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Nanotechnologies — Positron annihilation lifetime measurement for nanopore evaluation in materials

Nanotechnologies – Mesure d'annihilation de la durée de vie de positrons pour l'évaluation de nanopores dans des matériaux

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Foreword

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This document was prepared by Technical Committee ISO/TC 229, *Nanotechnologies*.

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

This document describes a method for measuring and reporting the lifetime of *ortho*-positronium utilizing the positron annihilation lifetime technique. Some of the positrons introduced into insulating materials, like oxides and organic polymers, can form the spin parallel positron-electron bound state *ortho*-positronium, which tends to localize in voids. In its trapped state, *ortho*-positronium annihilates with a lifetime that is less than its intrinsic lifetime of 142 ns in vacuum via a two-gamma annihilation process, where this lifetime component is well correlated with the void dimension. Based on this principle, one can evaluate the average porosity originating from nanometer size voids, such as free volumes in polymers. It is well documented that the positron annihilation lifetime technique is a powerful tool for characterizing the nanopores of various functional materials. Increased demands on the reliable evaluation of nanopores using this technique have emerged for various industrial applications.

This document describes a method for performing positron annihilation lifetime measurements to analyse the lifetime of the *ortho*-positronium ranging from 1 ns to 10 ns (ascribed to a pore size from approximately 0,3 nm to 1,3 nm in diameter), observed for polymeric materials. It also contains measurement procedures, data analysis, and reporting sections. In the annexes, the results of an interlaboratory comparison using two types of reference materials conducted by eight participating institutions, are described, followed by details of measurement systems that are based on the available analogue and digital methods, and a list of parameters and measurement conditions provided as a guide to the user.

Nanotechnologies — Positron annihilation lifetime measurement for nanopore evaluation in materials

1 Scope

This document describes a method for performing positron annihilation lifetime measurements using a ^{22}Na positron source that decays with β^+ emission. The β^+ (positron) lifetime is determined from a measurement of the lifetime of the *ortho*-positronium which ranges from 1 ns to 10 ns (ascribed to a pore size from approximately 0,3 nm to 1,3 nm in diameter), as observed for polymeric materials in which the positronium atoms mostly annihilate via a two-gamma annihilation process.

This document is not applicable to thin surface layers (that are less than several micrometers).

This document does not apply to measuring:

— non-positronium forming materials;

— positronium-forming materials that induce a spin conversion reaction;

— positronium-forming materials that contain chemicals influencing the annihilation process of *ortho*-positronium by chemical reactions;

— positronium-forming materials that contain mesoporous silica gels with a large contribution from the three-gamma annihilation process.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminology 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

3.1 General

3.1.1
positronium
bound state of a positron and an electron

3.1.2
positron lifetime
component lifetime corresponding to the annihilation of a large number of positrons or positroniums, and extracted from a measured lifetime spectrum

3.2 Experimental set-up

3.2.1
scintillator
material that luminesces when excited by radiation, wherein the luminescent energy is related to the energy deposited by the injected radiation

3.2.2
photomultiplier tube
vacuum phototube that converts incident light to an electronic signal, the magnitude of which is based on the energy and number of the incident photons, and subsequently amplifies that signal to provide an electrical output

3.2.3
counting rate
measured number of events per unit time where an event is the coincident detection of the photons generated during the production and annihilation of positrons

3.2.4
positron source
emitter of positrons due to nuclear transmutation via β^+ decay

Note 1 to entry: Sodium-22 (^{22}Na) transmuting to ^{22}Ne is a positron source, for example.

3.2.5
amplifier
module that increases the amplitude of a signal

3.2.6
gate and delay generator
module that generates a logic pulse of a desired duration (gate width) and with the desired delay relative to a reference event

4 Symbols and abbreviated terms

ADC analogue-to-digital converter

CFDD constant fraction differential discriminator

CRM certified reference material

DCFD differential constant fraction discriminator

GDG gate and delay generator

I relative intensity of lifetime component

LLD lower level discriminator

MCA multichannel analyzer

NIM nuclear instrument modules

PMT photomultiplier tube

Ps positronium

RI radioisotope

TAC time-to-amplitude converter

ULD upper level discriminator

***o*-Ps** *ortho*-positronium (triplet state)

***p*-Ps** para-positronium (singlet state)

τ positron or positronium component lifetime extracted from the measured lifetime spectrum

^{22}Na sodium with an atomic mass number of 22

^{22}Ne neon with an atomic mass number of 22

^{22}Ne* excited state of neon with an atomic mass number of 22

5 Principle

A fraction of the total number of positrons injected into an insulating polymer, such as polyolefins, can form positronium (Ps), the bound state of a positron and an electron. Ps forms either in:

— the singlet state, i.e. with antiparallel spins (called *p*-Ps);

— or in the triplet state with parallel spins (called *o*-Ps);

The positrons that do not form Ps will annihilate with the surrounding electrons with a mean lifetime of several hundred ps. The annihilation of *p*-Ps and *o*-Ps in vacuum have intrinsic lifetimes of 125 ps and 142 ns, respectively.

The *o*-Ps that is trapped in a pore will annihilate via the pick-off process with an electron at the pore walls and will have its lifetime shortened from the intrinsic lifetime of 142 ns. The annihilation lifetime of *o*-Ps decreases as the pore volume decreases, accordingly. An *o*-Ps lifetime of between 1 ns and 10 ns is correlated with the size of the pores. Based on this principle, the pore sizes can be estimated from the measured lifetime of *o*-Ps.

