TECHNICAL
REPORT

ISO/TR 23173

First edition
2021-06

Surface chemical analysis — Electron spectroscopies — Measurement of the thickness and composition of nanoparticle coatings

Analyse chimique des surfaces — Spectroscopies d'électrons — Mesurage de l'épaisseur et de la composition des revêtements de nanoparticules

Reference number
ISO/TR 23173:2021(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

Foreword iv

Introduction v

1 Scope 1

2 Normative references 1

3 Terms and definitions 1

4 Symbols and abbreviated terms 1

5 Overview 3

6 X-ray photoelectron spectroscopy 4

6.1 General 4
6.2 Coating thickness measurement 4
6.3 Nanoparticle coating thickness 5
6.4 Numerical methods 6
6.5 Descriptive formulae 9
6.6 Modelling and simulation software 11
6.7 Method comparisons 12
6.8 Inelastic background analysis 15
6.9 Elemental composition 16
6.10 Variable excitation energy XPS 18
6.10.1 General 18
6.10.2 Qualitative depth-profiling 19
6.10.3 Quantitative depth-profiling 22
6.11 Near-ambient-pressure XPS (NAP-XPS) 23
6.11.1 General 23
6.11.2 Internal structure of bimetallic NP catalysts 24
6.11.3 Measurement of NP's in liquid suspension 24

7 Auger electron spectroscopy 26

7.1 General 26
7.2 Coating thickness measurement 26
7.2.1 General 26
7.2.2 Destructive depth-profiling 27
7.2.3 Non-destructive depth-profiling 27
7.2.4 Elemental composition 27
7.2.5 Imaging and line scans 28

8 Complementary analysis 30

9 Deviations from ideality 33

9.1 General 33
9.2 Multilayered coatings 33
9.3 Other non-ideal cases 35

Annex A (informative) **Example script for modelling of XPS data from nanoparticles** 40

Bibliography 42

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).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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

For an explanation of 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 www.iso.org/iso/foreword.html.

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

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Recently, there has been increasing development and use of nanoparticles in a wide range of application areas, including catalysis, medicine, energy, optoelectronics and cosmetics[1]–[7]. In particular, nanoparticles having some form of coating layer, which is present either by design or due to incidental processes such as contamination or oxidation, are among the most commonly studied and utilised[8]–[11]. An essential part of the characterisation of nanoparticles is the measurement of the surface properties because a large proportion of the material is at a surface or interface. In the case of coated nanoparticles, the thickness and composition of the coating has a significant role determining its functional properties and defines the interaction of the particle with its environment. Many applications require nanoparticles to have coatings that are specifically designed in order to achieve a desired level of performance. Measurement of surface composition and coating thickness of nanoparticles is a challenge to which electron spectroscopies are well suited, due to high surface sensitivity, well-understood physical principles and accessibility. Such measurements can have a significant dependence on sample format and condition; sample handling and provenance of nanoparticle samples for surface chemical analysis are addressed in ISO 20579[12]. A general introduction to the challenges of surface chemical analysis of nanostructured materials is provided in ISO/TR 14187[13].

TECHNICAL REPORT **ISO/TR 23173:2021(E)**

Surface chemical analysis — Electron spectroscopies — Measurement of the thickness and composition of nanoparticle coatings

1 Scope

This document provides a description of 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. It identifies the assumptions, challenges, and uncertainties associated with each method. It also describes protocols and issues for the general analysis of nanoparticle samples using electron spectroscopies, specifically in relation to their importance for measurements of coating thicknesses.

This document focuses on the use of electron spectroscopy techniques, specifically X-ray photoelectron spectroscopy, Auger electron spectroscopy, and synchrotron-based methods. These cannot provide all of the information necessary for accurate analysis and therefore some additional analytical methods are outlined in the context of their ability to aid in the interpretation of electron spectroscopy data.

