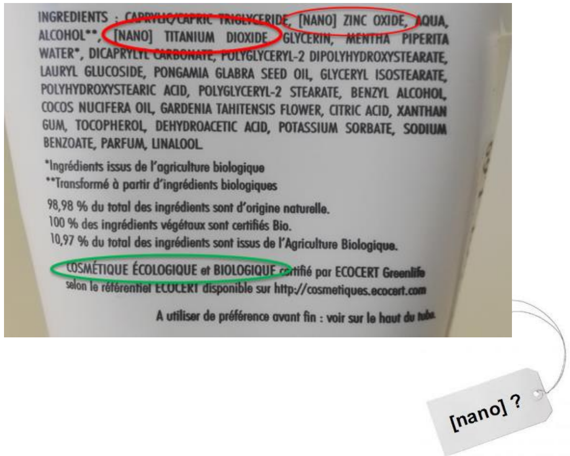
FOOD

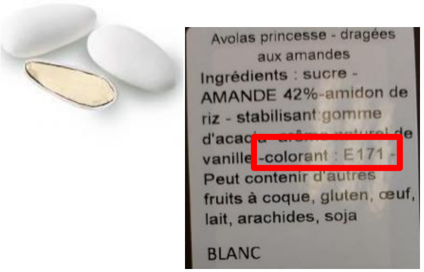
- EU n°1169/2011 (INCO): labelling of all **food products** which contain nanoparticles in their ingredients
- Since 2020, the use of **E171** is bannished in France and since 2022 in Europe

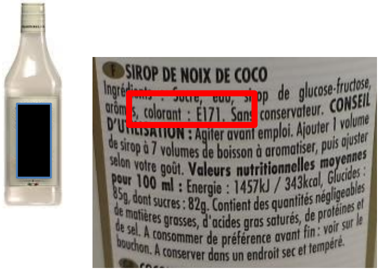
COSMETICS

- EU n°1223/2009: only black carbon, TiO_2 and ZnO are allowed as « insoluble NPs ». Labelling of **cosmetic products** which contain NPs in their ingredients
- Other EU legislation in April 2022 forbidden the use of NMs including Cu, Au, Pt (as NMs and colloids)

