EURAMET
European Association of National Metrology Institutes

Title: Measurement and characterisation of engineered nanoparticles in the environment

Abstract

Engineered nanoparticles (ENPs) are currently an unregulated constituent of environmental pollution, whose impact on quality of life and the environment is poorly understood. Measuring ENPs is key for the acceptance of nanotechnology, which also promises significant quality of life benefits. It is critical to be able to detect the presence of ENPs against ambient backgrounds. Investigation of the behaviour of ENPs in complex environmental media is limited due to the lack of suitable measurement tools. Proposals should support the development of a robust measurement infrastructure for a broad range of ENP characteristics and underpin the development and validation of novel measurement techniques to both quantify and determine the behaviour of nanoparticles in environmental matrices. An estimate of the toxicological impact, based on know correlations between toxicity and one or more physico-chemical characteristics (eg size, shape, chemical composition), can only be achieved when those physico-chemical characteristics can be determined accurately, reliably, and comparably.

Conformity with the Work Programme

This Call for JRPs conforms to the EMRP 2008, section on "*Grand Challenges*" related to *Environment* on pages 8-9, 25 and 38.

Keywords

Engineered nanoparticles (ENP), environment, eco-toxicity, particle characterisation, detection of engineered nanoparticles, air quality, ultrafine particles; particle shape, particle size distribution, chemical composition, chemical binding state, water quality, soil quality, sediments.

Background to the Metrological Challenges

Engineered nanoparticles are seen as a new industrial tool with the potential to make step changes in many sectors. Already, there are estimated to be over 1000 consumer products on the global market containing nanomaterials [1]. This rapid adoption of ENPs has occurred before a real understanding of the environmental hazards is in place and arguably in the absence of any significant regulatory regime, as the volumes produced of many, but not all, nanomaterials fall below the threshold for REACH [2]. Substantial concerns therefore remain about the adoption and safe use of nanomaterials. Available data indicate that ENP are likely to exhibit different properties compared to corresponding bulk materials. There is also evidence that some, but not all, types of ENP are toxic to living species.

Substantial research published over the past few years has often produced conflicting and contradictory results from different studies on the same nanomaterial. An example of this appears in a review of the work so far on nanosilver [3], an anti-microbial additive for everything from socks to deodorants. This review was performed by the UK's Advisory Committee on Hazardous Substances (ACHS) which concluded that *"it is not possible to fully rationalise often disparate (eco)toxicology results"*. A major problem with existing studies is the inability to adequately characterise the nanomaterials under test, as well as creating reproducible dispersions for both characterisation and dosing [4, 5, 6]. Substantial work is needed before the metrology framework in Europe can offer the necessary confidence in the characterisation data obtained by scientists in the field. A comprehensive review of measurement and characterisation for nanomaterials is given in the recently published EMERGNANO report [7], which highlighted many topics requiring development in the areas of measurement, characterisation and reference materials. The EU FP7 project "CO-NANOMET – Coordination of nanometrology in Europe" [8] has created a European Nanometrology Action Group addressing specifically Engineered Nanoparticles, which will deliver recommendations by the end of 2010. The ongoing EURAMET EMRP iMERA-Plus T3.J1.1 on 'Traceable characterization of nanoparticles' is developing some methods needed for traceable measurement of nanoparticles size, size distribution, shape, and composition. Proposed JRPs may build on this work but must demonstrate that the work proposed goes beyond, or is complementary to, the iMERA-Plus Joint Research Project T3.J1.1 and other projects.

Europe has a substantial economic interest in the development of appropriate metrology as many companies are heavily involved in the development and production of nanomaterials. The uptake of these technologies is to a large extent, dependent on the reliable characterisation of the nanoparticles, both for quality control purposes and so that properly quantified assessments of their health and environmental effects can be made. There could be significant implications for business and the wider community if potential risks are not identified and managed before any harm to the environment or human health can be done. Requirements for such characterisation have been detailed in studies such as the Defra-funded REFNano Study [9] commissioned by the UK Government, and international groups such as the OECD (Organisation for Economic Cooperation and Development) Working Party on Manufactured Nanomaterials [10]. Recently, in response to the EMERGNANO report [7], the requirements for research into measurement, characterisation and reference materials were reviewed by the UK's Nanotechnology Research Strategy Group and a summary was included in Annex A of the UK's Nanotechnologies Strategy published in March 2010 [11].

1) Characterisation of Nanomaterials for environmental research

Results depend on both the characteristic being measured and on the matrix in which the ENP is dispersed. Particle size is one of the few relatively well-understood parameters with a number of in-matrix methods available, but only for well-controlled systems such as mono-disperse spherical particles in deionised water. Typical industrially supplied ENPs are rarely spherical and have both polydisperse primary particle size and often a high degree of agglomeration. The matrices of interest such as river water are complex mixtures of salts and organic and biological molecules, which not only complicate the immediate particle size measurement but can also confer a time dependent size distribution. Measurement of ENP particle size distribution in sediments and soils is more complex, usually requiring pre-processing steps, which may affect the state of agglomeration, or binding to other soil constituents.

Particle size is probably the characteristic with the best metrology framework including a number of standardised measurement methods, several completed measurement intercomparisons and a limited number of reference materials.

