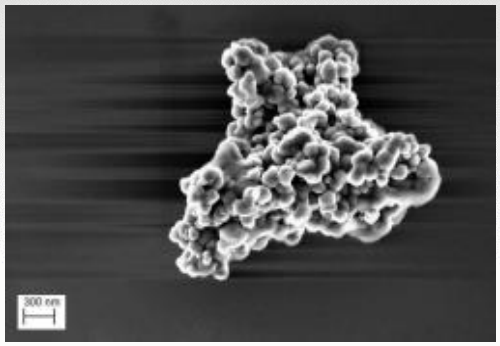
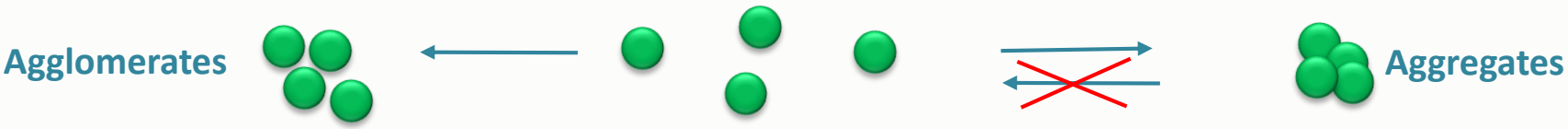
Nanomaterials
Legislation and analytical strategies

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

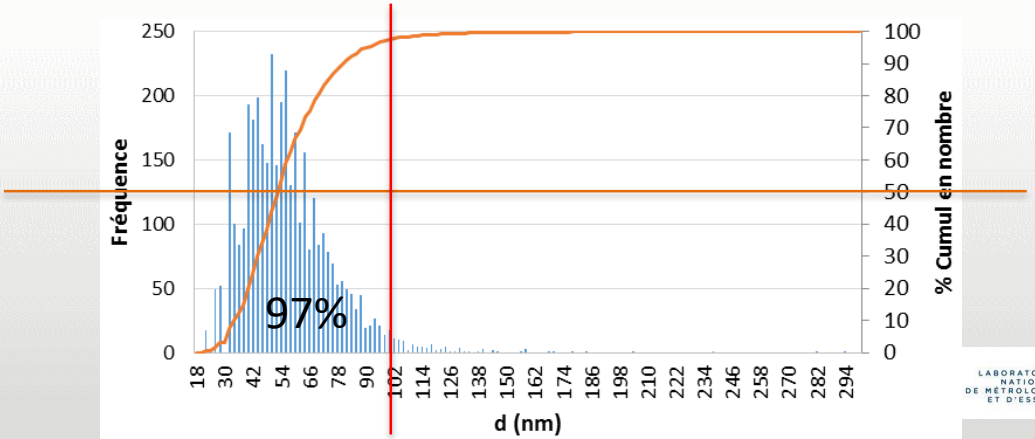


Nanomaterial definition according European Comittee 2011/696/UE

- **Natural** material
- Incidental or manufactured material containing particles in an unbound state or as **an aggregate or as an agglomerate**