In this document, radioactive ^{22}Na with a β^+ decay is used for the positron source. The ^{22}Na nucleus that emits a positron transmutes to ^{22}Ne* within a short time, which subsequently relaxes by emitting a gamma ray photon with an energy of 1,275 MeV (see Figure 1).

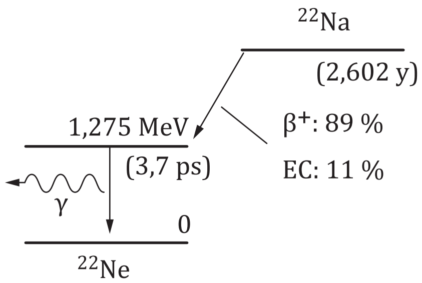

Figure 1 — Decay process of ^{22}Na

The lifetime of a single positron annihilated in a target specimen, placed in close proximity to the ^{22}Na positron source, is determined by measuring the time difference between the detection of the 1,275 MeV gamma ray photon and the 511 keV annihilation gamma ray photon in the specimen. The 1,275 MeV gamma ray photon is emitted almost simultaneously with the β+ decay. A lifetime histogram (also known as a positron annihilation lifetime spectrum) is obtained by accumulating the time differences over a large number of annihilation events, so that the mean lifetime of *o*-Ps annihilated in the sub-nanometer and nanometer-sized pores can be determined subsequently by data analysis.

The mean lifetime ($\tau = 1/\lambda$, where λ is the annihilation rate) and the respective fraction (relative intensity I) of each process can be determined by using a model function in the analysis and assuming a proper number of decay functions ascribed to the number of expected positron and Ps annihilation processes.

The number of surviving (unannihilated) positrons in the specimen at a laboratory time frame $t \geq 0$, is given by:

$$N(t) = N_0 \sum_{j=1}^{J} I_j \exp\left(-\frac{t}{\tau_j}\right) \qquad (1)$$

where N_0 is the initial number of the positrons, and J is the number of the annihilation components. Thus, the time dependence of the observed annihilation events, that is the positron annihilation lifetime spectrum [$C(t)$], is proportional to the rate of reduction of the positron number at a given time. It can be expressed as:

$$C(t) = \sum_{j=1}^{J} \frac{I_j}{\tau_j} \exp\left(-\frac{t}{\tau_j}\right) \qquad (2)$$

The *o*-Ps lifetime is obtained as the long-lived component (with a lifetime greater than 1 ns) in the experimental distribution (see Clause 10).

6 Overview of the positron annihilation lifetime measurement

A simplified schematic overview of a typical positron annihilation lifetime measurement system is shown in Figure 2.

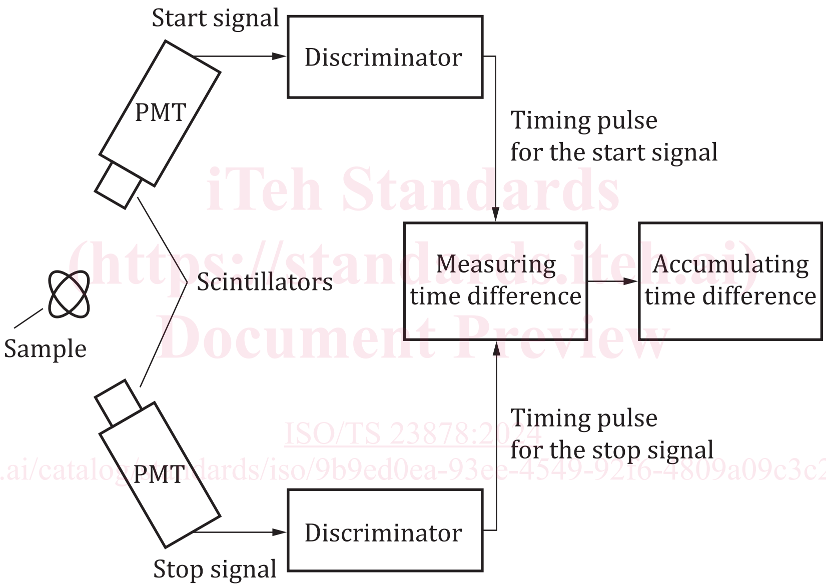

Figure 2 — Schematic overview of a positron lifetime measurement system

Start and stop signals, corresponding to the detection of the gamma ray photons from the production and the annihilation of a positron, are generated by a set of gamma-ray photon detectors. Each detector consists of a scintillator and a photomultiplier tube (PMT) that are placed on either side of the sample. Refer to Clause B.1 for guidance on detector placement. The detected signals are analysed to measure the time delay for each positron production and annihilation event.

The signals output from the PMT have amplitudes that range between a few mV to V, and are proportional to the energy of each gamma-ray photon (see Figure 3) and the scintillation and detection efficiency of that photon. The start and stop signals shall be selected by discrimination, that is, by processing only those signals with pulse amplitudes greater than the lower level discriminator (LLD) but less than the upper level discriminator (ULD), where the LLD and ULD are set differently for the start and stop signals.

The LLD and ULD assigned for each detector shall be set so that noise signals, as well as mismatch signals, are excluded from acquisition (see Figure 4). The timing pulses, which act as timing surrogates for the gamma-ray photons, can be produced by processing the PMT output signals according to several methods, such as a constant fraction discrimination (see Clause B.2). These timing surrogates are often necessary because: