FINAL PUBLISHABLE REPORT

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Project short name	ESCoShell
Project full title	An ISO Technical Report on the use of Electron Spectroscopy for Measurement of Core-Shell Nanoparticle Shell Thicknesses

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Primary Supporter: ISO TC201/SG1 c/o Pacific Northwest National Laboratory, USA, represented by Dr Don Baer, chair		
Internal Funded Partners: 1. NPL, UK 2. BAM, Germany	External Funded Partners:	Unfunded Partners:

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1 Overview

The aim of the project was to produce an ISO Technical Report on measurement of coating thicknesses (often referred to as the 'shell' thickness) on nanoparticles using electron spectroscopies such as X-ray spectroscopy (XPS) and Auger spectroscopy (AES). This has helped maximise the outputs of the EMRP BioSurf project which established the underlying metrology of key aspects of nanoparticle coating characterisation. The project has developed the ISO Technical Report and brought this to publication through ISO/TC 201 in 2021. This provides the user community with much needed validated methodology for measurement of nanoparticle coating thickness, increasingly needed in the fields of medical diagnostics, catalysis and optoelectronics.

2 Need

The Primary Supporter of this project, ISO/TC 201/SG1, "Nano-materials characterisation", represented by Don Baer (Pacific Northwest National Laboratory, USA) requested that the underlying metrology developed in HLT04 BioSurf on the measurement of nanoparticle coatings be conveyed into an ISO New Work Item to meet industry needs for progress towards standardisation of core-shell nanoparticle characterisation.

Coated nanoparticles are increasingly used in a wide variety of industries including medical diagnostics, catalysis and optoelectronics such as photovoltaic devices. In any application, knowledge of the thickness and surface chemistry of a nanoparticle coating is extremely important in understanding its behaviour and interactions with their environment. The capability to perform such measurements can be provided by electron spectroscopy. The ability to reproducibly and accurately characterise such nanoparticles is thus vital for the eventual development of nanoparticle systems for use in commercial applications. The ISO Technical Report produced by this project aids in the quick dissemination of protocols for sample preparation and analysis developed under HLT04 BioSurf, allowing for reproducible analysis of nanoparticle systems between instruments and laboratories.

3 Objectives

The objective of the project was to maximise the impact of BioSurf, specifically:

1. To publish an ISO Technical Report in ISO TC201 on methods for determination of nanoparticle coating thicknesses using electron spectroscopies.
2. To ensure the relevant user communities are aware of the ISO Technical Report and how it can improve the validity of their measurements and the development of their products.

4 Results

The purpose of the project was to maximise the impact of a previous EMPIR project BioSurf. Specifically, this was achieved via two objectives.

Objective 1. To publish an ISO Technical Report in ISO TC201 on methods for determination of nanoparticle coating thicknesses using electron spectroscopies

This objective was the main aim of the project.

A draft technical report on measurement of the thickness and nature of nanoparticle coatings measured using electron spectroscopies was written by NPL and BAM. This was reviewed and improved on by the international surface chemical analysis experts from USA, China, Japan and Europe. It was submitted for a new work item ballot in ISO TC201 (surface chemical analysis) sub-committee 7 on Electron spectroscopies. The document was approved as a new work item with multiple comments from experts. These expert comments were used to improve the draft standard. It then underwent iterative revisions where comments were received from the international experts and the document was improved by NPL and BAM. The document was then sent for draft technical report ballot and was approved for publication.

The document was then typeset by ISO central secretariat before being proofread by the project team and published in June 2021.

This objective was fully achieved. ISO 23173 Surface Chemical Analysis — Electron Spectroscopies — Measurement of the thickness and nature of nanoparticle coatings was published in June 2021, and can be accessed via ISO online: https://www.iso.org/standard/74821.html.

ISO Technical Report 23173, describes methods by which electron spectroscopies, including x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and synchrotron techniques, can be employed to calculate the coating thicknesses and compositions of nanoparticles. The document has been developed to review and outline the current state-of-the-art for such measurements. Such analyses of core-shell nanoparticles are common within the literature, however the methods employed are varied; the relative advantages and disadvantages of these methods, and the optimal usage of each may not be clear to the general analyst. ISO Technical Report 23173 aims to clarify the methods that are available, describe them in clear terms, exhibit examples of their use, and highlight potential issues users may face. The information provided should allow analysts of electron spectroscopy data to make clear choices regarding the appropriate analysis of electron spectroscopy data from coated nanoparticle systems and provide a basis for understanding and comparing results from different methods and systems.

Objective 2. To ensure the relevant user communities are aware of the ISO Technical Report and how it can improve the validity of their measurements and the development of their products.

NPL and BAM disseminated the information on the development of the ISO Technical Report to the community as widely as possible. This was done by giving presentations at national, European, and international conferences in surface analysis to maximise awareness amongst nanoparticle and electron spectroscopy analysts. In total 15 presentations at conferences and workshops were made including six invited oral presentations, which were presented in conferences in Europe, United states, Mexico, Japan and Korea.

Two publications have been published. The first on "Determining the thickness and completeness of the shell of polymer core-shell nanoparticles by XPS, SIMS and T-SEM" details characterization techniques that are used to distinguish an ideal from a non-ideal core-shell nanoparticle morphology as exampled by poly(tetrafluoroethylene)–poly(methyl methacrylate) (PTFE–PMMA) and poly(tetrafluoroethylene)–polystyrene (PTFE–PS) polymer core shell nanoparticles with a constant core diameter but varying shell thicknesses. Transmission scanning electron microscopy (T-SEM) was used for visualization of the shell, time-of-flight secondary-ion mass spectrometry (ToF-SIMS) was used for looking at systematic variations and XPS for determining the shell thickness of the nanoparticles.