- **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**



Nanomaterials omnipresence in daily life

Food

- Candies
- Ornament cake
- Frosting

Cosmetics

- Sunscreens
- Moisture
- Make-up

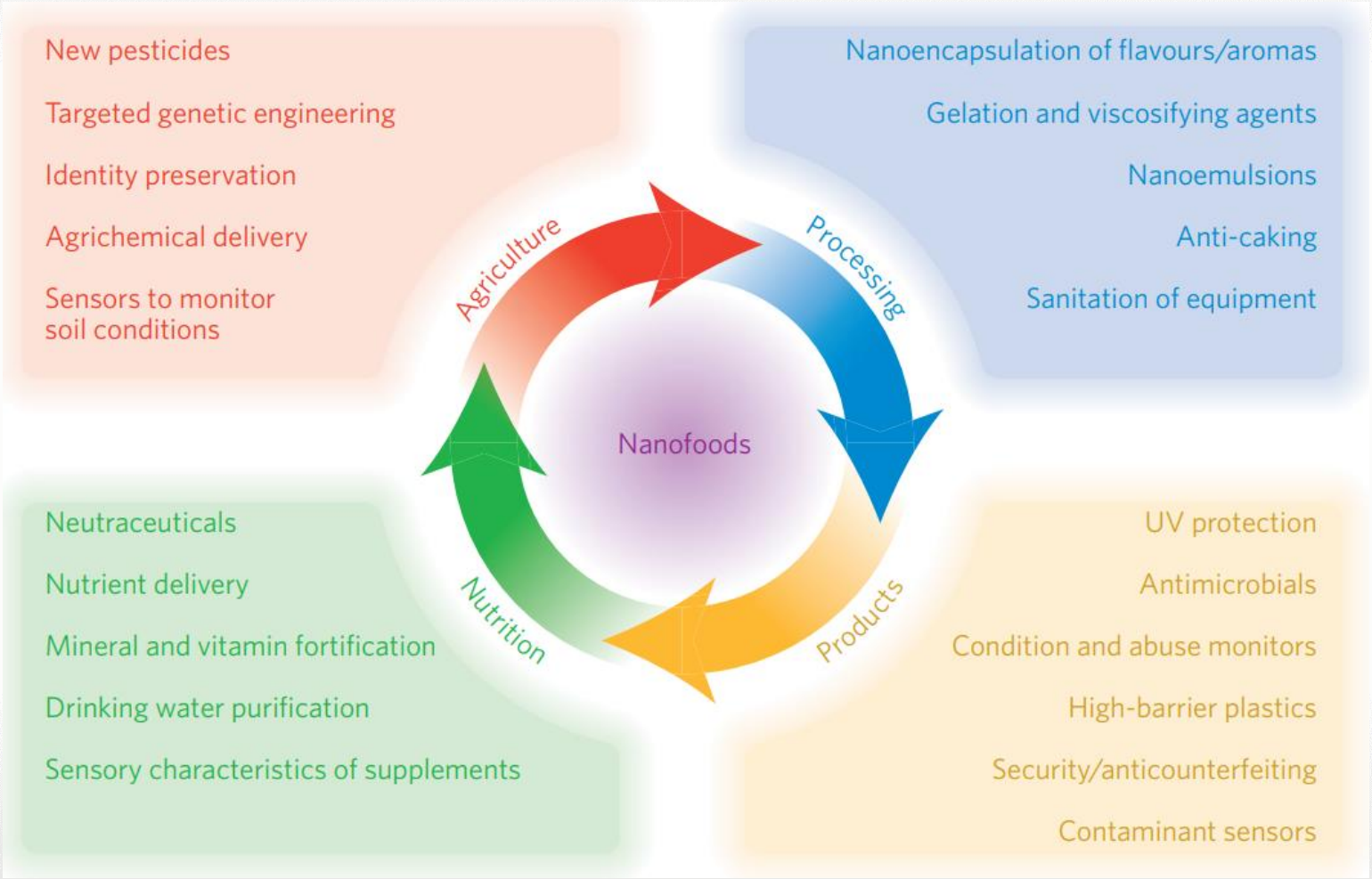
Contact materials

- Plastics
- Cardboard
- Ceramics

Biocides

- Disinfection

Nanotechnology and benefits to food industry



« Classic » Food colouring agents

micrometric powders containing a more or less significant fraction of fine particles

Titanium dioxide (E171)

- Confectionery
- Pastry
- Cream
- Yoghurt
- Ready meals

Iron oxides (E172)

- Charcuterie
- Confectionery
- Biscuits

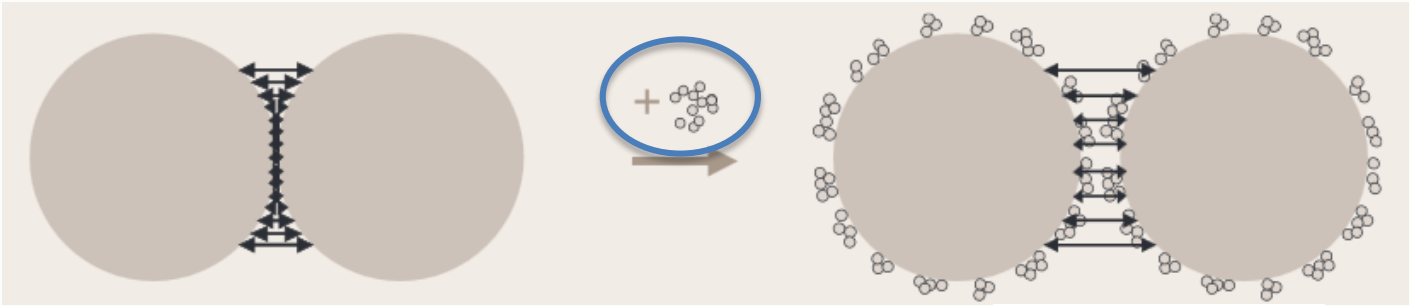
Silver or Gold (E174, E175)

- Decoration

Not designed to enhance fine particle fraction properties
BUT
Presence of fine particle = « **nanometric** » character

