Protocol for quantitative analysis of inorganic and organic MNM surface coatings Deliverable 2.4

Introduction

Manufactured nanomaterials (MNM) often are chemically modified to improve e.g., their stability or dispersibility in liquids by doping, coating, or functionalization of their surfaces. Such modification can dramatically change behavior and (eco-)toxicological effects of MNMs and should therefore be taken into account in relation to grouping, categorization and risk assessment. For this reason there is a need to be able to identify, quantify and group chemical modifications of MNMs according to their chemical composition and structure, extent and structural location.

This deliverable presents a Technical Guideline with several analytical SOPs that can be used to identify and quantify selected types of inorganic and organic chemical surface modifications, including doping and surface coatings. It also can be used to screen MNM for the presence of associated impurities, however, here the results require interpretation of a chemist to judge between intentionally added surface coating or unintentionally associated impurities. The proposed SOPs are also considered important and suitable for quality control of MNMs and for characterization in toxicological studies in general and are therefore also of interest for the NANoREG Toolbox.

Description of Work

Three SOPs for characterization of unknown MNM with unknown surface modification on the screening level have been developed. The first one is a method using thermogravimetric analysis (TGA) for determination of the amount of a possible organic coating on an inorganic core particle or the amount of carbon in a possible carbon based MNM. The second is a SOP for determination of water, organic and carbonate content (loss-on-ignition: LOI) using weighing and heating in drying oven and laboratory furnace and serves as a low cost alternative to TGA. The third one is a method using wavelength dispersive x-ray fluorescence spectroscopy (WDXRF) to determine the elemental composition and thus indicates or not a possible inorganic coating or a possible carbon based MNM.

An approach was developed for specific characterization of organic surface coatings on MNM based on quantification by TGA and identification by several extraction techniques and off-line mass spectrometry (MS) techniques.

Also for specific characterization of inorganic coatings an approach was developed. This approach involves quantification of the total elemental composition of an inorganic MNM using WDXRF and specific analysis of a possible inorganic surface coating using electron microscopy (EM).

Finally, an approach for specific characterization of oxygen containing functional groups attached to the outer walls of CNT was developed. This approach is based on the ability of oxygen containing functionalities on the CNT surface to decarboxylate, decarbonylate and/or dehydrate during heating using a TGA with mass spectrometric detector.

Main Results

A first proposal for general Technical Guideline and associated SOPs for identification and quantification of chemical surface modifications of MNMs has been established. The guideline and SOPs is intended to be proposed by NANoREG as a future work item for the OECD Working Party on MNM.

The Technical Guideline consists of an initial screening procedure using relatively simple methods to first identify MNM, which may have been chemically modified by doping and/or surface coating and/or

functionalization, which is then followed by more advanced specific analysis using different proposed SOPs depending on the type(s) of possible modifications observed.

The first step to be carried out before any of the SOPs is considered, is collection all possible information on the MNM of interest from manufacturer and other sources. This includes all available analysis results of such as for example electron microscopy in reports within the NanoReg consortium, from other projects, and in the peer-reviewed literature.

Analysis on the screening level includes TGA and WDXRF. LOI and water loss on heating may be used as a simpler alternative to TGA if such instrumentation is not available. TGA with infrared spectroscopy (IR) or MS detector will increase the application range by indications of the composition of the effluent gasses.

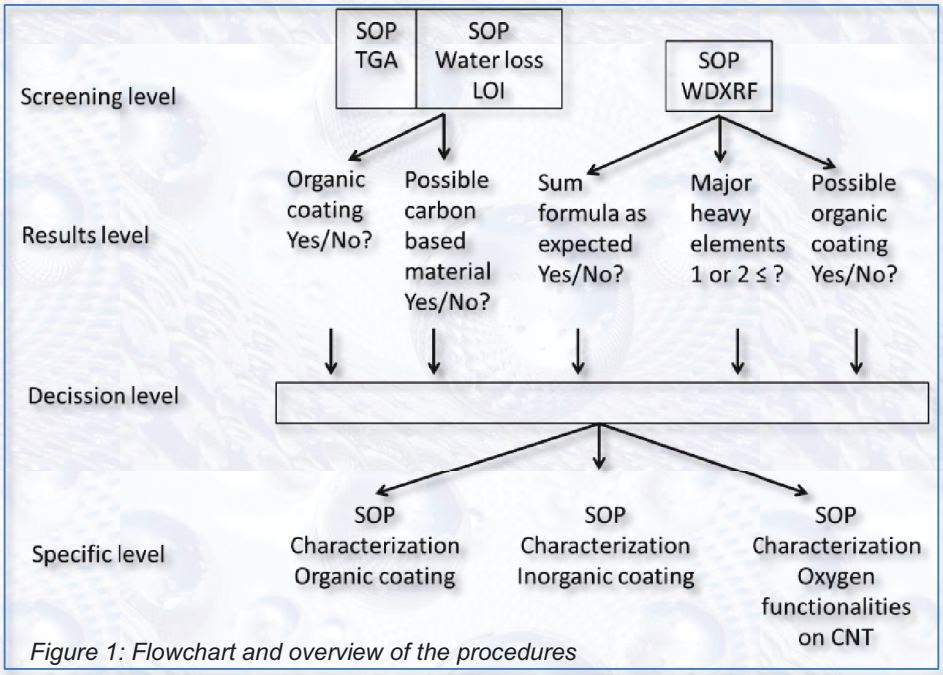

Figure 1: Flowchart and overview of the procedures

Decisions on further analysis depend on the results obtained on the screening level. If the results clearly point to an inorganic nanomaterial with an organic surface, an inorganic nanomaterial coated with an inorganic coating, or a carbon based MNM it is not difficult to decide to go further with the respective specific SOP. It may happen that the results are not conclusive, but here you have to go further with the type of MNM that are most likely.

After analysis on the specific level a combined interpretation of the screening and specific level results may be carried out to conclude on the identity and amount of surface coating on the MNM of interest. It may well happen that it is not possible to draw a final conclusion. Then it has to be decided on further analysis with methods not covered by the technical guidance document. There may be several reasons for such unsuccessful results. For inorganic MNM with organic surface coating this can be caused by reasons including covalently bound coating or a very complex structure of the MNM. Here not only surface techniques such as IR, x-ray photoelectron spectroscopy (XPS), and matrix assisted laser desorption ionization MS (MALDI-MS) may be considered, but also elemental analysis such as combustion elemental analysis (CEA) to determine the content of carbon, hydrogen, nitrogen and oxygen. For inorganic MNM with possible inorganic coating reasons include unknown, unusual, or complex crystal structure of the core MNM, of the coating or of both. Supplementary methods to be applied include x-ray diffraction to uncover the crystal structure. For carbon based materials the reasons include functionalizations containing elements other than carbon and oxygen and here CEA would be a help. Other important properties of carbon based MNM includes the content of amorphous carbon which can be deduced using Raman spectroscopy.

The Technical Guideline and associated SOPs have not been subject to interlaboratory- or full internal validation. The NANoREG core MNM does not include a sufficient number and variety of chemically modified MNM to allow validation.

For more details about NANoREG please visit the official website **www.nanoreg.eu**.

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