
**Nanotechnologies — Characterization
of single-wall carbon nanotubes using
ultraviolet-visible-near infrared (UV-
Vis-NIR) absorption spectroscopy**

*Nanotechnologies — Caractérisation des nanotubes à simple couche
de carbone par utilisation de la spectroscopie d'absorption UV-Vis-NIR*

STANDARDSISO.COM : Click to view the full PDF of ISO/TS 10868:2017



STANDARDSISO.COM : Click to view the full PDF of ISO/TS 10868:2017



COPYRIGHT PROTECTED DOCUMENT

© ISO 2017, Published in Switzerland

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

Contents

Page

Foreword	iv
1 Scope	1
2 Normative references	1
3 Terms, definitions and abbreviated terms	1
3.1 Terms and definitions	1
3.2 Abbreviated terms	2
4 Principle	2
4.1 General	2
4.2 UV-Vis-NIR absorption spectroscopy	2
4.3 Optical absorption peaks of SWCNTs in the UV-Vis-NIR region	2
4.4 Relation between SWCNT diameter and optical absorption peaks	4
4.5 Derivation of the purity indicator from optical absorption peak areas	4
4.6 Derivation of ratio of metallic SWCNTs from optical absorption peak areas	6
5 UV-Vis-NIR spectrometer	6
6 Sample preparation method	6
6.1 General	6
6.2 Preparation of D ₂ O dispersion for measurement of mean diameter and the ratio of metallic SWCNTs	7
6.3 Preparation of solid film dispersion for measurement of the mean diameter and the ratio of metallic SWCNTs	7
6.4 Preparation of DMF dispersion for determination of the purity indicator	8
7 Optical measurement procedures and conditions	8
8 Data analysis and results interpretations	9
8.1 Data analysis for characterization of SWCNT diameter	9
8.2 Data analysis for determination of the purity indicator	9
8.3 Data analysis for characterization of the ratio of metallic SWCNTs	9
9 Measurement uncertainties	9
10 Test report	10
Annex A (informative) Case study for derivation of the relation between optical absorption peaks of SWCNTs and their mean diameter	11
Annex B (informative) Case study for determination of the purity indicator	16
Bibliography	19

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 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 229, *Nanotechnologies*.

This second edition cancels and replaces the first edition (ISO/TS 10868:2011), which has been technically revised.

Nanotechnologies — Characterization of single-wall carbon nanotubes using ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectroscopy

1 Scope

This document provides guidelines for the characterization of compounds containing single-wall carbon nanotubes (SWCNTs) by using optical absorption spectroscopy.

The aim of this document is to describe a measurement method to characterize the diameter, the purity, and the ratio of metallic SWCNTs to the total SWCNT content in the sample.

The analysis of the nanotube diameter is applicable for the diameter range from 1 nm to 2 nm.

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/TS 80004-4, *Nanotechnologies — Vocabulary — Part 4: Nanostructured materials*

3 Terms, definitions and abbreviated terms

For the purposes of this document, the terms and definitions given in ISO/TS 80004-4 and the following apply.

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

- IEC Electropedia: available at <http://www.electropedia.org/>
- ISO Online browsing platform: available at <http://www.iso.org/obp>

3.1 Terms and definitions

3.1.1

purity indicator

optically defined indicator of the ratio of the mass fraction of SWCNTs to the total carbonaceous content in a sample

Note 1 to entry: Purity indicator is NOT “purity” itself which is defined as the percentage of mass of SWCNTs to the total mass of the sample. This guideline cannot evaluate this general purity because absorption spectroscopy cannot detect metallic impurities that are generally contained in any SWCNT sample. In order to characterize metal impurity content, there is a different Technical Specification on thermogravimetric analysis. Metallic impurity is defined as catalytic metal particle and does not include metallic carbon nanotube. See ISO TS 11308.

3.1.2

ratio of metallic SWCNTs

optically defined compositional ratio of metallic SWCNTs to the total SWCNTs contained in the sample

3.2 Abbreviated terms

For the purposes of this document, the following abbreviated terms apply.