« Classic » Texturizing agents

SiO_2 :Used as **anti-caking agent** or to improve texture/smoothness



Particles adhering because of van der Waals forces

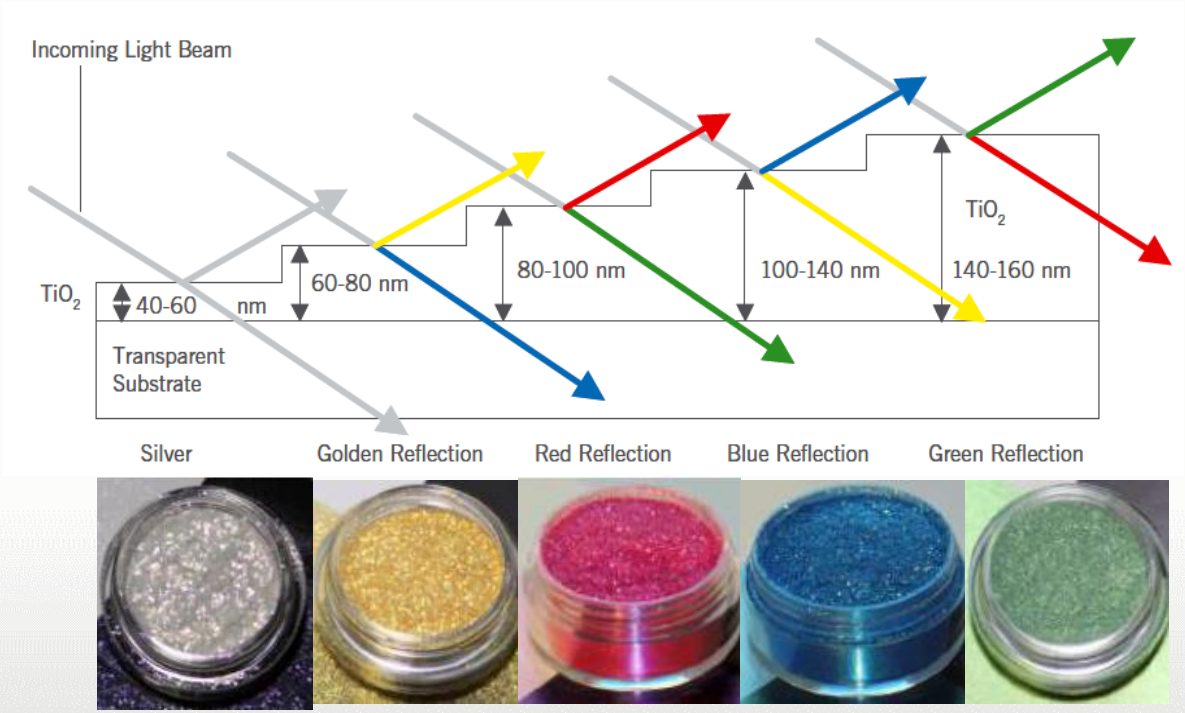
Free-flowing powder

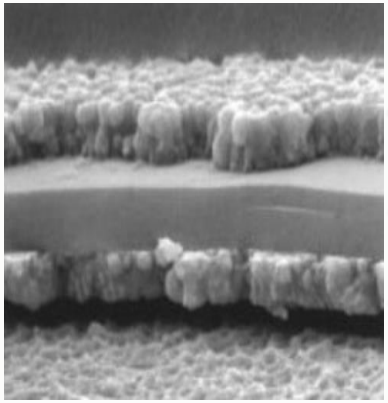
Silice SiO_2 (E551)
Calcium carbonate (E170)
Magnesium oxide

E171 + E172
(+E555)

INNOVATION
« New » Food colouring agents

New physico-chemical properties at the nanoscale such as : glitter/shiny effect

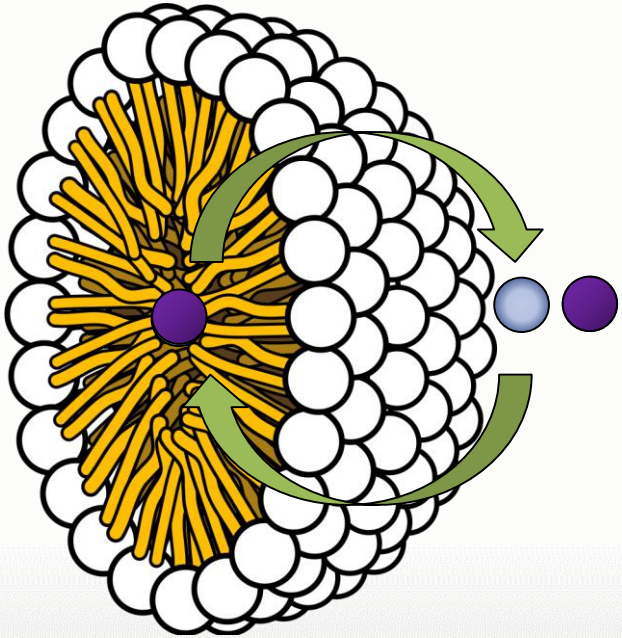


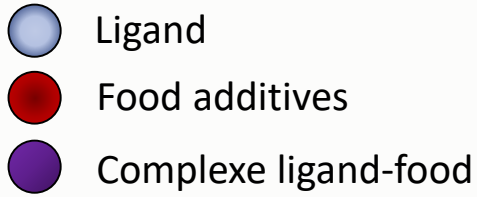


INNOVATION
R&D – Food nanotechnologie

Encapsulation of substances/food additives to :

- Improve their stability and bioavailability
- Improve their taste, nutrinional quality or retention of aromas
- Reduce the quantity needed





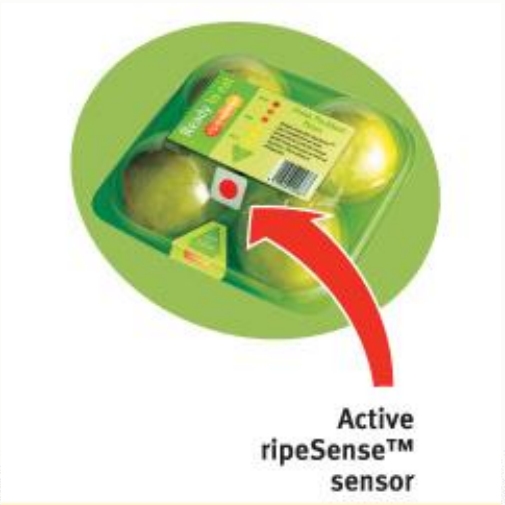
Enhancement of physico-chemical properties by selectively developing certain types of interactions, always in order to limit the quantities to be introduced into the formulation

Food contact materials

Nanomaterials	Properties	Application field
Titanium nitride	Improvement of « barrier » properties	Plastic packaging
Titanium dioxide	UV filter	Plastic and glass packaging
Calcium carbonate	Charge - Improvement of « barrier » properties	Plastic packaging
Carbon black	Black pigment	Printing
Magnesium silicate	Moisture absorber	Container
Silver	Anti-microbial agent	Food contact work surface/storage, packaging
Starch	Antistatic agent	Plastic film
Clay, aluminum and aluminum oxide	Charge - Improvement of « barrier » properties	Plastic packaging