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 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 https://www.electropedia.org/

4 Symbols and abbreviated terms

X subscripts	denote the material of the overlayer
Y subscripts	denote the material of the core
x subscripts	denote a specific photoelectron peak from material X
y subscripts	denote a specific photoelectron peak from material Y
I_i	intensity of electrons arising from a peak, i

$I_{i,I}$	intensity of electrons from peak i arising from pure material I
a	vertical thickness of the overlayer material at a given position
b	vertical thickness of the core material at a given position
$L_{i,J}$	effective attenuation length of electrons from peak i travelling through material J
R	nanoparticle core radius
T	thickness of the overlayer
d	horizontal displacement of a specific line of material
θ	angle between the central vertical axis of the particle and the point of the particle's surface which is at displacement x
$A_{x,y}$	normalised intensity ratio of the intensities of peaks x and y
γ	dimensionless scaling factor
T_∞	estimated overlayer thickness for a large sphere
T_0	estimated overlayer thickness for infinitesimally small particles
T_{NP}	estimated overlayer thickness for a nanoparticle
AES	Auger electron spectroscopy
AFM	atomic force microscopy
CSNP	core-shell nanoparticle
EAL	effective attenuation length
EDX	energy dispersive X-ray analysis
ICP-AES	inductively coupled plasma atomic emission spectroscopy
IMFP	inelastic mean free path
KE	kinetic energy
MPA	mercaptopropanoic acid
NAP-XPS	near-ambient-pressure x-ray photoelectron spectroscopy
NP	nanoparticle
SAM	scanning Auger microscopy
SANS	small angle neutron scattering
SAXS	small-angle X-ray scattering
SEM	scanning electron microscopy
TEM	transmission electron microscopy

TOP	trioctylphosphine
UHV	ultra-high vacuum
XPS	X-ray photoelectron spectroscopy

5 Overview

The methods described in this document are listed by clause and outlined in Table 1. The primary use detailed is the determination of the thickness of a nanoparticle coating from electron spectroscopy data, for which three main methods are described, with a specific example given for each. Methods for coating thickness determination that are described in detail include the use of descriptive formulae for calculation of coating thicknesses from X-ray photoelectron spectroscopy (XPS) peak intensities; numerical modelling of XPS intensities from nanoparticles, and general structure and layer thickness determination by the use of in-depth simulation software. Interpretation of sample composition from electron spectroscopy data for layered samples is discussed. Rudimentary analysis of the inelastic background in XPS data is described, alongside the relevant considerations for interpreting inelastic backgrounds from nanoparticle samples. Discussions of the use and potential benefits of synchrotron-XPS, near-ambient-pressure XPS (NAP-XPS), and Auger electron spectroscopy (AES) are included, along with any related issues and considerations. For all methods of analysis, additional characterisation is required before confident estimates of coating thickness or composition can be made. Therefore, a range of measurement techniques which are complementary to electron spectroscopy analysis, the benefits they provide, and any relevant concerns or disadvantages are outlined. A number of alternate morphologies and deviations from a uniform concentric core-shell structure are described. The effects these structural variations have on data from such samples are identified, and methods for their interpretation and analysis are discussed.

Table 1 — Summary of methods and analyses outlined in this document for the measurement of the thickness and composition of nanoparticle coatings

Clause	Details
6.4 Numerical methods	The use of simple numerical modelling to generate estimated XPS peak intensities from nanoparticles of a defined morphology. A method by which such modelling can be performed is provided, alongside a simple MathWorks® MATLAB script for performing such calculations.
6.5 Descriptive formulae	The use of methods for calculation of overlayer thicknesses using empirical or semi-empirical formulae derived from theory or modelling. Typically, these are methods whereby measured data can be input directly into a set of equations in order to derive a single calculated coating thickness value.
6.6 Modelling and simulation software	The use of electron spectroscopy modelling and simulation software. SESSA is described in detail as an example, and comparisons between it and the other methods herein are summarised, with examples.
6.8 Inelastic background analysis	Overview of the analysis of the inelastic background signal in XPS for planar overlayers, and the potential application of this for coated nanoparticles.
6.9 Elemental composition	Overview of the extraction of elemental compositions from electron spectroscopy data for coated nanoparticles And the challenges posed by systems with internal structure.
6.10 Variable excitation energy XPS	The use of variable-photon-energy XPS (e.g. utilising a synchrotron light source) for depth profiling of nanoparticles. The capabilities and applications of such methods are described, with examples.
6.11 Near-ambient-pressure XPS (NAPXPS)	An outline of the use of NAPXPS to coated nanoparticle systems, specifically regarding the potential differences between samples analysed in ultra-high vacuum conditions compared to those in an environment relevant to their application.