CMC	Sodium carboxymethylcellulose
DMF	Dimethylformamide
DOS	Density of states
NIR	Near infrared
NMP	N-Methyl-2-Pyrrolidone
SC	Sodium cholate
DOC	Sodium Deoxycholate
SDS	Sodium dodecyl sulfate
SDBS	Sodium dodecylbenzene sulfonate
SWCNT	Single-wall carbon nanotube
TEM	Transmission electron microscope
UV	Ultraviolet
VHS	van Hove singularity
Vis	Visible

4 Principle

4.1 General

All SWCNT samples contain both semiconducting and metallic SWCNTs, together with impurities consisting of carbon and other elements unless the samples have been altered after production. UV-Vis-NIR absorption spectroscopy can be used for the measurement of interband optical transitions specific to SWCNTs. The analysis of these optical transitions provides qualitative and semiquantitative information important for the characterization of SWCNT samples, such as mean diameter, purity, and the ratio of metallic SWCNTs to the total SWCNT content.

4.2 UV-Vis-NIR absorption spectroscopy

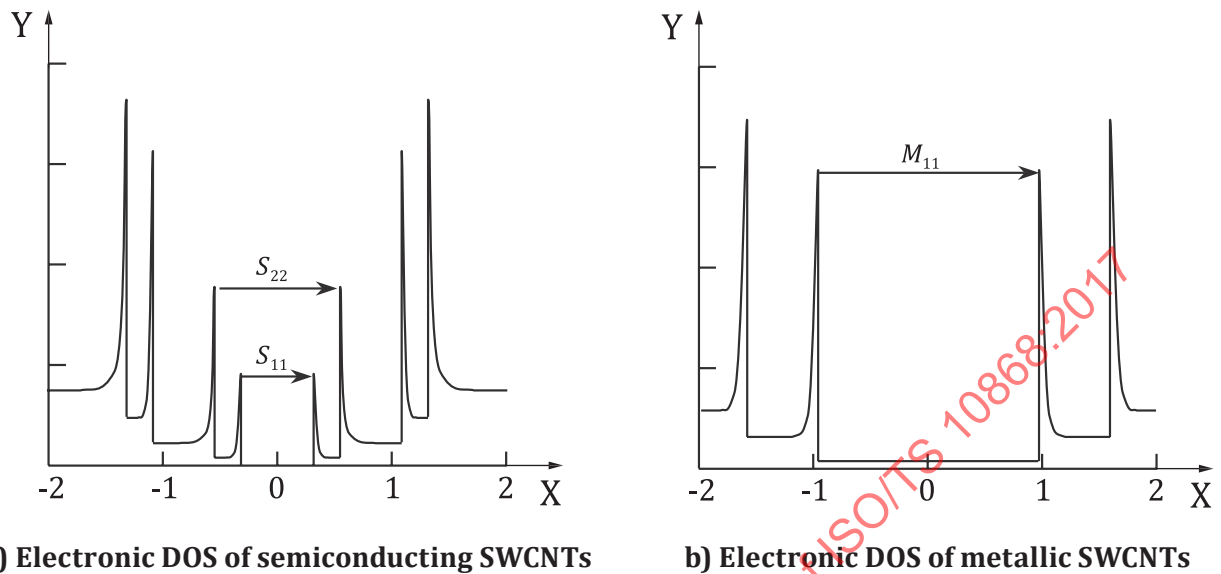
The intensity of light passing at a specified wavelength, λ , through a specimen (I) is measured and it is compared to the intensity of light before it passes through the specimen (I_0). The ratio I/I_0 is called a transmittance. The absorbance, A , is expressed as $-\log(I/I_0)$. The plot of the absorbance against wavelength for a particular compound is referred to as an absorption spectrum.

NOTE The relationship between transmittance and absorbance is only rigorously correct when reflectance is negligible and there is no scattering.

4.3 Optical absorption peaks of SWCNTs in the UV-Vis-NIR region

The shape of the electronic DOS of semiconducting and metallic SWCNTs shown in [Figure 1](#) is a series of spikes that are referred to as VHS. The peaks observed in the optical absorption spectra of SWCNTs are attributed to the electronic transitions between these VHSs as shown by arrows in [Figure 1](#). S_{11} and S_{22} are used as the symbols of the absorption due to the first and second interband transitions of

semiconducting SWCNTs, respectively [see Figure 1 a)]. M_{11} means the absorption arising from the first interband transition of metallic SWCNTs [see Figure 1 b)].



Key

X energy (eV)

Y electronic DOS (arbitrary unit)

S_{11} first interband optical transition attributed to semiconducting SWCNTs

S_{22} second interband optical transition attributed to semiconducting SWCNTs

M_{11} first interband optical transition attributed to metallic SWCNTs

NOTE 1 Arrows represent interband transitions that result in optical absorption.

NOTE 2 See Reference [2].