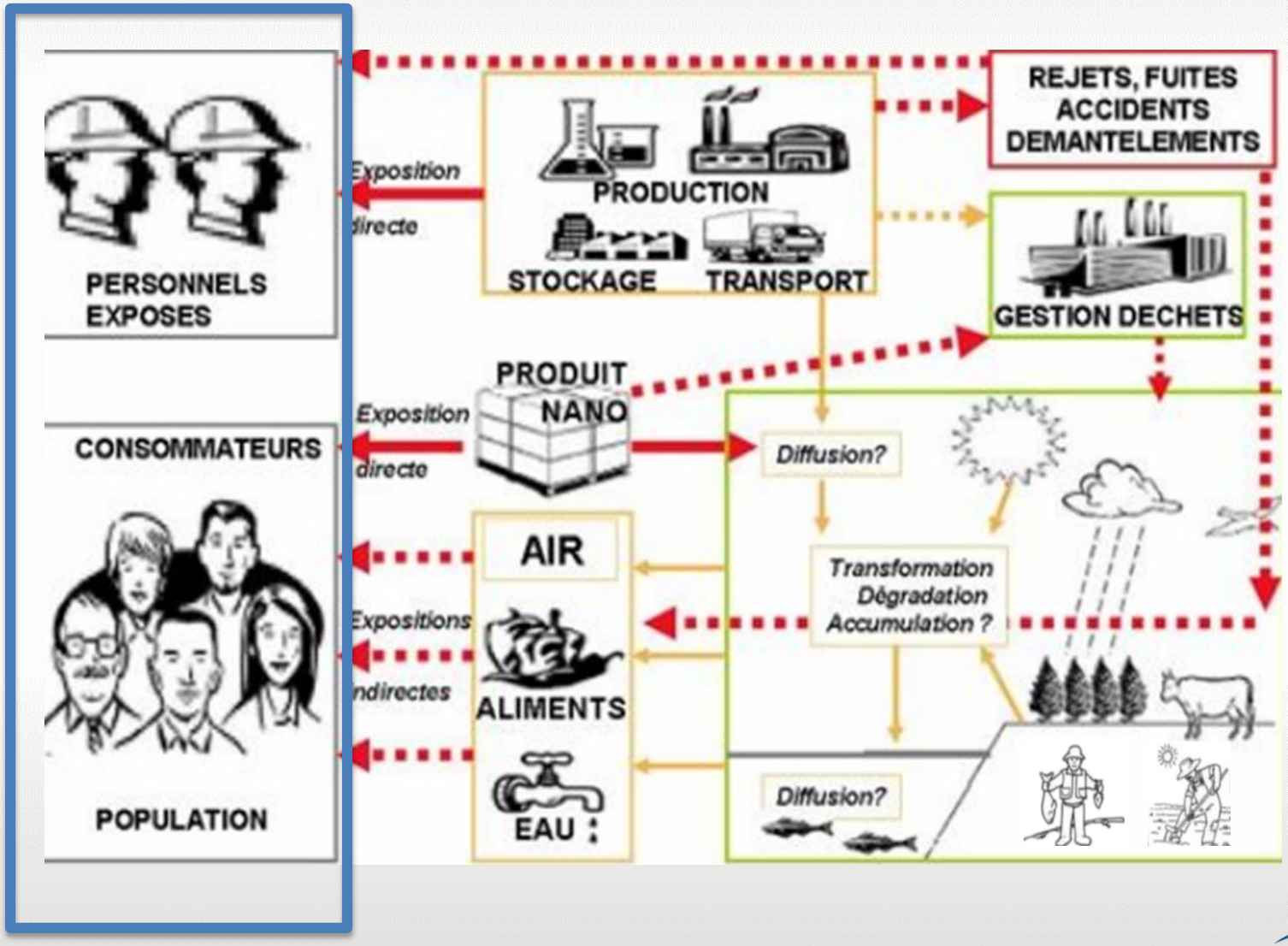
+

Intelligent packaging :
traceability, nanosensors

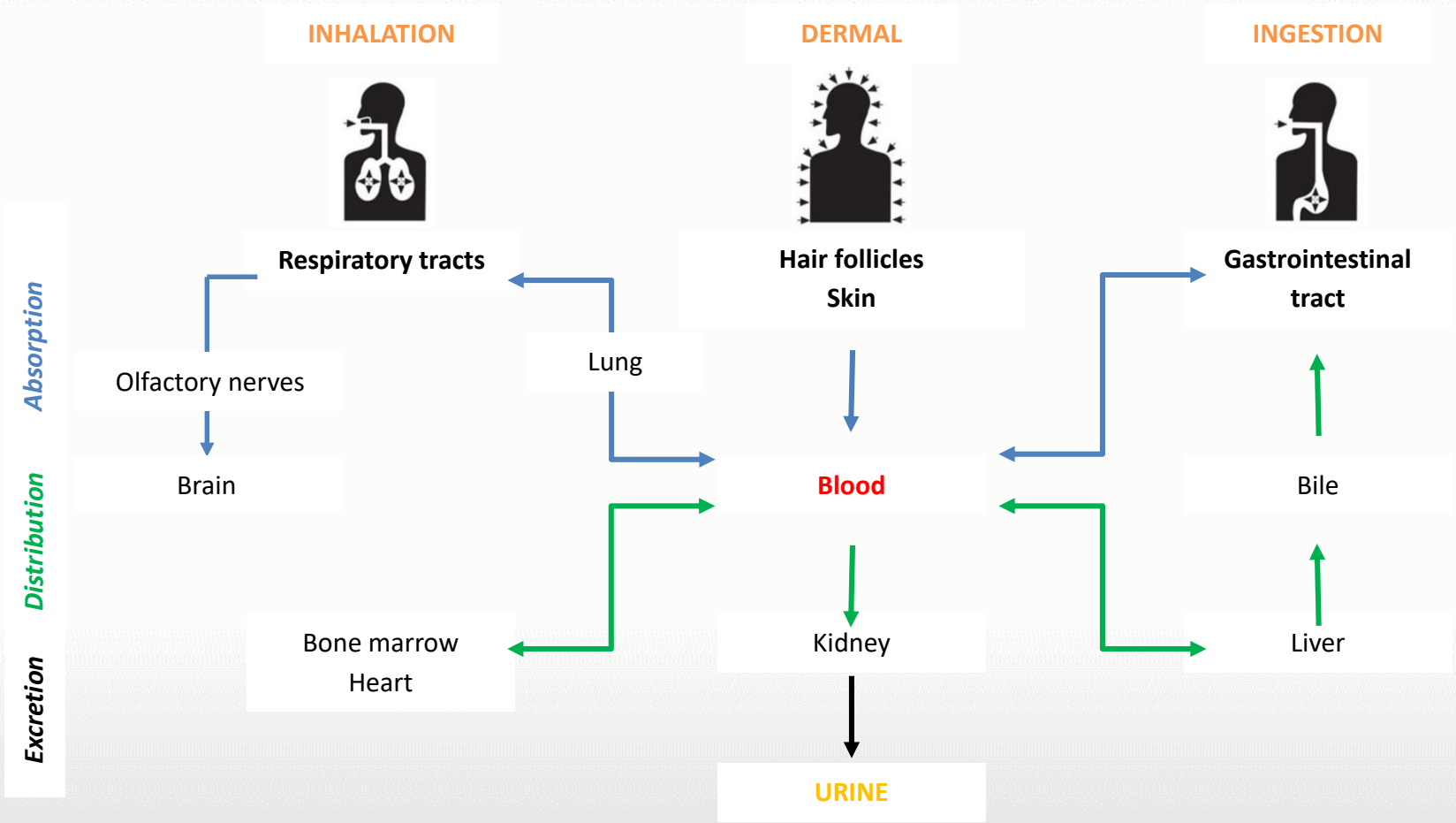


Sensor changing color according to the maturity of the fruit
(Source site Ripesense)

Nanomaterials : environment exposition and human hasards



Human exposure



Essential regulations for consumer protection

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.

Biocides	**R(UE)n°528/2012**	≠ Active or non active substance
Alimentation	**R(UE)n°1169/2011 (INCO)**	≠ **Intentionally** produced material + Aggregates/Agglomerates > 100 nm but retains nanoscale properties : • Large specific surface area • Different physico-chemical properties from the non-nanoform
Cosmetics	**R(UE)n°1223/2009**	≠ Insoluble or biopersistant and intentionally manufactured material **≠ List of authorized nanoparticles** + Internal structure in the size range 1-100 nm
