

ENVIRONMENTAL NANOTECHNOLOGY: An Analytical Platform for the characterization of Engineered Nanomaterials

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The lack of reliable methods to determine nanoparticles identity, characteristics and concentrations, as well as their transformations in complex systems (environmental and biological) is one of the most significant troubles in nanosciences. In the case of environmental nanosciences analysis at environmentally relevant concentrations adds an extra level of difficulty.

Inductively coupled plasma mass spectrometry (ICPMS) is a multielemental-specific technique, which is used routinely for the quantification of the elemental content of nanoparticles and nanomaterials. However, novel approaches based on the use of ICPMS are emerging. Direct analysis based on the detection of individual nanoparticles (single particle-ICPMS) [1] and hyphenation of flow field flow fractionation (FIFFF) techniques to ICPMS [2] are two of the most promising ones. Whereas FIFFF-ICPMS allows the separation and quantification of nanoparticles according to their size, single particle detection ICPMS provides information about dissolved and nanoparticle forms of an element, size distributions, and number and mass concentration without previous separation. The use of ultrafiltration in combination with ICP-MS analysis allows to fractionate an element in a suspension as dissolved and nanoparticle forms, complementing and supporting the information provided by the two other methods. A platform of analytical methods based in ultrafiltration-ICPMS, single particle-ICPMS and FIFFFICPMS is proposed to face and solve different types of nanometrological problems, which are current challenges in nanosciences, as well as in analytical chemistry.

When NPs reach a biological environment, medium components, especially proteins, compete for binding to the NP's surface, leading to development of a new interface, commonly referred to as the "protein corona". The rich protein shell gives the NPs a biological identity that can be very different from their synthetic one, in terms of their chemical-physical properties. There are many factors influencing the detailed nature of the NP biomolecule corona, with NP size, shape, surface charge, and solubility all playing a role in the interaction of the NPs with proteins. Understanding NP-protein interaction is crucial for both the bioapplications and safety of nanomaterials. Optimización of different electrophoretic methods (PAGE and especially AGE) will be shown for AgNP-proteins corona characterization.

The physicochemical characterization of CeO₂ NPs entails a series of analytical challenges related to their small size, nature, and solution physicochemistry, as well as to small concentration in environmental samples. Sensitive methods providing low limits of detection is required. We will shown methods to couple a fractionation technique (Field Flow Fractionation, FFF) to a sensitive detector (ICP-MS) to reach a fine characterization of CeO₂ NPs based on the particle size.

State of the art of the analytical platform methodologies will be presented, discussing their performance, challenges, limitations and complementarity. Application to selected cases about releasing of nanoparticles from nanocomposites will also be presented, specially for Ag and CeO₂ nanomaterials

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References

- [1] F. Laborda, E. Bolea, J. Jimenez-Lamana. Single Particle Inductively Coupled Plasma Mass Spectrometry: A Powerful Tool for Nanoanalysis. *Anal. Chem.*, 86, 2270, 2014.
- [2] E. Bolea, J. Jimenez-Lamana, F. Laborda, I. Abad-Alvaro, C. Blade, L. Arola, J. R. Castillo. Detection and characterization of silver nanoparticles and dissolved species of silver in culture medium and cells by AsFIFFF-UV-Vis-ICPMS: application to nanotoxicity tests. *Analyst*, 139, 914, 2014.