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Surface chemical analysis — Guidelines to sample handling, preparation and mounting —

Part 4: Reporting information related to the history, preparation, handling and mounting of nano-objects prior to surface analysis

Analyse chimique des surfaces — Lignes directrices pour la manipulation, préparation et montage des échantillons — Partie 4: Exigences de rapport sur les nanomatériaux, défis en matière d'analyse et méthodes d'extraction des solutions

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 201, *Surface Chemical Analysis*, Subcommittee SC 2, *General Procedures*.

A list of all parts in the ISO 20579 series can be found on the ISO website.

Introduction

Introduction to the ISO 20579 series

This series is intended to assist analysts and those seeking surface chemical analysis in the handling, storage, mounting and treatment of specimens. This is a multipart document, with the first two parts being general requirements for sample handling and storage in ISO 20579-1, and mounting and treatment of samples in ISO 20579-2. The ensuing parts combine new requirements of sample handling/storage and/or sample mounting/preparation for new materials classes. ISO 20579-3 focuses on biomaterials and ISO 20579-4 focuses on reporting needs for nano-objects. Each part of this document can be used independently of the other parts, although the general procedures described in Parts 1 and 2 are applicable to a wide range of materials and are not reproduced in the materials-specific documents.

Although primarily prepared for the surface-analysis techniques of Auger-electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and secondary-ion mass spectrometry (SIMS), the methods described in this document are also applicable to many other surface-sensitive analytical techniques such as ion-scattering spectrometry, scanning probe microscopy, low-energy electron diffraction and electron energy-loss spectroscopy, where specimen handling can influence surface-sensitive measurements. AES, XPS and SIMS are sensitive to surface layers that are typically a few nanometers in thickness. Such thin layers might be subject to severe perturbations caused by specimen handling or surface treatments that could be necessary prior to introduction into the analytical chamber. Proper handling and preparation of specimens is particularly critical for dependable analysis. Improper handling of specimens can result in alteration of the surface composition and unreliable data.

Introduction to this document

Although all types of samples requiring surface analysis need thoughtful preparation, as noted in ISO 20579-1 and ISO 20579-2[1], nano-objects present additional challenges in order to avoid artefacts due to the handling and preparation of materials prior to analysis[2]. The types of procedures described in ISO 20579-1 and ISO 20579-2 apply generally to nanomaterials, but because of the nature of nano-objects it is important to carefully document how these and other procedures are implemented. This document indicates the minimum information regarding sample preparation that needs to be reported about the handling and preparation for surface analysis that should become part of sample provenance information to help assure the reliability and usefulness of data obtained from surface-analysis methods[3]. Informative Annex A provides a background to some unique aspects of nano-objects that amplify the reporting needs. Informative Annex B provides an overview of practices used by research groups around the world to extract particles from solution in preparation for surface chemical analysis, and Annex C shows an example of a sample data form. Although focused on surface chemical analysis of nano-objects, many issues apply to nanomaterials more generally.

Nanomaterials include both materials with their internal or surface structures in the nanoscale, i.e. nanostructured materials, and objects with one or more external dimensions in the nanoscale, i.e. nano-objects. Nano-objects, in particular, present a range of characterization challenges that have the potential to inhibit or delay the scientific and technological impacts of nanoscience and nanotechnology[4-10]. The standardization of these characterization methods is led by ISO TC 229 (nanotechnologies) with many standards on particle size measurement produced by ISO TC 24/SC 4. Because nano-objects are comprised to a large degree of surfaces and interfaces, the importance of adequate characterization of their surfaces and interfaces has been highlighted by many[4][11] and the roles of surface chemical analysis methods for nanomaterial characterization are discussed in ISO/TR 14187[12].

Many nano-objects are produced and stored in conditions far from a state of equilibrium, making them particularly susceptible to change as a function of time, upon exposure to different environments, during handling and when subjected to different measurements[4]. Seemingly minor variations in synthesis, age or source of precursor chemicals, processing or storage have been found to produce materials with significantly different properties or lifetimes[13-15]. The large impact of such minor changes complicates the ability of experiments to be reproduced and emphasizes the importance of sample history in providing complete information about a sample and the impacts of analysis. These types of issues have led the Organisation for Economic Co-operation and Development (OECD) to prepare a

guidance document dealing with sample preparation and dosimetry for safety testing of manufactured nanomaterials. The guidance includes an indication of the many factors that can influence materials relative to safety testing and indicates information that should be reported. However, these issues have impacts well beyond safety testing.