Contact materials	**R(UE)n°10/2011**	≠ **List of authorized nanoparticles** + Aggregates/Agglomerates > 100 nm with nanosize properties

DG CCRF
DOUANES & DROITS INDIRECTS

R(UE)n°528/2012

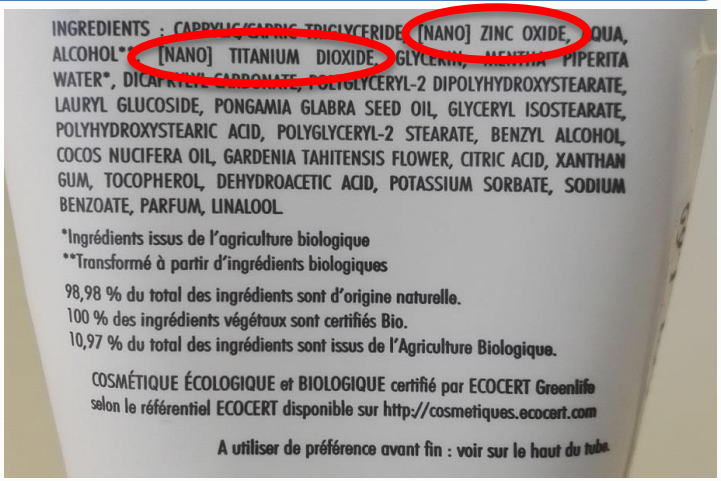
R(UE)n°1169/2011 (INCO)

R(UE)n°1223/2009

[Nano] mandatory labelling

Ingrédients pour 2 à 4 Gélules

Contenu: Extrait sec de pépins de Pamplemousse(300/600 mg), Curcuma (200/400 mg), Extrait sec de graines de Courge* (100/200 mg), Cumin (100/200 mg), Dioxyde de silicium [nano] E551.



National databases and registers

- **Consumer information**
- **Sample targeting**

R-Nano register:

Compulsory annual declarations (decrees n° 2012-232 et 2012-233) allow the authorities to better understand substances at nanoscale, their uses and quantities handled on national territory.

→ **Susbtances traceability** (from manufacturer or importer to the distributor)

→ **Better knowledge of the market**.