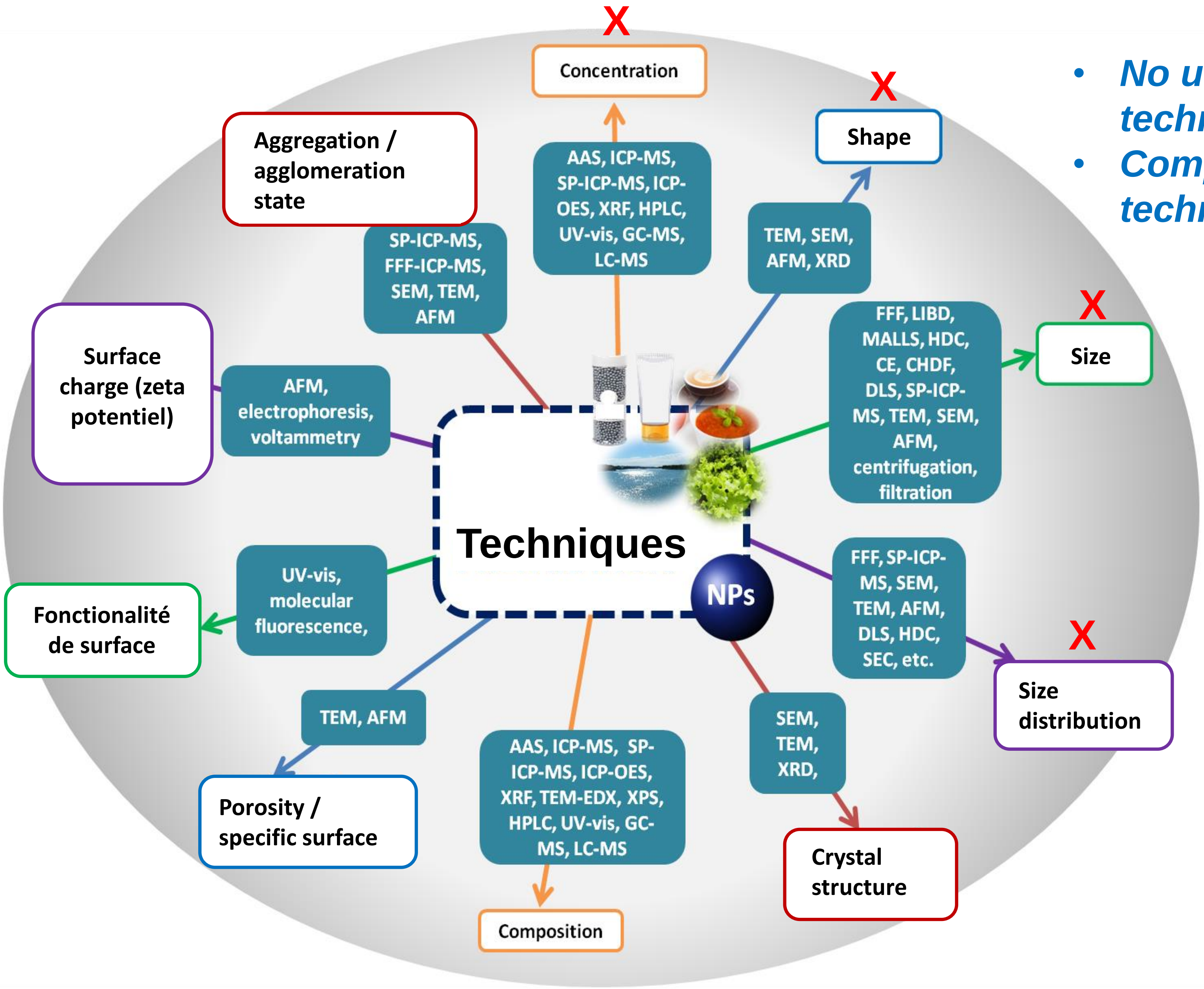
Product labelling





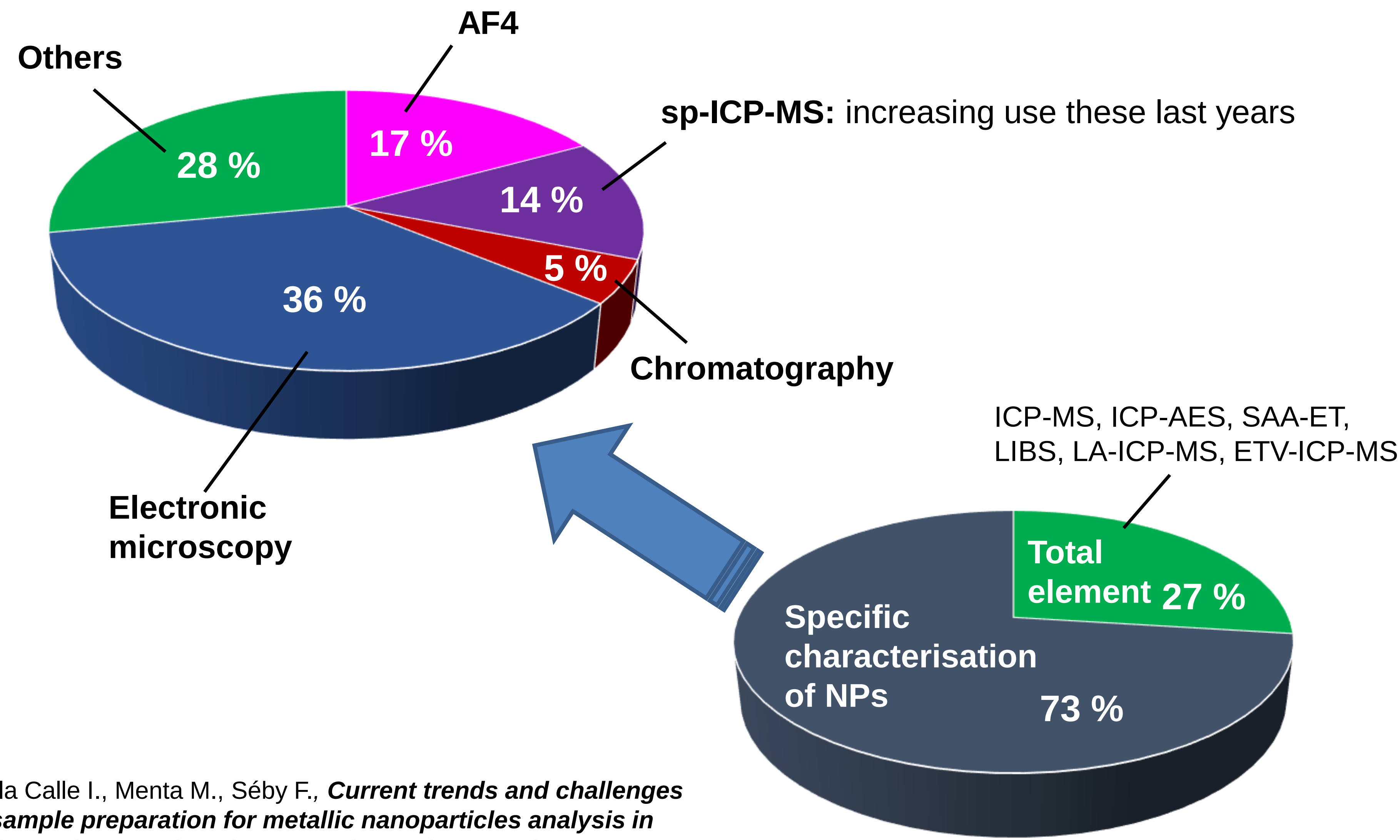


Techniques for NPs characterization



- ***No universal technique***
- ***Complementary techniques***

Main techniques used for inorganic NPs

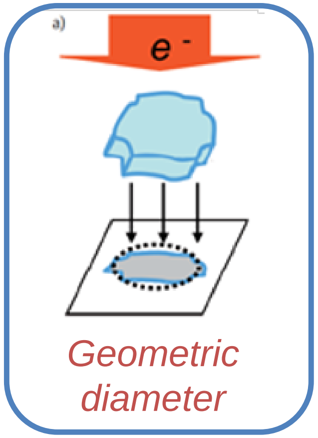


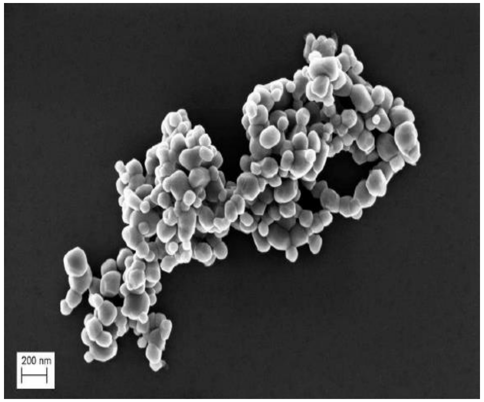
De la Calle I., Menta M., Séby F., ***Current trends and challenges in sample preparation for metallic nanoparticles analysis in daily products and environmental samples*****: a review**, *Spectrochim. Acta B,* **2016,** *125,* 66–96.