Many nano-objects are produced or stored in liquid environments. Although it is well recognized that it is important to analyse materials in their 'natural' environment when possible[4][9], methods often used to characterize surfaces of nano-objects involve removing materials from the natural or working environments and exposure to ambient and/or vacuum environments. A variety of approaches are being used to transport materials from the natural environment and to present the material for analysis, attempting to maintain or maximize the useful information that can be extracted from the analysis. Both care during the sample preparation, storage and processing, and accurate reporting of the process are critical to reliable understanding of the measurement results.

Accurate reporting of the sample handling and history of nano-objects is required to reproduce and validate experimental findings[3][4], mitigate contradictory information in the literature[15] and reliably address important issues such as product lifetimes and questions that are relevant to occupational and public health.

Surface chemical analysis — Guidelines to sample handling, preparation and mounting —

Part 4:
Reporting information related to the history, preparation, handling and mounting of nano-objects prior to surface analysis

1 Scope

This document identifies information to be reported in a datasheet, certificate of analysis, report or other publication regarding the handling of nano-objects in preparation for surface chemical analysis. This information is needed to ensure reliability and reproducibility of analyses needed to advance research and technology using these materials, and for obtaining appropriate understanding of potential nano-object environmental and biological impacts. Such information is in addition to other details associated with specimen synthesis, processing history and characterization, and should become part of the data record (sometimes identified as provenance information) regarding the source of the material and changes that have taken place since it was originated.

This document includes informative annexes that summarize challenges associated with nano-objects that highlight the need for increased documentation and reporting in a material data record (Annex A) and provide examples of methods commonly used to extract particles from a solution for surface chemical analysis (Annex B). An example set of relevant sample data is shown in Annex C.

This document does not define the nature of instrumentation or operating procedures needed to ensure that the analytical measurements described have been appropriately conducted.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 18115-1, *Surface chemical analysis — Vocabulary — Part 1: General terms and terms used in spectroscopy*

ISO 18115-2, *Surface chemical analysis — Vocabulary — Part 2: Terms used in scanning-probe microscopy*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18115-1 and ISO 18115-2 regarding surface analysis and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
nanomaterial
material with any external dimension in the *nanoscale* (3.4) or having internal structure or surface structure in the nanoscale

Note 1 to entry: This generic term is inclusive of nano-object and nanostructured material.

[SOURCE: ISO/TS 80004-1:2015, 2.4, modified – Note 2 to entry removed.]

3.2
nano-object
discrete piece of material with one, two or three external dimensions in the *nanoscale* (3.4)

Note 1 to entry: The second and third external dimensions are orthogonal to the first dimension and to each other.

[SOURCE: ISO/TS 80004-1:2015, 2.5]

3.3
nanoparticle
nano-object (3.2) with all external dimensions in the *nanoscale* (3.4) where the lengths of the longest and the shortest axes of the nano-object do not differ significantly

Note 1 to entry: If the dimensions differ significantly (typically by more than three times), terms such as nanofibre or nanoplate might be preferred to the term nanoparticle.

[SOURCE: ISO/TS 80004-2:2015, 4.4]

3.4
nanoscale
length range approximately from 1 nm to 100 nm

Note 1 to entry: Properties that are not extrapolations from a larger size are predominantly exhibited in this length range.

[SOURCE: ISO/TS 80004-1:2015, 2.1]

3.5
provenance information
information that documents the history of the content information

Note 1 to entry: This information tells the origin or source of the content information, any changes that might have taken place since it was originated, and who has had custody of it since it was originated.

Note 2 to entry: Examples of provenance information are the principal investigator who recorded the data, and the information concerning its storage, handling and migration.

[SOURCE: ISO 13527:2010, 1.4.2, modified — Explanatory part of definition converted to Notes 1 and 2 to entry.]

4 Provenance information to be collected or retained regarding the history, handling, storage and processing of nano-objects prior to submission for surface analysis

4.1 Information record

Surface analysis of nano-objects is usually undertaken to collect important information at specific stages during the lifetime or history of the material, such as after synthesis, before application or testing, or after application or testing. Because of the susceptibility of nano-objects to change as described in Annex A, it is important to retain as many relevant sample history and handling records as available to maintain the provenance[3][16][17] of the objects and data related to them. Information regarding the preparation of samples for surface analysis, as described in Clause 5, and the results of

surface analysis of nano-objects become part of this information record that provides the history of physical and chemical processes applied to a sample that would allow repetition of an experiment or the reproducible use of the material for other applications[18]. Appropriate information to be retained and passed along with analysis information, as indicated by the examples in 4.2 and 4.3, can vary depending on the history of the objects and the analysis objectives.