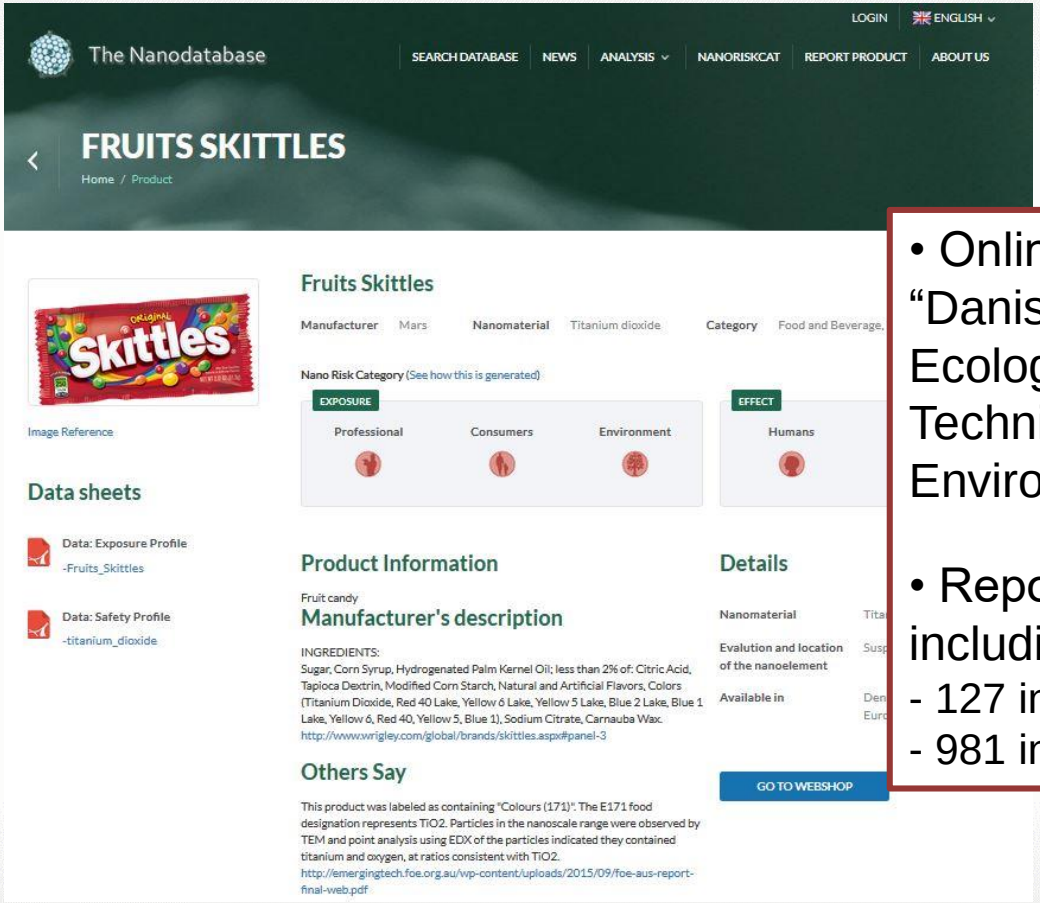
→ **Annual study report published on the R-Nano site :** general informations (declaration number, declared quantities, product families)

→ **Lack of accessible and precise datas** regarding properties ans uses of these substances.

→ **« Nanomaterial » definition : Commission recommandation!**

Inventaires et sources d'information de produits contenant des nanomatériaux

www.nanodb.dk



- Online database developped by the "Danish Consumer Council" & the "Danish Ecological Council in cooperation" with the Technical University of Denmark (DTU) Environment

- Reports 3036 products (au 08/10/2018) including:
  - 127 in « food and beverage »
  - 981 in « cosmetics and personal care »

Evaluation of the conformity

Manufacturers : know if the product meets regulatory requirements

Control authority : whether or not to accept the classification made by the manufacturer

Consumer : ensure that the product is properly labeled

Legislation

Regulation (CE) nº1169/2011

Conformity ?

Application in daily life

Regulation (CE) nº1169/2011

Control authority :

« Is the product proprely labeled ? »

- Presence of particles ?
- Particles composition ?
- « Nano » particles ? Which distribution ?

- **Analytical strategy for the numerical characterization in size of inorganic nanoparticles additives in food products and cosmetics (DLS,TEM,SP-ICP…)**

- **Development of analytical methods suitable for regulatory purposes (robust, rapid, not expensive)**

Reference method: MEB (+EDX)

EFSA statement (sept. 2016)

TiO_2

Recommendations

The Panel recommended that:

- The EU specifications for TiO_2 (E 171) should include a characterisation of particle size distribution using appropriate statistical descriptors (e.g. range, median, quartiles) as well as the percentage (in number and by mass) of particles in the nanoscale (with at least one dimension < 100 nm) present in TiO_2 (E 171) used as a food additive. The measuring methodology applied should comply with the EFSA Guidance document (EFSA Scientific Committee, 2011).

efsa European Food Safety Authority

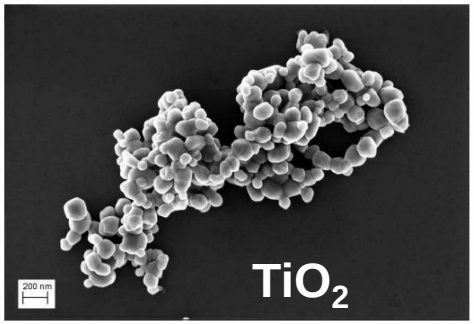
Guidance for risk assessment of engineered nanomaterials

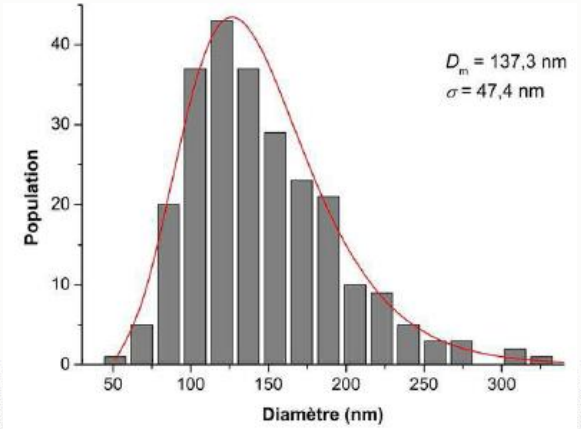
Table 1: Parameters for characterisation and identification of ENM (see appendix A for methods)

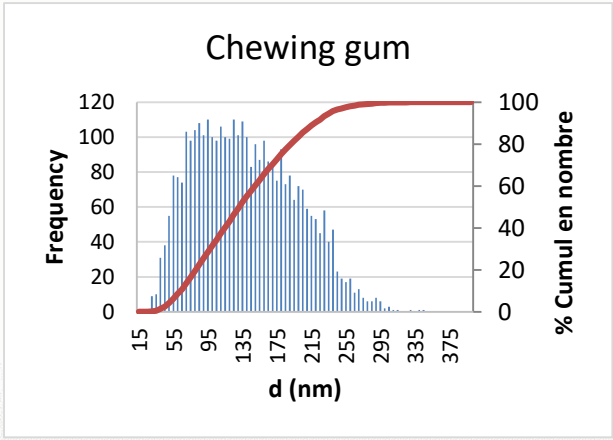
Parameter	Requirements	Description
Chemical composition/ identity	Essential	Information on chemical composition of the ENM – including purity, nature of any impurities, coatings or surface moieties, encapsulating materials, processing chemicals, dispersing agents and/or other formulants e.g. stabilisers.
Particle size (Primary/ Secondary)	Essential (two methods, one being electron microscopy)	Information on primary particle size, size range and number size distribution (indicating batch to batch variation – if any). The same information would be needed for secondary particles (e.g. agglomerates and aggregates) if present. .