Table 1 *(continued)*

Clause	Details
Clause 7 Auger Electron Spectroscopy (AES)	A summary of Auger electron spectroscopy for the analysis of nanoparticles, including destructive and non-destructive depth profiling, imaging, and line-scans of individual particles. Several examples of use are summarised.
Clause 8 Complementary techniques	A list of supporting measurement techniques which provide information that can be useful when analysing electron spectroscopy data from nanoparticles. The benefits and disadvantages of each suggested technique are outlined.
Clause 9 Deviations from ideality	A summary of how nanoparticle systems might deviate from the idealised model of a uniform, concentric, spherical coated nanoparticle, and the effects of such deviations on electron spectroscopy data.

6 X-ray photoelectron spectroscopy

6.1 General

XPS provides quantitative information of the surface composition of a sample by the collection of photoelectrons emitted under exposure to an x-ray beam. The information depth of XPS is limited by the attenuation of the electrons through the sample, which itself is determined by both the properties of the sample material, and the kinetic energy of the emitted electrons. Lab-based instruments typically use either aluminium or magnesium K_α x-rays at a photon energy of 1 486,6 eV or 1 253,6 eV, respectively, this corresponds to a maximum information depth for the elastic photoelectron peaks of approximately 10 nm. More recently, lab-based instruments with higher energy X-ray sources have also been developed, with correspondingly larger information depths due to the higher kinetic energies of the photoelectrons.

Due to this high surface sensitivity, XPS is an inherently nanoscale technique in terms of depth of analysis and is thus suited to the analysis and characterisation of nano-objects. It is commonly used to provide quantitative information on the relative concentrations of elements within the surface of a sample under the assumption of homogeneity, however with a proper understanding of the underlying theory and appropriate methodology, greater information on the surface structure of samples can be extracted.

In most lab-based XPS instruments, the analysis area under standard operating conditions is on the order of 0,01 mm^2 to 1 mm^2, with some instruments possessing lens-based area-limiting or micro-focussed x-ray beams that allow analysis areas down to 10^{-4} mm^2; thus for samples of nanomaterials XPS typically serves as a population measurement technique, where the measured intensities are an average of the material within the analysis area.

Given the high surface sensitivity of XPS, it is also of crucial importance that samples be prepared, handled, and cleaned with appropriate procedures. The presence of contaminants within a sample can drastically influence the results of any measurements made. This is of especial importance for nanomaterial samples, which may often require more careful preparation, or be susceptible to additional sources of contamination. ISO 20579-4 discusses the issues relating to the handling of nano-objects prior to surface analysis[12].

6.2 Coating thickness measurement

For flat, uniform surfaces measurement of overlayer thickness using XPS has been understood for some time. A formula for the calculation of oxide overlayer thicknesses was developed in the 1970s[14]. More recently, ISO 14701[15],dealing with the measurement of silicon oxide thickness using XPS, has been published. For reporting on measurements of overlayer thicknesses using XPS, ISO 13424[16] describes the information to be included. For cases where the overlayer and substrate peaks to be quantified are not of similar kinetic energy, a graphical method known as the "Thickogram"[17] was developed. In any calculation of an overlayer thickness, it is necessary that the peak areas corresponding to the overlayer and substrate materials are identifiable and measurable.

For samples which are not flat, such methods will be in error due to the effects of sample geometry on the path-length of electrons through the overlayer. Under the assumption of a uniform overlayer thickness, a sample with a flat surface oriented for normal emission to the detector presents the shortest possible direct path for electrons through the overlayer. For a conformal, uniform overlayer any topography therefore increases this path length, in a manner equivalent to tilting the sample. Analytical methods to determine the "effective average tilt" of the sample which results from the topography[18] have been developed if the topography is either known or can be measured, for example by atomic force microscopy (AFM). For generic morphologies such as spheres and cylinders, a simpler method using the concept of "topofactors" has been shown[19]. In methods of this type, a calculation is made treating the sample as if flat, and then the relevant "topofactor" is applied to correct for the known topography[19]–[21].