Electronic microscopy techniques

TEM, STEM, SEM or MEB, AFM

MEB (EDX)





Information obtained:

- Imaging of nano-objects
- Mean / median / modal diameters
- Particle number distribution
- Composition (if EDX)
- Aggregation and agglomeration state

Advantages	Drawbacks
✓ **Direct information on the shape**	▪ **Cost of the analysis**
✓ **Technique of reference**	▪ **Long and complex**

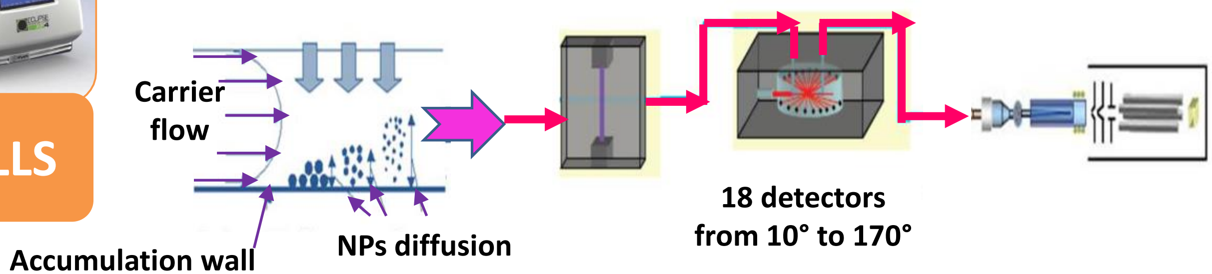
AF4-MALLS-ICP-MS coupling technique

Particles separation from **1 to 50 000 nm** as the function of the **size** and **mass**