Figure 1 — Electronic DOS diagram of SWCNTs near the Fermi level

To interpret the absorption spectra of SWCNTs, band structures calculated using the zone-folding method are frequently used. The electronic structure of an SWCNT is generally given by that of a two-dimensional graphite sheet expressed by the tight binding approximation as shown in Formula (1)[2]:

$$E_{2D} = \pm \gamma \left[1 \pm 4 \cos \left(\frac{\sqrt{3}k_x a}{2} \right) \cos \left(\frac{k_y a}{2} \right) + 4 \cos^2 \left(\frac{k_y a}{2} \right) \right]^{1/2} \quad (1)$$

where

E_{2D} is the two dimensional energy dispersion relation for a single graphene sheet;

a is the lattice parameter[3];

k_x and k_y are the components of the reciprocal unit vector;

γ is the overlap integral.

4.4 Relation between SWCNT diameter and optical absorption peaks

Within a simple tight-binding theory, in which the electronic band structure is assumed to arise from a pure p-orbital at each conjugated carbon atom, the low-energy band gap transitions take a simple analytical form. The energy gaps corresponding to the electron transitions are given by [Formula \(2\)](#) to [Formula \(4\)](#):

$$E_g(S_{11}) = \frac{2a\gamma}{d} \quad (2)$$

$$E_g(S_{22}) = \frac{4a\gamma}{d} \quad (3)$$

$$E_g(M_{11}) = \frac{6a\gamma}{d} \quad (4)$$

where

$E_g(S_{11})$,
 $E_g(S_{22})$,
 $E_g(M_{11})$

are the energy gaps corresponding to the transitions of S_{11} , S_{22} and M_{11} , respectively;

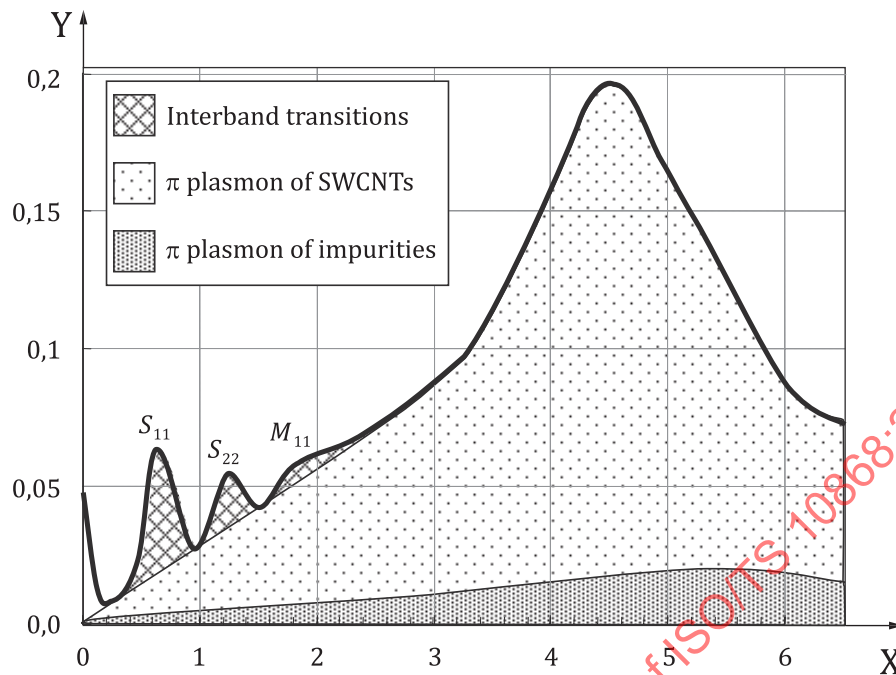
d is the diameter of SWCNTs[4].

[Formula \(2\)](#) to [Formula \(4\)](#) show a simple relationship between the diameter and the optical transition energies (and thus the peak wavelengths). This allows the estimation of the mean diameter of a SWCNT sample by the analysis of the absorption spectra originating from the optical transitions between VHSs.

[Formula \(2\)](#) to [Formula \(4\)](#) can give information related to the diameter within some limitations. One of the limitations is that the analysed peak(s) needs to be clearly resolved.