The second paper published is entitled "Determining nonuniformities of core-shell nanoparticle coatings by analysis of the inelastic background of X-ray photoelectron spectroscopy survey spectra". Here methods to identify and characterise deviations from the ideal in core-shell nanoparticles are discussed. Methodology is presented by analysis of the inelastic background in XPS survey spectra allowing the following types of deviations to be identified and quantified: the nonuniformity of the shell thickness within a nanoparticle sample and the incomplete encapsulation of the cores by the shell material.

In addition, in conjunction with the publication of the ISO Technical Report, NPL and BAM have submitted a summary version of the standard as a peer reviewed paper in the journal Surface and Interface Analysis. The paper summaries the ISO standard in that it briefly outlines the methods by which the coating thickness and chemical composition of "core-shell" nanoparticles (including some variant and non-ideal morphologies) can be determined using electron spectroscopy techniques, specifically X-ray photoelectron spectroscopy, Auger electron spectroscopy, and synchrotron-based methods. The paper was submitted in June 2021 and has been accepted for publication and thus will be published in due course. In addition, NPL have published a short summary and publicity information summary via social media (i.e. LinkedIn) in order to increase awareness and uptake by industry.

This objective was fully achieved.

5 Impact

Nanoparticles are being increasingly used in a wider variety of commercial applications including consumer healthcare, drug delivery, coatings, electronics and catalysis. These nanoparticles are becoming increasingly more complex and intentionally designed with specific characteristics. Thus, accurate and valid characterisation of nanoparticles is increasingly important with a broad array of both academic and industrial laboratories engaging in or specialising in the analysis of nanoparticulate samples.

The outcome of this project was an ISO Technical Report under the auspices of ISO/TC 201 that provides clear and comprehensive methods and best practice for the measurement of nanoparticle coating thicknesses using electron spectroscopy techniques. It creates further impact from the results of the EMRP HLT04 BioSurf project which established the underlying metrology of key aspects of nanoparticle coating characterisation. The technical report also provides guidance and validated methods, which streamline the ability of industry to bring effective nanoparticle-based products to market. The engagement with the members of ISO/TC 201 has increased the impact of these efforts and driven progression towards standardisation. This committee has a strong industrial focus and is the global leader in surface chemical analysis standardisation with international experts respected throughout the scientific community. Industrial participants include Kratos Analytical (UK), SPECS (Germany), Tascon GmbH (Germany), ThermoFisher Scientific (UK), the British Standards Institute (UK), the German Institute for Standardization DIN e. V., AWE (UK), and several other major international companies.

Wider economic impact - Nanoparticles are currently used in an extremely broad array of industries, with applications in fields including catalysis, composite materials, medical devices, diagnostics, and drug delivery, opto-electronics, and many others. The use of nanoparticles in medicine and pharmaceuticals is a large and rapidly growing industry. In the field of drug delivery alone, the total market size for nanoparticle/nanocarrier based technologies is expected to surpass $130 billion (USD) over the next 5 years. By providing validated methods for measurement of such coatings and progress towards standardisation of these kinds of measurement, the ISO Technical Report greatly facilitates the development of such products and helps to meet regulatory requirements.

Nanoparticles also have great potential application as catalysts for a variety of purposes. With an expected global worth of over $30 billion (USD) for the catalyst market within the next ten years the development of coated nanoparticle-based catalysts has a significant potential impact.
Wider social impact - The ISO Technical Report impacts on the broader quality of life through the utilisation of coated nanoparticles in the healthcare and medical industries, as well as some potential use in consumer goods, such as sun cream. As previously mentioned, coated nanoparticles for use in medical applications are a large and growing industry and are likely to significantly impact on early diagnostics and treatment outcomes for major illnesses such as cancer and viruses.

Wider environmental impact - This ISO Technical Report aids in the development of several nanoparticle-based technologies which may have direct environmental impact, such as for oil recovery and in the field of photovoltaics and lighting and display technologies. The published ISO Technical Report will thus have use in a variety of nanoparticle applications in energy-related markets, leading to significant positive environmental impact.

Initial consultations with commercial XPS service providers and academics suggested that there will be a good uptake of this technical report for the determination of nanoparticle coating thickness and chemistry. Publicity of the development of this ISO document has been undertaken via social media and a submitted peer-reviewed publication. The document was discussed in 2018,2019 and 2020 at the annual meetings of the ISO TC 201 plenary and sub-committee meetings. Here, in each year the experts were informed about progress of the technical report and input received. Experts included NMIs, instrument vendors, measurement service providers and industry stakeholders. During the project, 15 presentations on the project were made at national, European, and international conferences. This includes six invited talks.

In conclusion, the main impact of this project is the usage of this ISO technical report, which will become a reference point for nanoparticle coating thickness and chemistry in order to aid products in key industrial sectors and accelerate innovation.

6 List of publications

- Determining the thickness and completeness of the shell of polymer core-shell nanoparticles by XPS, SIMS and T-SEM, The journal of Physical Chemistry C, *https://doi.org/10.1021/acs.jpcc.9b09258*
- Determining nonuniformities of core-shell nanoparticle coatings by analysis of the inelastic background of X-ray photoelectron spectroscopy survey spectra, Surface and Interface Analysis, *https://doi.org/10.1002/sia.6865*

This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/

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