Such methods for measurement of overlayers on topographic samples apply only in the case where the topography is on the macroscopic scale – that is, they cannot account for topography on the scale of the electron IMFP’s within the material. At this length scale the volumetric contribution of the coating to the XPS data becomes significant and the assumption of a continuous underlying substrate becomes invalid. For nanoparticle samples, the presence of overlayer material on the sides and underside of the particles, and potentially even particles beneath the outermost layer, can contribute to the measurement result.

6.3 Nanoparticle coating thickness

Several methods for the determination of nanoparticle coating thicknesses from XPS data are available. These can broadly be categorised into three types: simple numerical modelling, empirically determined formulae and the use of more rigorous simulation software. When any analysis of XPS data from nanoparticles is considered however, there are several assumptions which are typically made. Hereafter, particles conforming to these assumptions are described as "ideal" core-shell particles.

- The analysis area is assumed to be representative of the whole sample, exhibiting no macroscopic variation. In situations where this is not the case, multiple non-overlapping analysis areas can be used to assess the effect of any variation.
- Unless specifically accounted for, the nanoparticles are assumed to be randomly deposited, with no large-scale ordering[22]. This assumption is not necessary if the analysis method requires, or is capable of modelling, particles in a specific distribution.
- All of the measured XPS peak intensities are assumed to arise from the nanoparticles, with no significant contribution from the substrate or contaminants[10].
- The core material and coating are each assumed to be uniform in density, i.e. possess no gaps, density gradients, or similar. It follows from this assumption that the boundary between the core and coating materials is abrupt, with no mixing layer.
- The core and coating are assumed to form a pair of concentric spheres.
- All the particles in the analysed population are identical in both chemical and physical structure.
- There is no significant contribution to the signal from particles below the outermost layer, i.e. the electron path lengths do not exceed the particle size.

Depending on the analysis method selected, some of these assumptions might not be necessary, or deviations can be accounted for. This is particularly true for more advanced simulation methods, as these can be capable of accounting for many possible structural variations. Because there are a large number of possible structural variations which are indistinguishable directly from XPS data, it is important that deviations from the typical assumed case are understood and characterised using relevant analytical techniques. In some cases, variation in the XPS measurements taken can be used to corroborate or disprove these assumptions; for example the use of multiple separate analysis areas to judge sample homogeneity. Sample rotation (with respect to the analyser) may be used to identify the presence, or lack, of signal arising from the substrate, or to indicate structural discrepancies; for spherical, randomly deposited particles, angle-dependant XPS should not observe differences in the relative signal observed from the core and shell. Any discrepancy would therefore be due either to signal from the substrate, or structural deviations.

In most realistic scenarios, many of these assumptions are invalid to some degree. The effects of deviations from the assumed morphology are discussed in Clause 9.

6.4 Numerical methods

In general, a numerical modelling approach involves writing a simple script or program to calculate relative XPS intensities for the core and overlayer materials arising from a nanoparticle. By performing such calculations programmatically, for a large array of core/shell sizes, and then comparing to experimental data, an estimate of overlayer thickness can be made. Numerical modelling of the attenuation of electrons through material can be used in order to generate expected XPS peak intensities for any given material and can be applied to a broad range of sample morphologies. Despite this, there are relatively few examples of numerical modelling in the literature[23]–[25]. An understanding of the attenuation of electrons through material is required in order to correctly apply this method; this information can be readily found throughout the literature[14],[17],[19],[22]–[25]. Likewise, a rudimentary understanding of the relevant geometrical calculations is necessary, particularly if non-ideal morphologies are being considered.

