Nuclear Instruments and Methods in Physics Research B 381 (2016) 122–131

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Energetic electron processes fluorescence effects for structured nanoparticles X-ray analysis and nuclear medicine applications

A. Taborda[a], A. Desbrée[a], A. Carvalho[b], P.C. Chaves[c], M.A. Reis[b,c,*]

[a] Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PRP-HOM/SDI/LEDI, BP-17, 31, Avenue de la Division Leclerc, 92262 Fontenay-aux-Roses, France
[b] IEQUALTECS, Lda, Rua Dr. Francisco Sá Carneiro, 36, 2500-065 S. Gregório CLD, Portugal
[c] C^2TN, Campus Tecnológico e Nuclear, Instituto Superior Técnico, Universidade de Lisboa, EN10 km 139.7, 2685-066 Bobadela LRS, Portugal

ARTICLE INFO

Article history:
Received 28 April 2016
Received in revised form 27 May 2016
Accepted 31 May 2016
Available online 16 June 2016

Keywords:
Electron fluorescence
X-ray fluorescence
PIXE
Dose deposition
SPIO
Nanoparticles

ABSTRACT

Superparamagnetic iron oxide (SPIO) nanoparticles are widely used as contrast agents for nuclear magnetic resonance imaging (MRI), and can be modified for improved imaging or to become tissue-specific or even protein-specific. The knowledge of their detailed elemental composition characterisation and potential use in nuclear medicine applications, is, therefore, an important issue. X-ray fluorescence techniques such as particle induced X-ray emission (PIXE) or X-ray fluorescence spectrometry (XRF), can be used for elemental characterisation even in problematic situations where very little sample volume is available. Still, the fluorescence coefficient of Fe is such that, during the decay of the inner-shell ionised atomic structure, keV Auger electrons are produced in excess to X-rays. Since cross-sections for ionisation induced by keV electrons, for low atomic number atoms, are of the order of 10^3 barn, care should be taken to account for possible fluorescence effects caused by Auger electrons, which may lead to the wrong quantification of elements having atomic number lower than the atomic number of Fe. Furthermore, the same electron processes will occur in iron oxide nanoparticles containing ^{57}Co, which may be used for nuclear medicine therapy purposes. In the present work, simple approximation algorithms are proposed for the quantitative description of radiative and non-radiative processes associated with Auger electrons cascades. The effects on analytical processes and nuclear medicine applications are quantified for the case of iron oxide nanoparticles, by calculating both electron fluorescence emissions and energy deposition on cell tissues where the nanoparticles may be embedded.

1. Introduction

In PIXE, secondary fluorescence corrections to prevent the overestimation of the concentration of elements in thick targets have been proposed by several authors [1–6]. The secondary fluorescence effects taken into account are, however, usually limited to the case of secondary fluorescence induced by the primary emission of X-rays, disregarding secondary fluorescence induced by primary electrons, even though these are in a larger number than the primary X-rays in the case of low energy transitions.

Literature regarding the quantification and correction of effects of the emission of secondary X-rays induced by primary Auger electrons, or secondary Auger electrons induced by primary X-rays or Auger electrons induced by proton impact in PIXE or XRF, to the best of our knowledge does not exist yet. In the case of the calculation of dose deposition the situation is different (as is the case of the work of Wälzlein et al. [7]) but existing works have focus mostly on Monte Carlo algorithms, which are not always appropriate to some applications such as its use in quantification codes for analytical methods [8].

When macroscopic samples are being dealt with, this is not an expected problem since the lack of intensity of X-rays is expected to be compensated by its much larger range in the material. On the other hand, as the dimensions of the samples being analysed are reduced, primary X-rays get less and less absorbed in the sample, but primary electrons keep losing most, or even all, of their energy inside the sample. When very small dimensions are reached, a significant fraction of these electrons will lead to the potential emission of secondary X-rays or of additional electrons that will further enhance the effect, while X-rays escape essentially without interaction with the matrix of the particle emitting them. Such

---

* Corresponding author at: C^2TN, Campus Tecnológico e Nuclear, Instituto Superior Técnico, Universidade de Lisboa, EN10 km 139.7, 2685-066 Bobadela LRS, Portugal.

E-mail address: mareis@ctn.tecnico.ulisboa.pt (M.A. Reis).

http://dx.doi.org/10.1016/j.nimb.2016.05.031
0168-583X/

processes are expected to become of particular importance in nano- and/or microparticles possessing an important fraction of light elements in their composition.

In this paper, we address the particular cases of particles having a core containing elements that emit 5–10 keV X-rays and Auger electrons, surrounded by an encapsulating layer composed of light X-ray emitting elements, which one can classify as core inhomogeneous samples. An analytical model to account for these effects is developed, discussed and applied to two particular application cases, namely the PIXE and XRF analysis of superparamagnetic iron oxide (SPIO) nanoparticles and their application in nuclear medicine.