Instrument	Scheme

A4F membrane | Detector UV | Detector MALS | Detector ICP-MS

A4F-MALLS



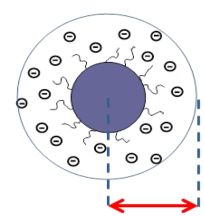
AF4

- **MALLS**
- **ICP-MS**

Information obtained:

MALLS:
- ✓ **Hydrodynamic diameter**
- ✓ **Radius of gyration**

ICP-MS:
- ✓ **Composition**
- ✓ **Concentration**



Hydrodynamic radius

Advantages

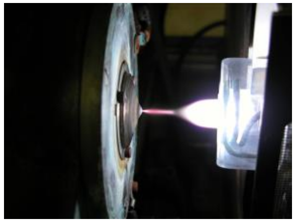
- ✓ Analysis of a wide range of sizes
- ✓ Good separation efficiency
- ✓ Wide variety of particles

Drawbacks

- Particle-particle and particle-membrane interactions
- Long optimization and data interpretation often difficult

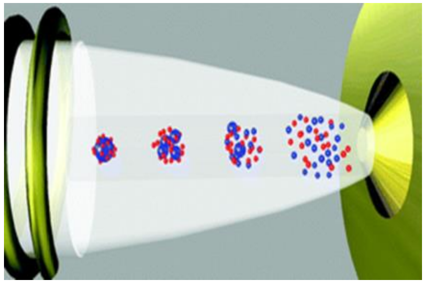
TUNTWIN

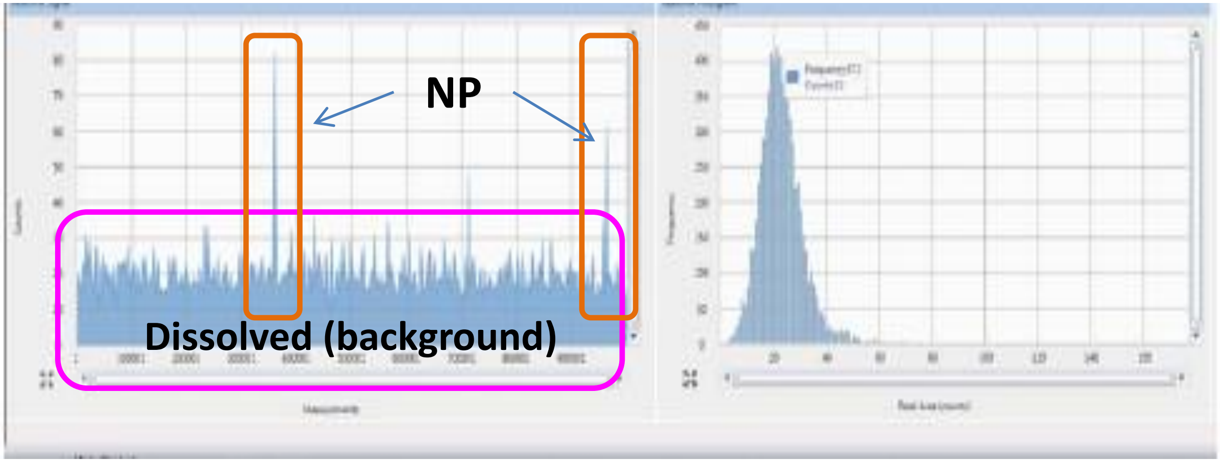
The spICP-MS technique



The basics for NPs analysis by spICP-MS

- **Spherical particles**
- **Low dwell time**
- **High dilution of samples: *1 particule → 1 pulse***