Numerical modelling of this type can be performed using a broad range of software. Scientific scripting environments such as MATLAB are ideally suited, however the procedure can be translated to the majority of common programming languages and is simple enough to be implemented within common spreadsheet manipulation software. It is suited for use with most types of nanoparticle system and is particularly beneficial for systems which cannot be resolved using any descriptive formula, but which still possess a well-understood geometry.

Typically, the first step in using numerical modelling involves calculating the relative XPS intensities for the core and overlayer materials arising from a vertical line through the particle. The signal from this line can be considered equivalent to a stack of planar overlayers. The effects of elastic scattering can be corrected for by the use of effective attenuation lengths (EALs) in calculations of electron attenuation through the material. In this case, the intensities for the core and overlayer materials arising from a single line of material within an ideal particle are given by Formulae (1) and (2):

$$I_x = I_{x,X}\left[1 - e^{\left(\frac{-a}{L_{x,X}}\right)}\left(1 - e^{\left(\frac{-b}{L_{x,Y}}\right)}\left(1 - e^{\left(\frac{-a}{L_{x,X}}\right)}\right)\right)\right] \tag{1}$$

$$I_y = I_{y,Y}\, e^{\left(\frac{-a}{L_{y,X}}\right)}\left(1 - e^{\left(\frac{-b}{L_{y,Y}}\right)}\right) \tag{2}$$

where

X, Y	are the materials of the overlayer and core, respectively;
x and y	are the specific photoelectron peaks from materials X and Y;
I_i	is the intensity of electrons arising from a peak, i;
$I_{i,I}$	is the intensity of electrons from peak i arising from pure material I;

a is the vertical thickness of the overlayer material at a given position;

b is the vertical thickness of the core material at a given position;

$L_{i,J}$ is the effective attenuation length of electrons from peak, i, travelling through material J.

For lines which do not pass through the core, where $b=0$, Formulae (1) and (2) are still valid. For situations in which one of the elements within a sample is present within both the core and overlayer, simply summing the outputs of both equations will provide the total intensity for that element.