4.2 As-synthesized and as-prepared materials

Information about the nano-objects as synthesized or as prepared for application or property testing should be retained in the information record. See Annex C for an example data set.

In addition to analysis data, such information should include:

a) Record of sample synthesis

Reference or details of synthesis as known (e.g. vendor, lot number, chemical sources, temperature). (Subtle differences in process or initial chemicals can impact sample properties.)

EXAMPLE 1 Silver nanoparticles were produced by homogenous nucleation process via borohydride reduction.

EXAMPLE 2 Bio-Clean XY particles were purchased from ABC Company and received month/year, lot number 12345.

EXAMPLE 3 Single-layer graphene was grown on 25 µm 99,99 % pure Cu foil using chemical vapor deposition with methane precursor. The graphene layers cover both sides of the Cu foil.

b) Important dates: synthesis, arrival in laboratory, opening of sample container, primary measurements, expiry date.

EXAMPLE Silver nanoparticles were produced at XYZ University on December 12, 2012, and received at TUW Laboratory on December 17, 2012, then placed in a dark refrigerator for storage. The sample container was first opened on January 2, 2013. The sample was prepared for dynamic light scattering (DLS) analysis by dilution in purified water (resistivity 18,2 MΩ·cm at 25 °C) on January 5 and the first DLS measurements at TUW confirming size distribution were conducted on January 5, 2013. A set of particles were prepared for electron microscopy on January 18, 2013, with images collected the same day. The sample appeared to be stable with regard to size as observed by DLS measurements. However, it was observed to have agglomerated and formed precipitates in April 2013[19].

c) Storage time, conditions and containers (temperature, temperature variations, light shielded, shipping or transport).

EXAMPLE 1 Sample was stored in refrigerator at 3 °C upon receipt.

EXAMPLE 2 Particles were stored in initial glass packaging at ambient room temperature in dark conditions.

EXAMPLE 3 Initial suspension of particles was divided into five equal portions in new glass containers and stored under refrigeration.

d) Additional processing (e.g. dried, washed, heated, sonicated or functionalized, including method and number of times processed).

EXAMPLE 1 Dry particles were dispersed in a citrate saturated solution for storage. To assist dispersion, 50 ml of the particle suspension was sonicated for 30 min with bath/probe sonicator model 1A (effective energy input Joules/litre, probe type, operation mode) at frequency 20 kHz[17][20].

EXAMPLE 2 Samples were removed from solution using the flash dry method[21].

EXAMPLE 3 Particles formed in nitrate solution were dispersed in citrate-saturated solution (or x M solution if not saturated) to stabilize the suspension for short-term storage.

EXAMPLE 4 Graphene was transferred from 25 µm Cu foil onto NiTi stents using a 50 nm layer of poly(methyl methacrylate) 4 % in anisole and etching in 0,5 M copper nitrate solution.

4.3 After testing, exposure, treatment or retrieval

Information related to characterization of nano-objects being examined after some type of testing, environmental exposure or retrieval or after treatment by some type of deliberate or accidental process (e.g. agglomeration as a result of solution exposure, oxidation or reduction based on the working environment, coating formation or removal) should be retained in the information record.

Such information should include:

a) Information about the origin of the nano-objects, as noted in 4.1, before property testing or environmental exposure.

EXAMPLE 1 Au nanoparticles stabilized in citrate were purchased from ABC Incorporated in July 2011 for toxicity testing.

EXAMPLE 2 Physicochemical characterization measurements of the particles used in this study were conducted at 123 Laboratory in June 2013 and are summarized in report 123.

b) Record of the testing, exposure or sampling process prior to the planned measurements, including dates of testing, sampling or processing, storage conditions and any processing before storage or presentation for measurement not covered below.

EXAMPLE 1 Silver nanoparticles were suspended in cell culture media for 24 hours at 37 °C.

EXAMPLE 2 Iron nanoparticles were suspended in water containing CF_4 for 6, 12, 24, 36 and 48 hours.

EXAMPLE 3 Carbon nanotubes were suspended in solvent QRX and sonicated (type of device, operating conditions, effective energy input and time) for use in the formation of composite films.

5 Information to be reported related to preparing and mounting of nanomaterials for surface chemical analysis

5.1 General

The methods of sample handling and storage in preparation for analysis described in ISO 20579-1 and ISO 20579-2 will apply in many circumstances. Information about the following shall be provided as part of the material information record.

5.2 Initial form or packaging of sample

The nature of the sample as received shall be described (e.g. dry powder, liquid suspension).

EXAMPLE 1 Material was received as dry powder in a sealed container with an argon atmosphere.

EXAMPLE 2 Particles were received in citrate solution at a concentration of X mg/ml.

