TECHNICAL REPORT

ISO/TR 14187

Second edition
2020-06

Surface chemical analysis — Characterization of nanostructured materials

Analyse chimique des surfaces - Caractérisation des matériaux nanostructurés

Reference number
ISO/TR 14187:2020(E)

Contents

Foreword

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This document was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 7, *Electron spectroscopies*.

This second edition cancels and replaces the first edition (ISO/TR 14187:2011), which has been technically revised.

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Introduction

As engineered nanomaterials of many types play an increasing role in many different technologies[1], international organizations (including ISO, ASTM, the International Bureau of Weights of Measures (BIPM), Consultative Committee for Amount of Substance: Metrology in Chemistry (CCQM) and the Organization for Economic Cooperation and Development (OECD))[1] are working to identify critical properties[2] and measurements that must be understood to adequately and reproducibly define the nature of the materials being used.

A large percentage of any nanomaterial is associated with a surface or interface. Therefore, surface composition and chemistry have been identified as being part of a minimum set of chemical parameters needed to characterize nanomaterials and it would naturally seem that the wide range of tools developed for surface characterization could or should be routinely applied to these materials. Two different issues, however, have limited the impact of traditional surface analysis tools in some areas of nanoscience and nanotechnology. First, many of the tools do not have sufficient spatial resolution in three dimensions needed to analyse individual nanostructured materials (or, equivalently, variations of composition within that material). For this reason, some researchers do not consider application of the tools even though they can often provide very important information. Second, surface analytical (and other) tools are often applied to nanostructured materials without appropriately considering several analytical challenges or issues that these materials present. Such challenges include environmentally altered behaviours of nanoparticles (including effects of making measurements in vacuum), time-dependent characteristics of nanostructured materials, the influence of particle shape on analysis results, and the increased possibility of altering the structure or composition of the nanomaterial by the incident radiation (typically electrons, X-rays, or ions) during the analysis.

As noted by others including Linkov et al.[3] there are new challenges associated with understanding and characterizing nanomaterials, “the study of nanostructures and nanomaterials requires special protocols that take into account the physical [and chemical] phenomena that occur in nanosized systems.” This document gives information on these important issues. The report first describes the types of information that can be obtained about nanostructured materials, sometimes using analytical approaches beyond those in standard applications. Second, the report examines the technical challenges generally faced when applying surface analysis tools (and often other tools) for characterization of nanostructured materials as well as those specific to each technique.

Because of the expanding use of nanostructured materials in research, development, and commercial applications as well as their natural presence in air, surface, and ground water, there is an increasing need to understand the properties and behaviours of nanostructured materials as they are synthesized or as they evolve in a particular environment. The novel and unusual properties of nanostructured materials excite scientists, technologists and the general public. However, the sometimes surprising properties of many of these materials raise reproducibility, analysis or characterization issues that sometimes are unexpected by analysts, scientists, and production engineers[4-6]. There is an increasing awareness of reproducibility issues in many areas of science including those associated with materials, biological, computational, and chemical research[7-11]. Inherent characteristics of nanoparticles (NPs) that make them interesting and potentially useful also make them susceptible to reproducibility challenges associated with their production, characterization, and delivery. Inconsistencies and conflicts caused by these challenges have stimulated editorials and commentaries[5-12], scientific news items, and journal articles[4,15-18]. Careful analysis, including surface analysis as described in this report, along with data records such as described in ISO 20579-4 for preparation of nano-objects for surface analysis can help establish the provenance of a batch of nano-objects[19,20] providing a tool to address nano-object reproducibility issues.