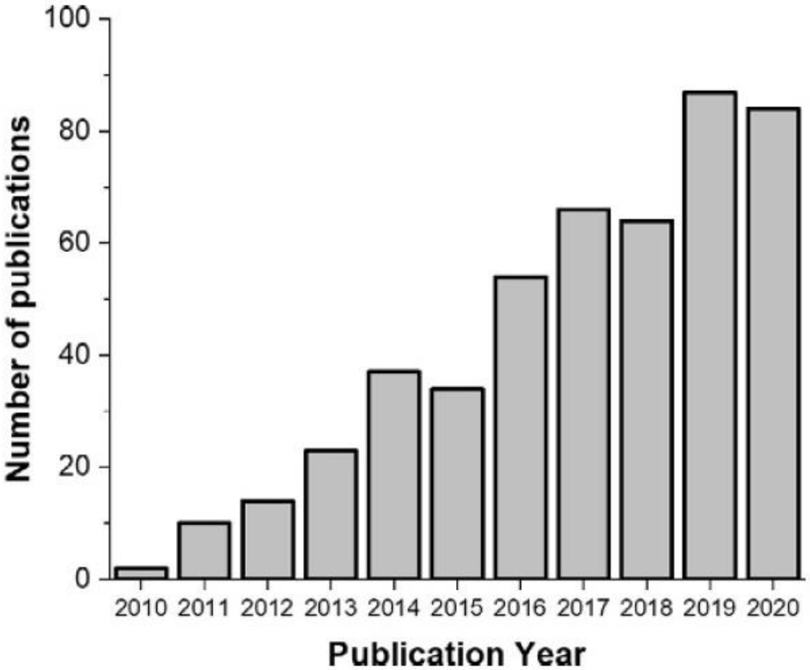
Information obtained:

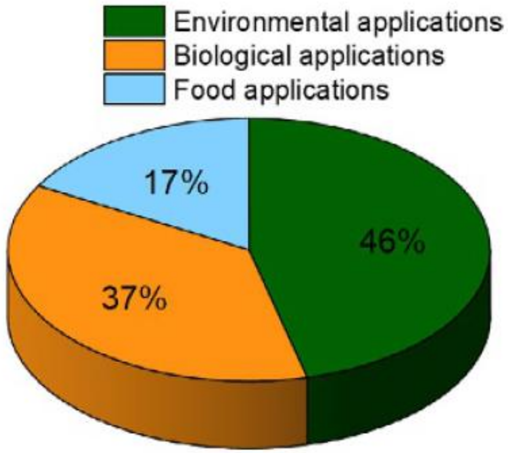
- Mean / median diameter
- Particle size distribution
- NPs concentration
- Dissolved element concentration

Equivalent spherical diameter

Advantages	Drawbacks
✓ **Simple**	▪ **Limited to ICP-MS element detectable**
✓ **Fast**	▪ **Supposedly spherical shape**
✓ **Sensitive**	▪ **Minimal diameter different as the function of the NPs type**
✓ **Specific**	▪ **Same interferences than those observed by ICP-MS**

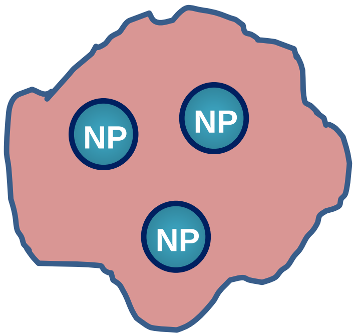
Use of the spICP-MS technique





Vidmar et al., Detection and characterization of metal-based nanoparticles in environmental, biological and food samples by single particle industively coupled plasma mass spectrometry, In: Analysis and characterization of metal-based nanomaterials, **2021,** 93, 345–380.