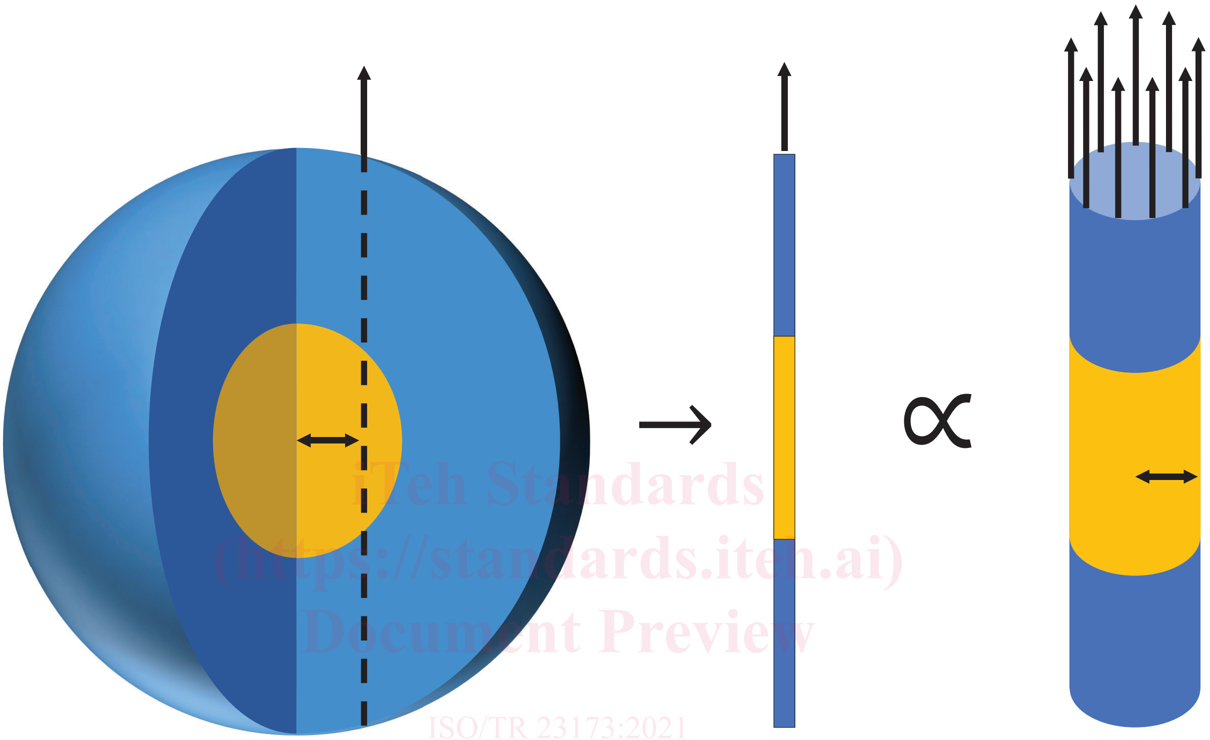

Figure 1 — Schematic illustration of the equivalence of the XPS intensity observed from an infinitesimal line at a fixed horizontal displacement to that of the hollow cylinder describing all lines at identical horizontal displacement

This calculation is repeated for an array of parallel lines through the particle and the intensities for each line summed across the entire geometry of the particle with appropriate weighting for the area represented by each line. For spherically symmetrical particles, the relative intensities arising from a vertical line of material are equivalent to those originating from the hollow cylinder described by the rotation of this line around the central vertical axis of the particle, as shown in Figure 1. Therefore, the calculation reduces to a one-dimensional summation of displacements from the central axis of the particle, with correction factors applied to account for the differing circumferences of the cylinders.

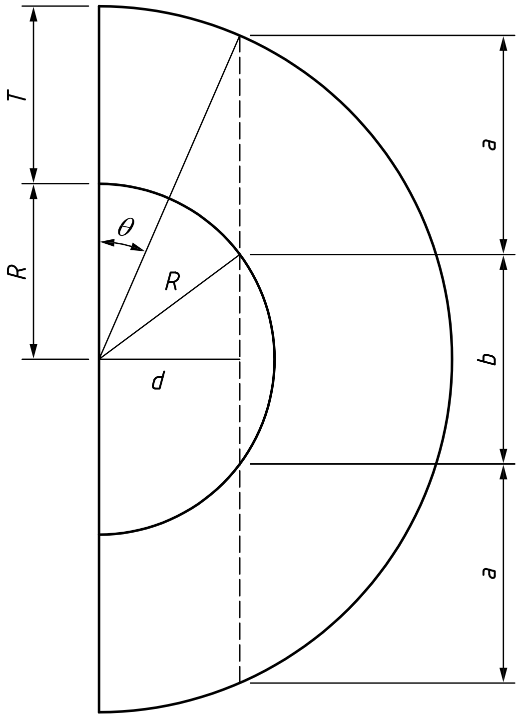

Figure 2 — Schematic of the geometry relevant to calculation of intensities from a specific line of material at a horizontal displacement x from the central vertical axis of the particle

Figure 2 depicts the relevant geometry for calculating the dimensions of an individual line of material, It is most efficient to perform the intensity calculations given in Formulae (1) and (2) in a loop from $\theta = 0$ rad to $\theta = \frac{\pi}{2}$ rad. Using this method, the parameters in Figure 2 are related by Formulae (3) to (6).

$$d = (R + T)\sin\theta \tag{3}$$

$$2a + b = 2(R + T)\cos\theta \tag{4}$$

$$b = \begin{cases} 2\sqrt{R^2 - d^2}, d < R \\ 0, d > R \end{cases} \tag{5}$$

$$a = (R + T)\cos\theta - b/2 \tag{6}$$

where

R is the nanoparticle core radius;

T is the thickness of the overlayer;

d is the horizontal displacement of a specific line of material;

a is the vertical thickness of the overlayer at displacement d;

b is the vertical thickness of the core at displacement d;

θ is the angle between the central vertical axis of the particle and the point of the particle's surface which is at displacement d.

If performing the geometry summation in this way (i.e. summing for a range of values of θ) two correction factors need to be applied. Firstly, the intensities from each individual line will be equivalent