4.5 Derivation of the purity indicator from optical absorption peak areas

As mentioned in [4.3](#), there are the specific absorptions of SWCNTs originating from interband transition between VHSs. These absorption peaks are typically observed in the Vis-NIR region. On the other hand, in the UV region, most SWCNT samples present optical absorption with the peak at 200 nm to 300 nm[5]. This absorption is attributed to the collective excitations of π electron systems (π -plasmons) and can also be observed in most graphitic compounds[5]. Therefore, the π -plasmon absorption observed in most SWCNT samples is due to both SWCNTs and carbonaceous impurities. The π -plasmon absorption is extremely broad and is superposed on the above-mentioned specific absorption of SWCNTs as a featureless background extending to the Vis-NIR and IR region. To summarize, the absorption spectrum of SWCNT samples in the Vis-NIR region is composed of the interband transitions of semiconducting and metallic SWCNTs and π -plasmon absorbance (see [Figure 2](#)).

**Key**

X photon energy (eV)

Y absorbance (absorbance unit)

NOTE The relative contribution from each component is arbitrary and also has differing chiral angle distributions.

Figure 2 — Typical UV-Vis-NIR absorption spectrum of an SWCNT sample^[6]

In [Figure 2](#), the absorption from S_{nn} and M_{11} gives rise to the absorption peak areas, $AA(S_{nn})$ and $AA(M_{11})$, and that of π -plasmon as $AA(\pi)$. In addition, the total absorption [$AA(S_{nn}) + AA(\pi)$ or $AA(M_{11}) + AA(\pi)$] is designated as AA_t (see [Annex B](#)). As long as samples of concern have similar mean diameters and diameter distributions, the relative magnitude of $AA(S_{nn})$ [or $AA(M_{11})$] to AA_t can be used as an indicator of purity, $P_i(S_{nn})$ or $P_i(M_{11})$ ^{[7][8]}, which is given by [Formula 5](#):

$$P_i(S_{nn}) \text{ or } P_i(M_{11}) = AA(S_{nn} \text{ or } M_{11}) / AA_t \quad (5)$$

[Formula 5](#) gives information related to purity within some limitations. One of the limitations is that the analysed peak(s) needs to be clearly resolved. Another is that samples need to have almost similar mean diameters and distributions as determined by the locations of the peak positions.

NOTE Surfactants and/or dispersing agents could also add complexity to the spectra.

4.6 Derivation of ratio of metallic SWCNTs from optical absorption peak areas

On the basis of the analogy of 4.5, an analysis of the area under the peak for semiconducting and metallic SWCNTs provides an indicator of the ratio of metallic SWCNTs to the total SWCNTs, which is given by [Formula \(6\)](#):

$$R_{\text{Metal}} = \frac{AA(M_{11})}{AA(S_{11}) + AA(M_{11})} \quad (6)$$

Furthermore, [Formula \(6\)](#) can be converted into [Formula \(7\)](#) for R_{Metal} as the function of $AA(S_{22})$ and $AA(M_{11})$:

$$R_{\text{Metal}} = \frac{AA(M_{11})}{1,2AA(S_{22}) + AA(M_{11})} \quad (7)$$

Use of [Formula \(7\)](#) is frequently more favourable than use of [Formula \(6\)](#) because $AA(S_{11})$ is sensitive to the charge transfer^[9].

R_{Metal} does not literally represent the ratio of metallic SWCNTs, because integrated molar extinction coefficients in the M_{11} and S_{11} regions (or their relative magnitude) are not completely clarified. In the case of the SWCNT sample with the diameter distribution of 1,1 nm to 1,3 nm, [Formula \(6\)](#) and [Formula \(7\)](#) provide the actual ratio of metallic SWCNTs because these coefficients have been determined to be equal experimentally^[10].

R_{Metal} , nonetheless, can be utilized as an indicator of the ratio of metallic SWCNTs in the comparison of different samples within some limitations. One of the limitations is that all the peaks involved need to be clearly resolved. Another is that samples need to have similar mean diameters and distributions.

NOTE Most UV-Vis-NIR absorption spectra of SWCNTs show separate groups of peaks each of which can be assigned to optical transitions in the metallic or semiconducting components. At the present stage, however, determining their compositional ratio by spectral analysis is not possible, because of experimental difficulties such as the unavailability of their extinction coefficients and ambiguity in background subtraction. A qualitative comparison could still be made as to the relative abundance of each component using a certain standard sample. For example, some SWCNT samples are known to have the ratio of 0,33, as theoretically predicted under the assumption of equal synthetic probability^[11], or the ratio of 1 in the sample treated by the special separation process^[10], which can be used as a reference.

5 UV-Vis-NIR spectrometer

A calibrated standard spectrophotometer covering a broad, ultraviolet to NIR wavelength range shall be used. The long wavelength limit shall be 3 000 nm or longer to cover SWCNT diameter up to 2,5 nm. The spectrophotometer shall be turned on 1 h prior to the measurement to allow the baseline to stabilize.

