Detection and characterisation of ENM in complex matrices

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Detection and characterization of ENM in complex matrices

Challenges

- Detection and characterization of ENM is a vast and challenging domain: nature and properties of ENM pushes all techniques to their current limits.
- The situation in complex matrices is even more challenging due to the sheer variety of possible matrices and ENM concentrations
- One of the first challenge for some projects was to determine which properties could be addressed and to prioritize the properties list.

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Challenges

- PSD were challenging and some of the first projects found the determination of PSD highly challenging.
- Surface charge characterisation were highly problematic for most of the first projects and specific WPs were devoted to challenge this specific issue. Surface charge – zeta potential still confusing discussion…

Questionnaire sent to project coordinators

- Which methods were used to detect and characterize ENM
- Major problems encountered on detection and characterization of NM
- Sample preparation for detecting ENM in complex matrices is a problem? If yes, how it has been tackled?
- How the project has contributed to advance the state of the art in the detection and characterization of ENM in complex matrices
- Open issues

1. Particle size distribution and surface charge characterisation

- Size and aggregation state can be determined by different techniques that provide different results.
- Most of ENM suspensions are not stable over time and that it is difficult to decompose signal from agglomerate to individual size of ENM within the agglomerate
- Most progress obtained by FP7 projects came from samples preparation in biological and environmental media prior to toxicological assays with inter-laboratories common protocols. Those protocols are currently discussed at the regulation and normalization levels (NANOREG).

1. Particle size distribution and surface charge characterisation

- Many efforts remain to better educate research community. For example Dynamic Light Scattering is not suited for polydisperse samples.
- X-ray based scattering tools are still poorly known, but they can provide size of individual particles and agglomerate size. Access to X-ray based tools is still difficult and European or national common platforms would help.
- The combination of size separation techniques (such as FFF) with online size measurement (such as DLS and MALS) has given promising results (for example in the SMARTNANO and NanoLyse projects)

2. Surface properties

- Surface properties (charge, redox state, chemical reactivity, coated layer structure and composition) are almost lacking from FP7 projects. It is possible to obtain such characterisation in simple aqueous systems, however it remains a fantastic challenge in complex media.
- Most FP7 projects nicely integrated the surface charge properties generally through the measurement of zeta potential.
- Protein corona: even in complex media can be now measured.

3. Quantification and location in complex matrices

- FP7 funded research has helped in applying new techniques to the detection of ENM in complex matrices. FP7 results reveal major improvement to locate and quantify ENM in complex media.
- Major improvements came from the neat combination of separation and quantification techniques. One of the most powerful methodologies combines Field Flow Fractionation to separate and isolate ENM from their matrix and to ICP-MS for their quantification.
- Recent results from FP7 projects clearly demonstrated that it is possible, even if still complex, to quantify and identify the presence of ENM in food for instance and in sediments (NanoLyse).

Progress example: NanoLyse

- Developed methods for inorganic (SiO2, Ag), carbon (fullerenes) and organic (micelles, liposomes, protein complex) NP in real food matrices
- Characterisation (size, PSD, chemical identity), quantification
- Various techniques used (EM, SPR biosensor, ELISA, FFF-LS-ICPMS, spICPMS, HDC-MALDI-ToF-MS, pDMA)
- Sample preparation tailored to matrix (chemical + enzymatic digestion, SEC, ...)
- All methods validated

Novel approaches to NP detection

- Based on advanced Surface Plasmon Resonance (SPR) microscopy. The technology provides a real-time detection of nanoparticles adsorbed to the sensor surface (NANODETECTOR)
- Combination of electroanalytical with optical method to characterize and identify, and perhaps even quantify ENMs (INSTANT)
- Miniaturized modular technology platform based of combination of FFF-UV-MALS-DLS-ICPMS and application-specific cartridges (SMARTNANO).

Novel approaches to sample preparation

- Innovative sample preparation using ionic liquid in combination with nanomaterial (INSTANT).
- Supercritical CO_2 treatment to simplify matrix. It effectively remove water and CO_2 -soluble compounds from each material, resulting in a residue that contained the ENPs (SMARTNANO).

4. On-going activities

Cross-projects measurement of common samples

- The SMART-NANO, NANODETECTOR and INSTANT projects are executing a campaign of common measurements.
- Running at the moment: measurement of commercially-available NP standards (AuNP. AgNP, TiO2-NP).
- Second stage (summer 2015): measurement of “real” NM-containing samples (including sample preparation).

- Inventory of dispersion protocols and SOPs for analytical methods (NanoDefine)

5. Future Issues

Detection of ENM

- Improvements in techniques: more robust, more sensitive and chemically specific (X-ray based tools may help for inorganic ENMs).
- Particle counting techniques (EC definition)
- Metrology issues: determination of method performance characteristics (validation), harmonised validation guidelines. (Certified) Reference Materials (NP in complex matrix).
- Detection of non-metallic (organic) ENM (ICP-MS basically works only for metallic NP).

5. Future Issues

Sample preparation

- Sample preparation is a key issue for most methods for the analysis of NP in complex matrices.
- More general sample preparation approaches are needed.

Characterization of ENM Surfaces

- Properties of ENM heavily depends on the functionalization of the ENM surface and the same core material can exhibit very different properties based on differences in their coatings.
- Need for techniques, guidance and approaches to measure surface coating and surface properties of ENM.

CONCLUSIONS

- 5 years ago importance and challenges of analysis in complex matrices largely underestimated –
  now better recognised, but still needs more attention
- Cross-talk between toxicology and physico-chemical characterisation improved –
  establish interdisciplinary collaboration within projects and beyond
- Most work on method development carried out in WPs of projects has focued on hazard, exposure, release etc. using existing technologies
- Dedicated focused projects for technology improvement + innovation needed to deliver tools for tailored methods in other projects