5.3 Analysis objective or special requirements

The objectives of analysis or any special sample requirements shall be described (e.g. determine thickness of an adsorbed layer, verify presence of a specific coating, determine the surface chemical state, measure the particle shape or examine the state of particles after specific reaction time).

EXAMPLE XPS measurements were used to examine the nature of surface coatings on the particles and determine the thickness of surface coatings.

5.4 Description of method used to prepare samples for analysis

A description of the procedure and any chemicals used to prepare the material for analysis shall be included. Appropriate detail shall be provided to enable the procedure to be reproduced. It is sufficient to provide a reference to a procedure that is available in the literature if that description meets this

criterion. (See Annex B for example methods, e.g. filtered from solution, washed three times in purified water, dried in a vacuum desiccator, dispersed in biological or other media).

Depending on the initial form of sample and the requirements of the analysis method, an appropriate sample preparation might be needed. Special attention needs to be paid to the dispersion of material, especially for dispersion of powders in a liquid with a focus on the stability of the dispersion. Because it can influence particle behaviour, the whole dispersion procedure, including fluid composition (water or other solvent, content of dispersant aids) and specific energy input (e.g. stirring, mixing, ultrasound) shall be described in detail. For particles in dispersions that need to be analysed in a dry state, the opposite procedure is necessary: particles have to be separated from liquid, i.e. by centrifugation or filtration, and washed, where appropriate (see Annex B). Again, the whole procedure shall be recorded.

EXAMPLE 1 Solution containing particles was washed three times using centrifugation and resuspended in purified water (see Annex B).

EXAMPLE 2 Particles were removed from solution before XPS and TEM analysis by the flash drying process described by Nurmi et al.[22]

EXAMPLE 3 Particles received in a dry state were dispersed in media to break up agglomerates before analysis.

5.5 Method of mounting sample for analysis (see ISO 20579-1 and ISO 20579-2 for examples)

EXAMPLE 1 Dispersion of cleaned particles was deposited on a cleaned silicon wafer and dried in a laminar flow cabinet with HEPA filter.

EXAMPLE 2 Drops of suspension containing nanoparticles were placed on a cleaned silicon wafer and dried[23][24]. Multiple deposits were made to fully cover the substrate.

Annex A
(informative)

Needs for enhanced documentation and application of surface chemical analysis methods to assist in identifying and avoiding artefacts and misinterpretations involving research and applications of nano-objects

A.1 Overview of challenges

A.1.1 General

In spite of the rapidly increasing numbers of publications[4], patents[25], and consumer and other products associated with nanoscience and nanotechnology, there are important underlying issues or challenges that need to be solved to enable nanotechnology to significantly impact some of the biomedical, energy and environmental challenges that confront the world community. As indicated later in this subclause, research papers, critical review articles, editorial perspectives and scientific press news articles have highlighted a variety of issues[4][11][26-33] associated with reproducible synthesis, properties and characterization.

Fundamentally, the ability, or rather inability in many circumstances, to reproducibly supply nanomaterials with repeatable and well-controlled properties impact, in many cases, the ability to manufacture, process and store nano-objects as well as the shelf life and functional lifetime of 'products' that use them. These issues affect the ability to reliably design new materials and systems as well as determine the impact of nano-objects on health and safety as they undergo transformations in the environment and in biological systems. These characteristics of nano-objects present challenges to safety testing.

ISO TC 229 has prepared guidance on physico-chemical characterization of engineered nanomaterials for toxicological assessment[34] and the OECD has prepared a document dealing with sample preparation and dosimetry for safety testing of manufactured nano-objects[17]. The document discusses many issues identified in this annex (and others) and highlights the importance of recording a wide variety of information as identified in this document.

Publication titles highlighting challenges associated with nanoscience and nanotechnology:

— 'Identification and Avoidance of Potential Artifacts and Misinterpretations in Nanomaterial Ecotoxicity Measurements' (Reference [27] Peterson);

— 'Nanosafety Research – Are we on the Right Track?' (Reference [32] Krug);

— 'Common pitfalls in nanotechnology: lessons learned from NCI's Nanotechnology Characterization Laboratory' (Reference [26] Crist);

— 'Discriminating the states of matter in metallic nanoparticle transformations: What are we missing?' (Reference [29] Pettibone);

— 'The characterization bottleneck' (Reference [31] Richmond);

— 'Nanobiomaterials and nanoanalysis: Opportunities for improving the science to benefit biomedical technologies.' (Reference [11] Grainger);

— 'The potential toxicity of nanomaterials – The role of surfaces' (Reference [30] Karakoti).