Potential health and environmental concerns related to materials with unusual or unique properties increase the need to understand the chemical, physical and biological properties of these materials throughout their life cycle. It is now recognized that some early reports on the properties of nanoparticles and other nanostructured materials, including their toxicity and environmental stability, were based on inadequate characterizations[13]. In some cases, important characterizations appear not to have been attempted or reported[21,22]. A March 2006 article in Small Times magazine described a workshop designed to identify roadblocks to nanobiotech commercialization[13] at which several experts reported that many of the important physical characteristics needed to understand the physical and chemical properties of nanoparticles were not reported and apparently often unmeasured, especially in assessments of particle toxicity. The article further notes that the changes that these particles undergo when exposed to the environment where they are stored or used are especially important and usually unknown. In many cases, nanoparticles are coated with surfactants or contaminants, and these are often not well characterized and sometimes not adequately identified. As a result, the validity of the conclusions may be questionable. Inadequate characterization of the surface chemistry of nanoparticles has been identified as one of the areas where appropriate characterization is often lacking[5,22]. This issue was identified also by the OECD Working Party on Manufactured Nanomaterials (WPMN) and new projects are launched under the umbrella of the Malta Initiative. One of them is the "Identification and quantification of the surface chemistry and coatings on nano- and microscale materials" where surface chemical analysis will substantially contribute.

The ISO definition of a nano-object (ISO/TS 80004-1:2015) is that, in at least one dimension, the size of the object or structure must be approximately 100 nm or less. Considerable attention is being given to the characterization of nanosized-objects (particles, rods or other shapes) that might be released into the environment and a set of minimum characterization requirements for nanoparticles for use in toxicity studies has been identified[2]. However, the needs for nanomaterials characterization include the wide variety of nanostructured materials that are used in computers, as sensors, in batteries or fuel cells and many other types of applications. Nonetheless, the minimum characterization requirements for nanoparticles can be generalized to a wider range of materials and potential applications as shown in Table 1.

Surface-analysis methods of various forms (described later) can provide information that relates to many elements in Table 1 including those that appear obvious (such as surface composition and chemistry) but also includes particle or component size, presence of surface impurities, nature of surface functionality (including acidity), surface structure/morphology, near-surface variation of composition (both laterally and with depth, coating/film thickness, and electronic properties of nanostructures/films.

Surface characterization is only a subset of several nanomaterials analysis needs that are being examined by ISO/TC 229. This report on surface chemical analysis methods prepared by ISO/TC 201/SC 7 has been prepared in coordination with the overall characterization needs identified by experts in TC 201 and TC 229 as well as awareness of the objectives being addressed by ISO/TC 229. This document describes the information that can be obtained (and by which techniques), and examines some of the issues and challenges faced when performing such analyses.

Table 1 — Physical and chemical properties for characterization of nanostructured materials

*Items in **bold** font are properties for which surface chemical analysis can provide useful information, as described in this document.*

What does the material look like?

— **Particle/grain/film/structural unit size**(s) /size distribution

— **Grain, particle, film morphology** (shape, layered, roughness, topography)

— Agglomeration state/aggregation (e.g., do particles stick together)

What is the material made of?

— Bulk composition (including chemical composition and crystal structure)

— Bulk purity (including levels of impurities)

— **Elemental, chemical and/or phase distribution** (including surface composition and surface impurities)

What factors affect how a material interacts with its surroundings?

— Surface area

— **Surface chemistry**, including reactivity, hydrophobicity

— Surface charge

Overarching considerations to take into account when characterizing engineered nanomaterials (for toxicity studies and other applications):

— **Stability**—how do material properties (especially the surface composition, particle agglomeration, etc.) change with time (dynamic stability), storage, handling, preparation, delivery, etc.? Include solubility and the rate of material release through dissolution

— Context/media—how do material properties change in different media or during processing (**environmental effects**); i.e., from the bulk material to dispersions to material in various biological matrices? ("as administered" characterization is considered to be particularly important)

— Where possible, materials should be characterized sufficiently to interpret **functional behaviours.** For toxicology studies, information is required on the response to the amount of material against a range of potentially relevant dose metrics, including mass, surface area, and number concentration

This table is adapted from [2]. The recommendations in the initial table were developed at a workshop on ensuring appropriate material characterization in nanotoxicology studies, held at the Woodrow Wilson International Center for Scholars in Washington, DC, USA, between 28 October and 29 October, 2008; http://www.characterizationmatters.org.