Analytical strategies & methods – Conformity

Method	MEB	SP-ICP-MS
Size	✓	✓
Size range	✓	✓
Number size distribution	✓	✓
Agglomeration/Aggregation states	✓	✓

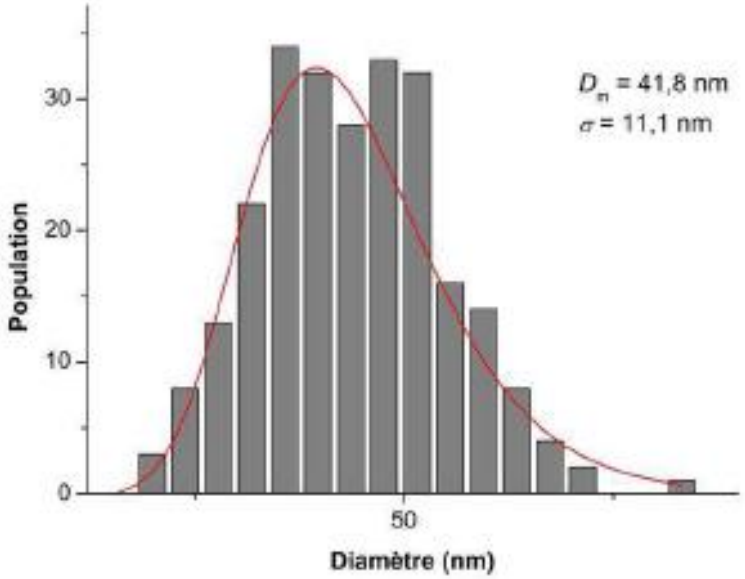


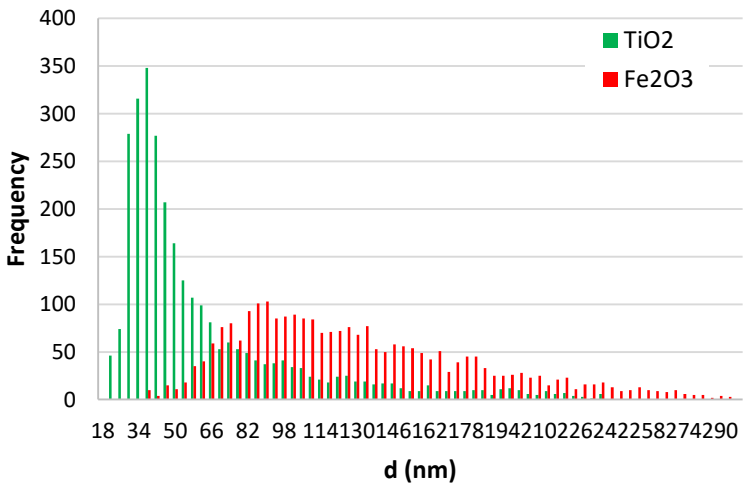




	MEB	SP-ICP-MS
Average	137 nm	140 nm
Median	127 nm	135 nm
Mode	120 nm	114 nm
<100 nm	23%	29%

Analytical strategies & methods – Conformity





	MEB	SP-ICP-MS TiO_2	SP-ICP-MS Fe_2O_3
Average	42 nm	69 nm	134 nm
Median	42 nm	46 nm	121 nm
Mode	36 nm	38 nm	70 nm
<100 nm	100 %	83 %	34 %

- × No distinction between E171/E172
- × 250 NP - Manual counting

- ✓ Differenciation E171/E172
- ✓ 3000 NP/60s
- ✓ **Selectivity & specificity**

Analytical strategies & methods – Complementarity

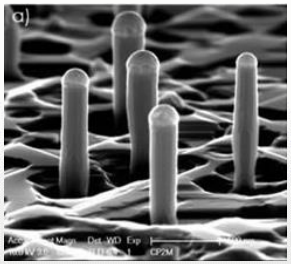
Method	MEB	SP-ICP-MS
Size	✓	✓
Size range	✓	✓
Number size distribution	✓	✓
Agglomeration/Aggregation states	✓	✓

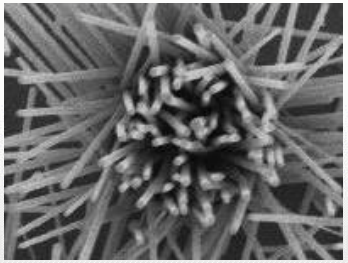
- Ferret diameter
- Various shapes

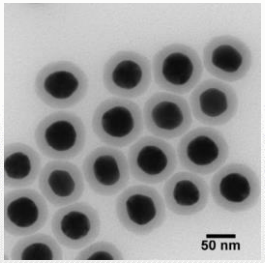
- No discrimination
- Expensive

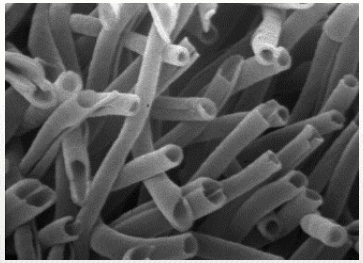
- Sphere of equivalent diameter
- Spherical