2) Measurement and characterisation of the nanoscale behaviour of ENPs

Currently capabilities for the measurement of ENPs in-situ within environmental matrices and organisms are extremely limited. Researchers have started to develop some techniques, but these rely on bulk samples and generally samples must include labelled nanoparticles in order to distinguish them from the naturally occurring background. Future techniques should be able to readily distinguish ENPs from a large background with sufficient resolution to be able to determine the agglomeration state and binding to soil particles or other matrix components as well as the alteration to the chemistry of the local environment (particularly important when ENPs are found in, or bound to, organisms).

3) Reference materials (RMs)

There are currently few reference nanomaterials available. They include a few mono-disperse particle size RMs, one for zeta potential and several for specific surface area (in air). Apart from the many surface area RMs for BET, availability of suitable RMs is inadequate or non-existent. Even currently available size and other reference materials do not suit the diversity of media, instrumentation and nanomaterials in use. A major need is for reference materials to aid the physicochemical characterisation of ENPs.

Scientific and Technological Objectives

Proposers should address the objectives stated below, which are based on the PRT submissions. Proposers may identify amendments to the objectives or choose to address a subset of them, in order to maximise the overall impact, or address budgetary or scientific / technical constraints, but the reasons for this should be clearly stated in the JRP protocol.

The focus of this topic is the traceable measurement and characterization of engineered nanoparticles in the environment, especially in water and in air, providing robust, and reliable measurement standards for NMIs, regulators and the eco-toxicology community.

The specific objectives are;

1. Traceable measurement where possible and characterization of key ENP quantities such as particle size distribution, number density, agglomeration/aggregation potential, water solubility/dispersibility, specific surface area (air/liquid), chemical composition
2. Development of measurement techniques to enable the detection, quantification and investigation of the behaviour of ENPs in complex environmental matrices like river water, sediments and soils
3. Development of suitable reference materials to enable calibration and validation of instrumentation, required for key eco-toxicological assessments

The proposers shall prioritise the developments and the quantities under study according to documented stakeholder needs and include measures to facilitate the development of European standards and Directives.

Proposers should establish the current state of the art including that associated with the iMERA-Plus project T3.J1.1 on 'Traceable characterization of nanoparticles', and explain how their proposed project goes beyond this.

Potential Impact

Proposals must demonstrate adequate and appropriate participation/links with the "end user" community. This may be through the inclusion of unfunded JRP partners or collaborators, or by including links to industrial/policy advisory committees, standards committees or other bodies. Evidence of support from the "end user" community (eg letters of support) is encouraged.

Where a European Directive is referenced in the proposal, the relevant paragraphs of the Directive identifying the need for the project should be quoted and referenced. It is not sufficient to quote the entire Directive per se as the rationale for the metrology need. Proposals must also clearly link the identified need in the Directive with the expected outputs from the project. In your JRP submission please detail the impact that your proposed JRP will have on any Directives:

You should also detail other Impacts of your proposed JRP as detailed in the document "Guidance for writing a JRP"

You should detail how your JRP results are going to:

- feed into the development of urgent standards through appropriate standards bodies
- transfer knowledge to the relevant industrial sectors and the environmental, health and regulatory communities.
- engage the manufacturers of the relevant materials, instrumentation and analytical techniques developed in the project.

You should also detail how your approach to realising the objectives will further the aim of the EMRP to develop a coherent approach at the European level in the field of metrology. Specifically the opportunities for:

- improvement of the efficiency of use of available resources to better meet metrological needs and to assure the traceability of national standards
- the metrology capacity of Member States and countries associated with the Seventh Framework Programme whose metrology programmes are at an early stage of development to be increased
- outside researchers & research organisations other than NMIs and DIs to be involved in the work

Time-scale

The project should be of 3 years duration.

Additional information

The references were provided by PRT submitters; proposers should therefore establish the relevance of any references.

[1] Woodrow Wilson Project on Emerging Nanotechnologies – see http://www.nanotechproject.org/inventories/consumer/

[2] DG Environment - Nanomaterials on the market: What Regulators need to Know conference report – see http://www.nanomaterialsconf.eu/

[3] Advisory Committee on Hazardous Substances – Report on Nanosilver – see http://www.defra.gov.uk/environment/quality/chemicals/achs/documents/achs-report-nanosilver.pdf

[4] DG Research: Proceedings of the workshop on research projects on the safety of nanomaterials: reviewing the knowledge gaps, 2008

[5] ENRHES: Engineered Nanoparticles: Review of Health and Environmental Safety – see http://nmi.jrc.ec.europa.eu/project/ENRHES.htm

[6] Richman E.K and Hutchison J.E, The Nanomaterial Characterisation Bottleneck, Nano, 3, 2441-2446, 2009

[7] Defra, EMERGNANO:A review of completed and near-completed environment, health & safety research on nanomaterials & nanotechnology - B0409, 2009

[8] CO-NANOMET http://www.co-nanomet.eu/page1198/Training-Resources/Nanometrology-Discussion-Papers

[9] DEFRA 2007. REFNANO, Reference Materials for engineered nanoparticle toxicology and metrology

[10] Plans for testing of a representative set of manufactured nanomaterials, OECD, Dec 2007

[11] UK Technology Strategy Board: http://www.innovateuk.org/_assets/pdf/Corporate-Publications/NanoscaleTechnologiesStrategy.pdf