6 Sample preparation method

6.1 General

Because all the SWCNT samples are generally produced as powder or solid aggregates, they shall be processed into a form that enables optical absorption measurements. Homogeneous, non-scattering and stable dispersion of SWCNTs in liquid or solid media is best suited for this purpose, the preparation of which requires a solvent and a dispersant. As they have their own optical absorption that can disturb a spectral measurement of SWCNT, solvents and dispersants shall be properly chosen as follows.

For measurement of the mean diameter and ratio of metallic SWCNTs, the dispersing method using water or heavy water (D_2O) and water-soluble surfactants shall be used because of high dispersing ability. Furthermore, for measurement in the wavelength region from UV-Vis to 1 800 nm, dispersion in D_2O shall be used because of its optical transparency over this region. Beyond 1 800 nm, however, because of the unavailability of such optically transparent solvents, solid films shall be used in which

SWCNTs are homogeneously dispersed. Because the positions of the absorption peaks are mainly determined by diameter as described in 4.4, this translates into a guideline in terms of SWCNT diameter. That is, if the diameter is known to be less than 1,4 nm, liquid dispersion shall be used. If the diameter is known to be greater than or equal to 1,4 nm, or if it is unknown, solid film dispersion shall be used.

NOTE For the preparation of D₂O dispersion of SWCNT, see 6.2, and for the preparation of solid film dispersion of SWCNT, see 6.3.

For measurement of the purity indicator, DMF dispersion shall be used instead of aqueous dispersion in order to disperse both SWCNTs and carbonaceous impurity efficiently. The procedures are separately described for the preparation of DMF dispersion in 6.4.

6.2 Preparation of D₂O dispersion for measurement of mean diameter and the ratio of metallic SWCNTs

For the preparation of D₂O dispersion of SWCNTs for measurements of mean diameter and the ratio of metallic SWCNTs, the following procedure shall be performed.

- a) Use D₂O as the solvent, which transmits light in the broad range from UV-Vis to 1 800 nm.

NOTE H₂O is unsuitable above 1 400 nm because it strongly absorbs light.

- b) Use water-soluble surfactants such as SDS, SDBS, SC and DOC as the dispersant.

The surfactants should preferably be anionic.

- c) Prepare a D₂O solution of the dispersant, at a concentration from 1 % to 2 % mass fraction.

- d) Add over 1 mg of a compound containing SWCNT into the dispersant solution of 20 ml.

- e) To facilitate the process and to obtain homogeneous SWCNT dispersion, sonicate the mixture using an ultrasonic homogenizer for a total of 30 min, continually preventing the dispersion solution from boiling by using an ice bath.

NOTE Even after ultrasonic homogenization, some SWCNTs still remain bundled, which broaden absorption peaks that are originally sharp for isolated SWCNTs, inhibiting detailed spectral analysis.

- f) To prevent such disturbance, perform ultracentrifugation with a swing rotor typically at $120\,000 \times g$ to $150\,000 \times g$ for 2 h to 5 h, or with a fixed angle (e.g. 23°) rotor at $55\,000 \times g$ to $170\,000 \times g$ for 2 h, where bundled SWCNTs can be selectively sedimented due to their slightly larger density. The rate and time depend on the purity and dispersibility of the sample, and hence should be chosen empirically so the resultant supernatant shows well-resolved absorption peaks.

- g) Collect the supernatant and use it for the subsequent absorption measurement.

6.3 Preparation of solid film dispersion for measurement of the mean diameter and the ratio of metallic SWCNTs

For the preparation of gelatin film dispersion of SWCNTs for measurements of mean diameter and the ratio of metallic SWCNTs, perform the following procedure.

- a) Use H₂O as a solvent and otherwise follow the same procedures as described in 6.2 including sonication and ultracentrifugation to obtain the supernatant.
- b) Mix the supernatant with the same volume of an H₂O solution of gelatin with a typical concentration of 10 % mass fraction. Use gelatin as a film-forming agent.
- c) Cast the mixed solution on to a quartz substrate and leave it still for 10 h or longer until it dries.

NOTE This results in the formation of an optically uniform film in which SWCNTs are homogeneously dispersed^[12]. The spectral disturbance due to the solvent absorption is now eliminated. Overnight oven drying at 50 °C can also be used for drying the films.

- d) Use the gelatin film for the subsequent absorption measurement.

