ACEnano—Hydrophobicity, Solubility and Reactivity Monitoring of Nanomaterials

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Engineered nanomaterials are being produced in exponentially increasing quantities, due to their unique physical and chemical properties and the improved performance of final products, and therefore spur technological and economic progress. A comprehensive risk assessment of these new materials is crucial to create new adequate regulations. In the frame of the European ACEnano project, CSEM is developing innovative techniques for the characterization of nanoparticles. In particular, CSEM focuses on three key properties of nanomaterials, namely their surface hydrophobicity, solubility and reactivity.

The European project ACEnano is improving nanomaterial risk assessment by developing a widely implementable and robust tiered approach to nanomaterials physicochemical characterization, which will simplify and facilitate contextual (hazard or exposure) description and its transcription into a reliable nanomaterial grouping framework [1]. Among the key properties of nanomaterials are surface hydrophobicity, particle solubility and particle reactivity, for which there is a substantial lack of techniques for reproducible assessment.

Within the frame of ACEnano, the rose Bengal assay, and more generally, the dye partitioning method (the main technique for nanomaterial (NM) surface hydrophobicity assessment) has been tested for automation using a field-flow fractionation (FFF) system. The technique was chosen for its potential to combine partitioning coefficient assessment and size distribution measurement to refine the hydrophobicity of the NMs as a function of their size.

We demonstrated that this method is limited by the nature of the hydrophobic interaction, which is a weak and reversible affinity binding and leads to dye losses by contact with the FFF membrane. Therefore, the FFF–dye partitioning assessment method is not suitable for hydrophobicity assessment. However, this study raised several useful key points to consider for the dye partitioning method for surface hydrophobicity measurement such as the influence of the dye on the NM stability, the impact of the NM on the dye (*e.g.*, chemical degradation) and the general strong influence of the pH on the results.

CSEM investigated two alternative approaches, based respectively on hydrophobic interaction chromatography (HIC) with elution investigation in hydrophobic columns and on 2D surface analysis with CSEM's waveguide interrogated optical sensor (WIOS) instrument [2]. These approaches showed very promising results that will be published in a peer-reviewed journal.

For both NM solubility assessment and reactivity monitoring, CSEM developed a simple and low-cost automated mixing and colorimetric measurement system for 24 parallel assays, based on a SLAS/ANSI standard-sized disposable custom-designed microfluidic chip (well plate) as well as a standalone unit for pneumatic actuation and readout, into which the chip is placed. Nanomaterials in solution and solvents/reactants of interest can be pipetted manually or by robot into the well plate, where they are automatically and rapidly mixed 1:1 (<0.4 s) and incubated in-plate.

For solubility assessment, NMs are mixed in the system with a solvent and then the chip is placed on a plate shaker, from where an auto-sampler feeds the mixtures into an external inductively coupled plasma mass spectrometer (ICP-MS) for analysis of concentration and particle size distribution (in single particle operation mode), as depicted in Figure 1.

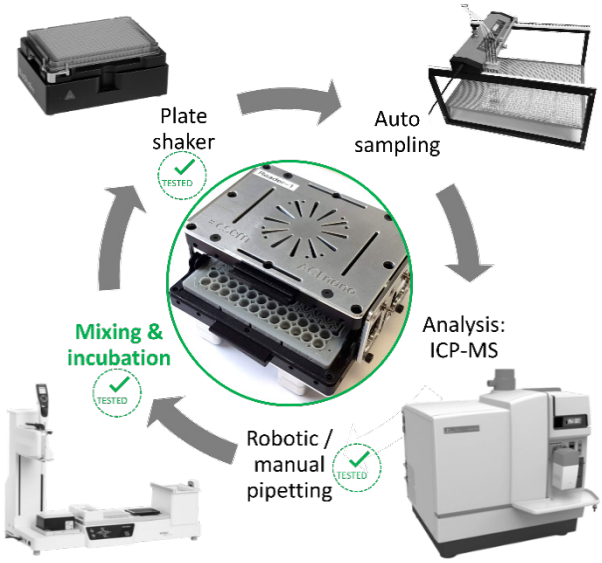

Figure 1: CSEM's automated sample preparation system (microfluidic chip inside the control unit) at the core of a new nanomaterial solubility assessment.

For reactivity monitoring, the control unit's 24 optical readout channels were used, compatible with a colorimetric assay for determining catalytic reactivity developed by Wageningen Food Safety Research (former RIKILT) [3]. For this assay, the control unit mixes and incubates the nanomaterials in the chip with a dye and reducing agent, and also determines the reactivity colorimetrically.

Both, the microfluidic chip and control and readout unit are currently being characterized at CSEM, while the ICP-MS solubility analysis method is being further developed by our consortium partners.

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[1] www.acenano-project.eu

[2] J. Adrian, S. Boder-Pasche, J. Diserens, S. Sánchez-Baeza, H. Gao, M. Marco, G. Voirin, "Waveguide interrogated optical immunosensor (WIOS) for detection of sulfonamide antibiotics in milk, Biosens. Bioelectron. 2009, 24, 3340-3346.

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