2. General considerations of the proposed model

The general model for secondary fluorescence and secondary Auger electron emission proposed here for spherical samples is based on one of the models presented in the MSc thesis of M. A. Reis, in 1992, namely the penetration function model, published, in its form limited to the use on infinite thickness targets, in the subsequent paper on matrix corrections in PIXE analysis [6].

In Reis' penetration function model [6], the secondary fluorescence emitted by the whole sample is set as function of the point of origin of the primary radiation, an approach particularly useful in cases where at least one of the characteristic dimensions of the sample is small, of which small spherical samples are but a particular case.

Established originally for infinite thickness and for infinite foils, Reis' penetration function model still needs to be adapted to be applicable to core inhomogeneous particles. Furthermore, since in the cases dealt with in the present work, the particles' core is usually much smaller than the whole particle, itself having also nano or micrometre size dimensions, some geometrical considerations are applied.

The nanoparticles of interest in this work are typically constituted by a crystalline core with a coating composed of light elements, such as silicon, silica, phospholipids, etc. The crystalline core's dimensions are usually much smaller than the total dimension of the nanoparticle ($\varnothing_{core} \approx 5-10\,\text{nm}$, $\varnothing_{nanoparticle} \approx 50-100\,\text{nm}$).

This makes possible the adoption of the ideal geometry of a point source emission as a good approximation, as shown schematically in Fig. 1, which then allows one to consider an homogeneous sphere (of coating material) as the nanoparticle where the primary radiation is emitted from the centre of the sphere. The secondary effects that could arise from the interaction with the core material are thus disregarded.

Two different situations must be taken into account regarding the effects.

In the case of analytical processes, namely PIXE and XRF, it should be noted that the number of secondary X-rays calculated corresponds solely to the fraction of X-rays that reach the detector.

In the case of potential energy deposition, as consequent absorbed dose, such as in medical applications, the most important secondary particles to account for are electrons and the interest is on the number and mean energy of electrons that are emitted from the surface of the sphere to the surrounding media.

In the X-ray case, and since the dimensions of the nanoparticles are much smaller than the dimensions of the detector, one can also consider that all the detected X-rays will be emitted in a direction parallel to the detector direction, eliminating the need to include a detection angle in the geometric description of the problem, as shown in Fig. 2.

In the case of electrons, taking into account the spherical geometry of the problem, one can assume that the most important case to consider is that of secondary particles being emitted along the radial direction towards the nearest point at the surface of the sphere. The reasoning for this will be discussed later on, since it bears its roots on details of the model being proposed.

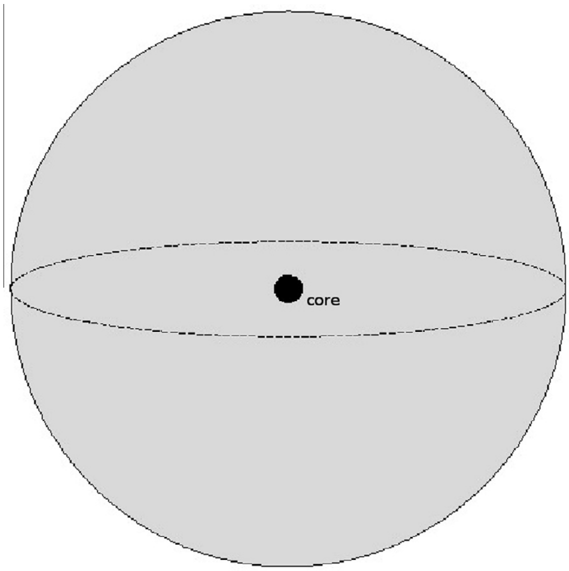

Fig. 1. Schematic representation of a typical nanoparticle: small core + thick coating. Assuming that the radius of the core is much smaller than the global radius of the particle an ideal geometrical model of point source emission at the centre of an homogeneous sphere, can be used as a good approximation.

Fig. 2. Schematic representation of the detector (on the left) and the nanoparticle/sphere (on the right).

Under these assumptions, and following the penetration function model presented by Reis et al. [6], the number of secondary X-rays, X_s, induced in a volume dV inside the target (Fig. 3) by the primary particles p_p produced at the centre of a sphere with radius r_S and emitted by the nanoparticle as a whole, in the direction of the detector can be written as:

$$d\chi^{p_p,X_s} = \frac{\Omega}{4\pi} P^{p_p}(E_{p_p}, r) R^{p_p,X_s} Q^{p_p}(r) T_d^{X_s}(r_S, r, \theta) dV \qquad (1)$$

where $p = e, X$ refers to the emitted particle being an Auger electron or a X-ray photon, respectively. The indexes p, s refer to the primary and secondary particles, respectively, $\frac{\Omega}{4\pi}$ is the detectors solid angle fraction and $P^{p_p}(E_{p_p}, r)$ is the number of primary particles p_p, of energy E_{p_p}, produced at the centre of the sphere, which reach out