TECHNICAL REPORT

# ISO/TR 14187

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# Surface chemical analysis — Characterization of nanostructured materials

*Analyse chimique des surfaces — Caractérisation des matériaux nanostructurés*



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## Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

In exceptional circumstances, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example), it may decide by a simple majority vote of its participating members to publish a Technical Report. A Technical Report is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO/TR 14187 was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 5, *Auger electron spectroscopy*.

 

# 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 define the nature of the materials being used. An inherent property of any nanostructured material, whether a particle, fibre or other object, is that a large percentage of the material 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 need 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. This Technical Report 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 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 analysis or characterization issues that sometimes are unexpected by analysts, scientists, and production engineers [3-5].

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 [6]. In some cases, important characterizations appear not to have been attempted or reported [7, 8]. A March 2006 article in Small Times magazine described a workshop designed to identify roadblocks to nanobiotech commercialization [6] 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 [4, 8]. One of the definitions of a nanostructured material is that, in at last one dimension, the size of the object or structure must be 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 5 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 Technical Report 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 Technical Report.*

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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

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*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.*



 

# Surface chemical analysis — Characterization of nanostructured materials



## 1 Scope

This Technical Report provides an introduction to (and some examples of) the types of information that can be obtained about nanostructured materials using surface-analysis tools (Section 4). Of equal importance, both general issues or challenges associated with characterizing nanostructured materials and the specific opportunities or challenges associated with individual methods are identified (Section 5). As the size of objects or components of materials approaches a few nanometres, the distinctions among "bulk", "surface" and "particle" analysis blur. Although some general issues relevant to characterization of nanostructured materials are identified, this Technical Report focuses on issues specifically relevant to surface chemical analysis of nanostructured materials. A variety of analytical and characterization methods will be mentioned, but this report focuses on methods that are in the domain of ISO/TC 201 including Auger Electron Spectroscopy, X-ray photoelectron spectroscopy, secondary ion mass spectrometry, and scanning probe microscopy. Some types of measurements of nanoparticle surface properties such as surface potential that are often made in a solution are not discussed in this Report.

Although they have many similar aspects, characterization of nanometre-thick films or a uniform collection of nanometre-sized particles present different characterization challenges. Examples of methods applicable to both thin films and to particles or nano-sized objects are presented. Properties that can be determined include: the presence of contamination, the thickness of coatings, and the chemical nature of the surface before and after processing. In addition to identifying the types of information that can be obtained, the Technical Report summarizes general and technique-specific Issues that must be considered before or during analysis. These include: identification of needed information, stability and probe effects, environmental effects, specimen-handling issues, and data interpretation.

Surface characterization is an important subset of several analysis needs for nanostructured materials. The broader characterization needs for nanomaterials are within the scope of ISO/TC 229 and this report has been coordinated with experts of TC 229 Joint Working Group (JWG) 3.

This introduction to information available about nanomaterials using a specific set of surface-analysis methods cannot by its very nature be fully complete. However, important opportunities, concepts and issues have been identified and many references provided to allow the topics to be examined in greater depth as required.

## 2 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18115 parts 1 and 2 apply.

## 3 Symbols and abbreviated terms

| | |
|---|---|
| AES | Auger electron spectroscopy |
| APT | atom probe tomography |
| AFM | atomic force microscopy |
| ARXPS | angle resolved X-ray photoelectron spectroscopy |
| CNT | carbon nanotube |
| CVD | chemical vapour deposition |