- Selectivity and specificity
- Rapid-Routine



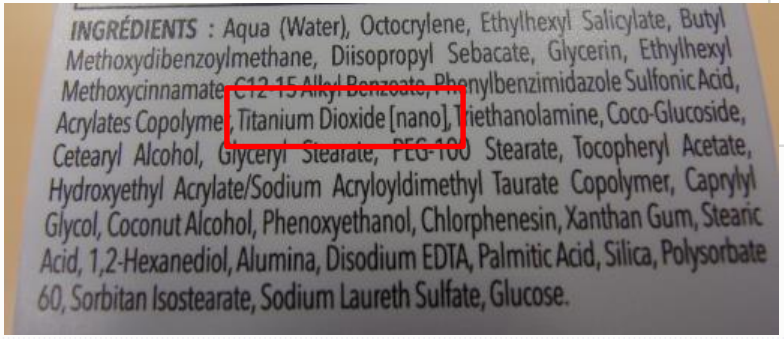


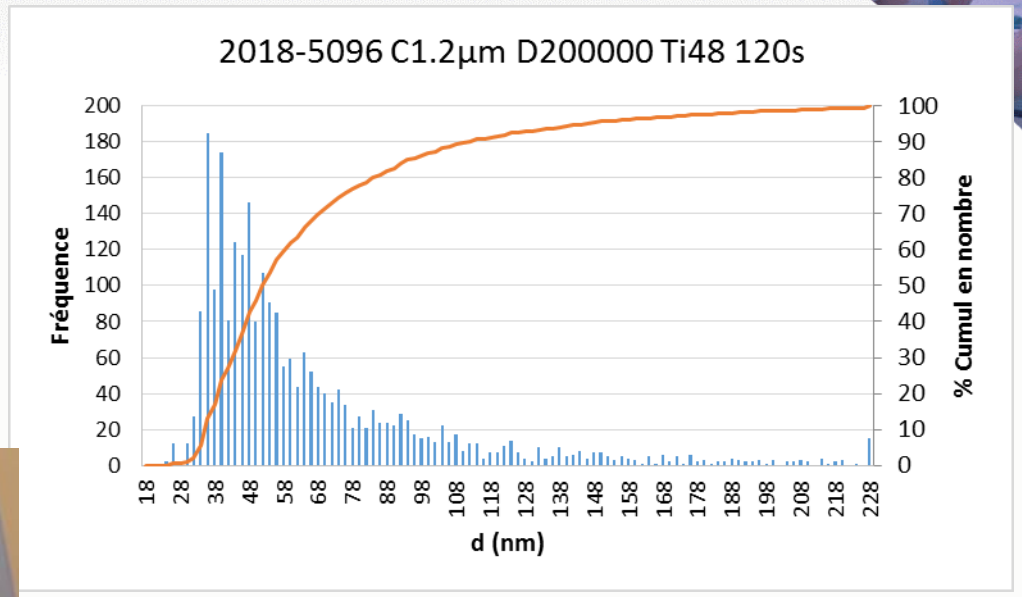




Analytical strategies & methods – Conformity

Cosmetics Real sample



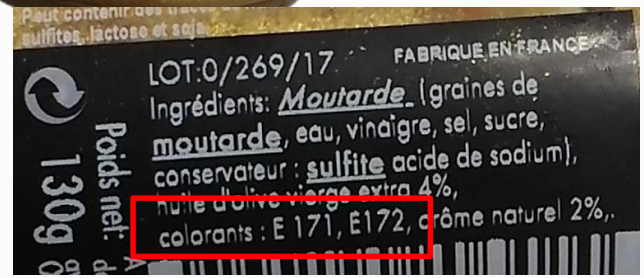


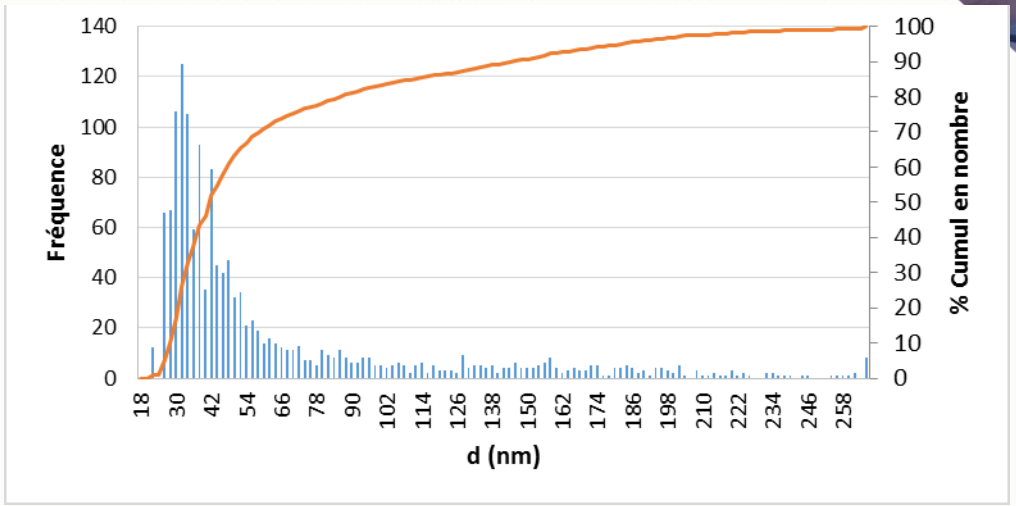
Parameters	TiO2 (E171)
Median (D50)	50 nm

D50 < 100 nm ?	Labeling [nano] ?	Conclusion ?
YES	YES	CONFORM

Analytical strategies & methods – Conformity

Food Real sample





Parameters	TiO2 (E171)
Median (D50)	49 nm

D50 < 100 nm ?	Labeling [nano] ?	Conclusion ?
YES	NO	NO CONFORM