Sample preparation before NPs analysis



Sample

Objectives

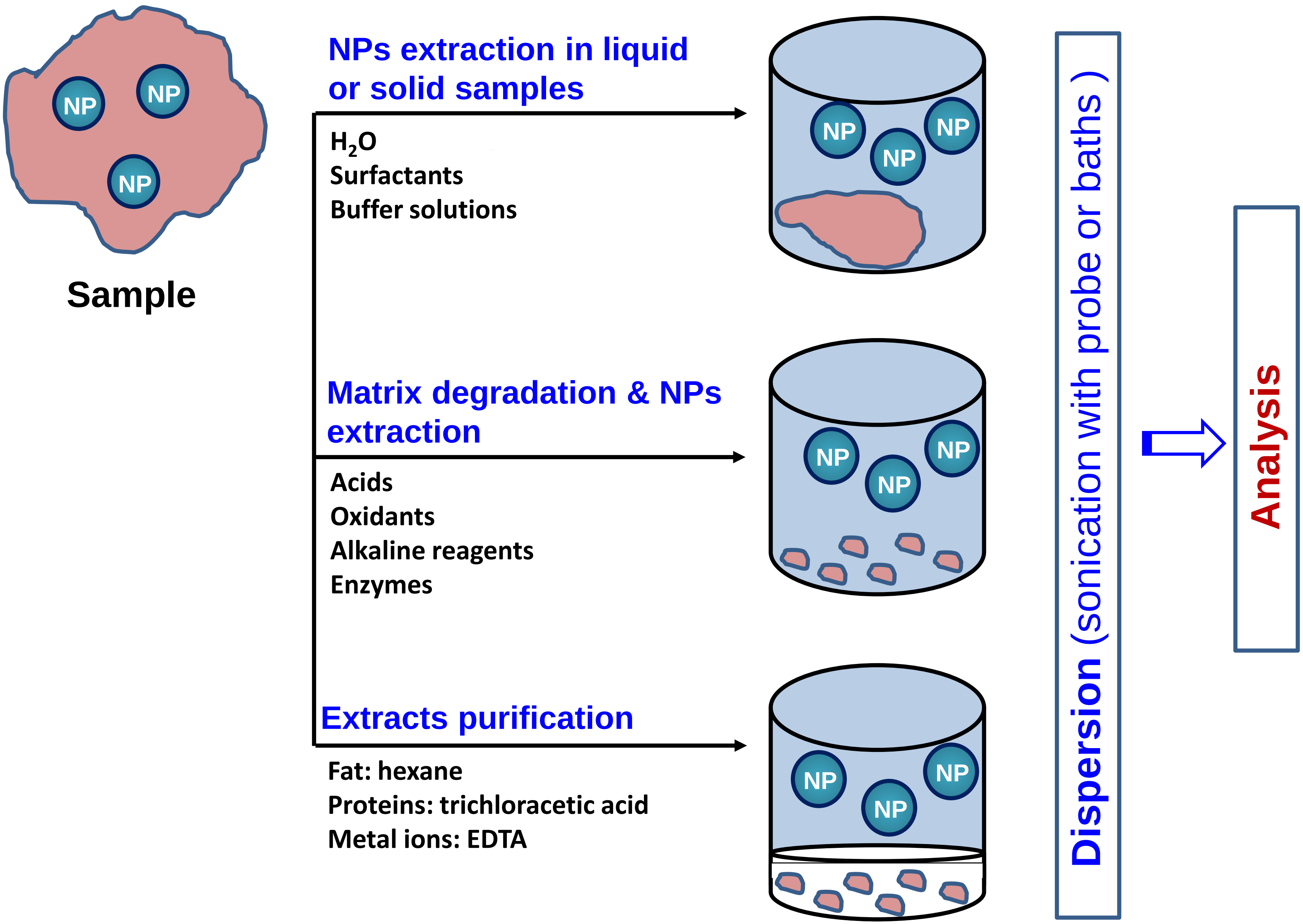
- Obtain a representative suspension
- Reduce the complexity of the sample
- Isolate NPs from the matrix
- Preconcentrate

Difficulties

- High reactivity of the NPs (aggregation/agglomeration)
- Isolate NPs from the matrix
- Avoid NPs dissolution

⚠ Centrifugation and filtration are not recommended

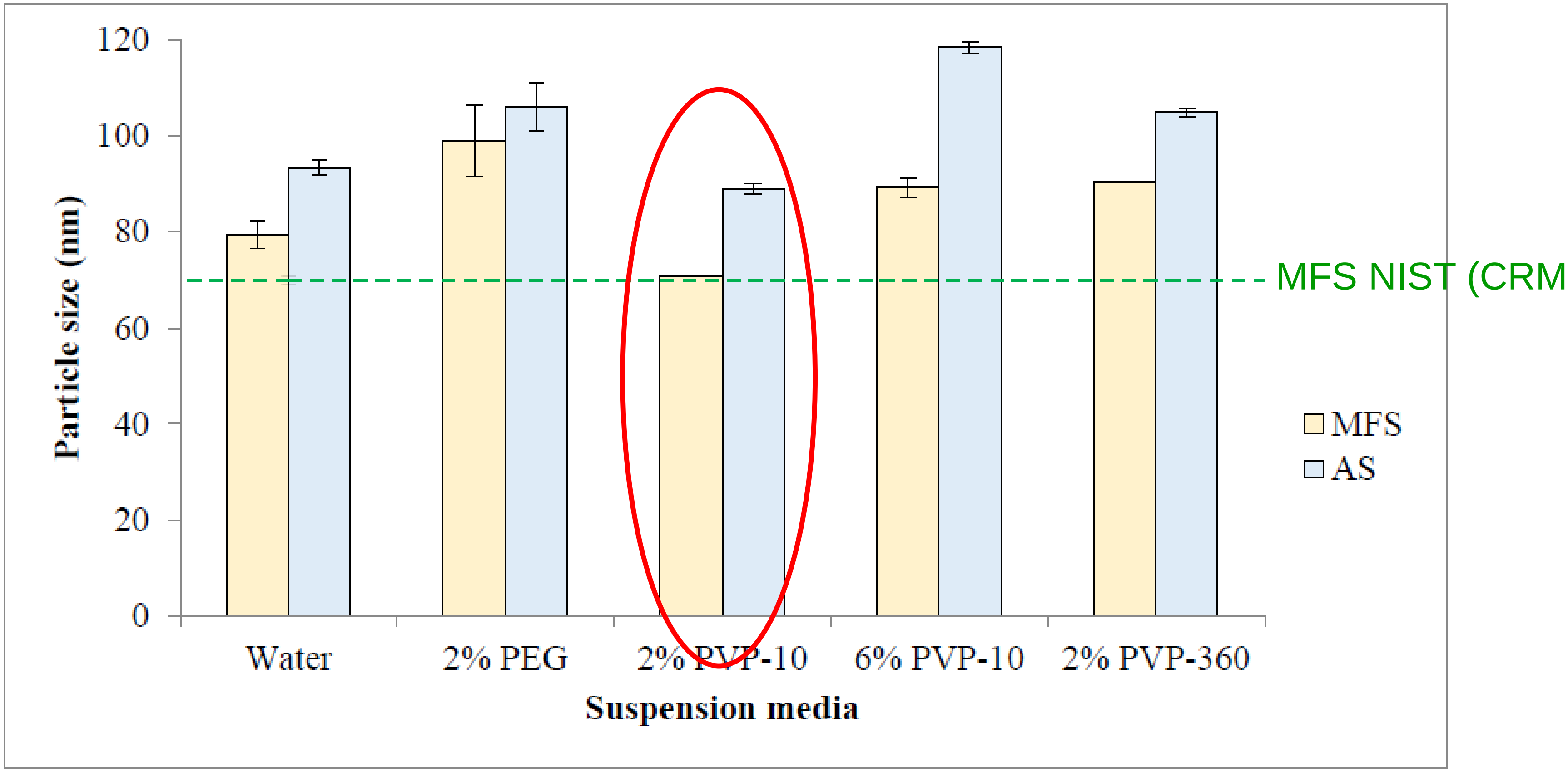
Sample preparation



TiO_2 NPs analysis in urine samples

Influence of the dispersion media on TiO_2 NPs size in urine samples assisted by sonication (probe) before spICP-MS analysis

Presence of salts resulting in NPs aggregation/agglomeration



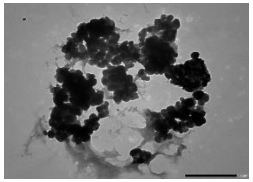
MFS: most frequent size
AS: average size

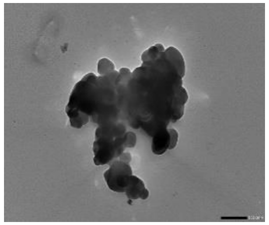
Salou et al., Anal. Bioanal. Chem., **2020,** *412,* 1469–1481.

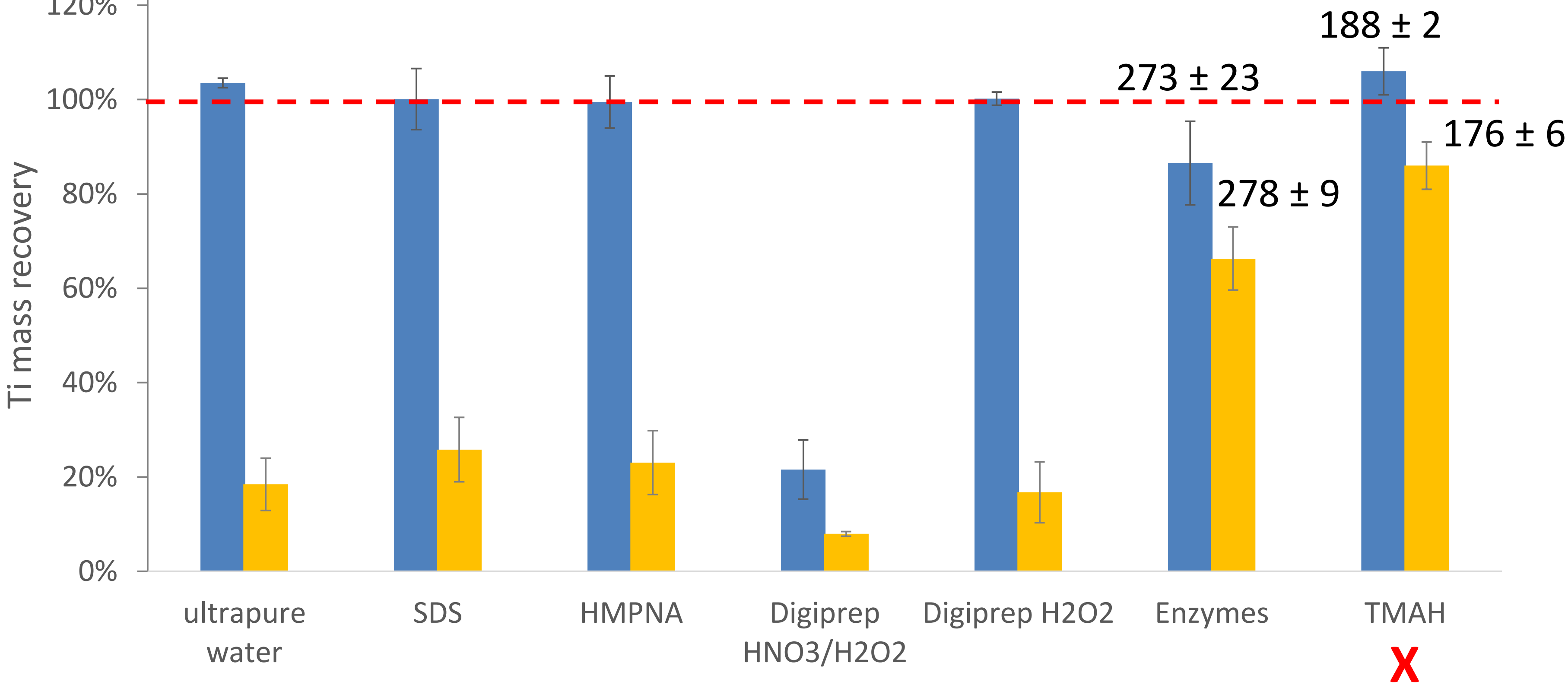
TUNTWIN

TiO_2 NPs extraction in fat food samples

Results consistent with TEM







Klein et al., study not yet published

Conclusion

- Nanoparticles in food and cosmetic products:
  - Industrial use since a long time

    before E*XXX* and now « nano »
  - Toxicity not well known yet
- Analytical techniques now available:
  - Inorganic NPs: spICP-MS
  - Organic NPs: AF4-MALLS
- Urgent needs for quality control tools:
  - Standardised methods
  - Certified Reference Materials
  - Interlaboratory exercices

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