Alternatively, CMC may be used for the preparation of solid film dispersion of SWCNTs for measurements of the mean diameter and the ratio of metallic SWCNTs without using surfactants.

NOTE CMC itself works both as a dispersant and a film-forming agent^[3], simplifying the sample preparation process.

For the preparation of CMC film dispersion of SWCNTs, perform the procedures e) to i) instead of a) to d).

- e) Prepare an H₂O solution of CMC usually at a concentration of 1 % mass fraction.
- f) Add a small amount (typically 1 mg) of the compound containing SWCNT into the dispersant solution, typically 20 ml.
- g) Perform sonication and ultracentrifugation as described in 6.2.
- h) Cast the supernatant on to a quartz substrate and leave it still until it dries, resulting in the formation of homogeneous film dispersion of SWCNT.
- i) Use the CMC film for the subsequent absorption measurement.

NOTE In some cases, the combined use of a surfactant and gelatin can yield better resolved absorption spectra of the film as compared with CMC used alone^[11].

6.4 Preparation of DMF dispersion for determination of the purity indicator

For the purpose of preparing dispersion samples for measurement of P_1 , perform the following procedure.

- a) Use dimethylformamide (DMF) or n-methylpyrrolidone (NMP) as a solvent, which can disperse SWCNT in a relatively efficient way without any dispersant.

NOTE This method has a limitation in dispersing ability necessary to sufficiently isolate individual SWCNTs and dispersion stability as compared with the dispersant-aided methods.

- b) Mechanically homogenize the SWCNT material to give a dry powder for accurate evaluation of bulk quantities of SWCNT material of more than 10 g. For purified SWCNT samples, the amount of material used for the purity evaluation test may be reduced to 1 mg.
- c) Disperse 50 mg of homogenized SWCNT material in 100 ml of DMF by use of an ultrasonic bath for 10 min to 20 min. Mechanical stirring facilitates homogenization during this step which should lead to a homogeneous concentrated slurry of SWCNTs in DMF.
- d) Collect a few drops of the concentrated SWCNT slurry by a pipette from different regions of the sample and dilute to 10 ml with fresh DMF and sonicate it for 10 min. By use of one or two additional 10 ml scale dilution-ultrasonication cycles, reduce the concentration to 0,01 mg/ml, which provides a stable, visually non-scattering dispersion with an optical density close to 0,2 at 12 000 cm⁻¹ (833 nm) in a 10 mm path-length cell.
- e) Use the dispersion for the subsequent absorption measurement. The dispersion shall be sonicated just before the spectral measurement in order to ensure high quality dispersion.

7 Optical measurement procedures and conditions

Measure the absorption spectrum by using the UV-Vis-NIR spectrometer. Use quartz cuvettes for solution samples. For film samples, mechanically fix them in the sample compartment of the spectrophotometer. In principle, an absorption spectrum of a SWCNT sample is defined against an appropriate reference. For a solution sample, use a solution of the dispersant with the same concentration without SWCNT as a reference. For a film sample, use a film with the same thickness without SWCNT as a reference. Perform measurements in air at room temperature.

8 Data analysis and results interpretations

8.1 Data analysis for characterization of SWCNT diameter

The procedure for determining the mean diameter of the SWCNT sample is as follows.

- Pick the peak wavelengths of maximum S_{11} , S_{22} , or M_{11} absorptions.
- Convert these wavelengths into photon energies (eV) and substitute them into [Formula \(8\)](#).
- Calculate the value of d as the mean diameter from [Formula \(8\)](#):

$$\begin{aligned} E_g(S_{11}) &= \frac{0,96}{d} \\ E_g(S_{22}) &= \frac{1,7}{d} \\ E_g(M_{11}) &= \frac{2,6}{d} \end{aligned} \quad (8)$$

NOTE The derivation of these relations is given in [Annex A](#).

8.2 Data analysis for determination of the purity indicator

The procedure for determining the purity indicator of the SWCNT sample is as follows.

- If the spectrum data is a function of wavelength (nm), convert the data to be as a function of photon energy (eV) or wavenumber (cm^{-1}).
- Integrate the total area under the absorption spectrum as AA_t .
- Draw a tangent line between the minima of the absorption curve at the low and high energy sides of the S_{nn} or M_{11} transition and calculate the area between the spectrum curve and the straight line as $AA(S_{nn})$ or $AA(M_{11})$ (see [Figure 2](#)).
- Calculate purity indicator, P_i , by using [Formula \(5\)](#).

8.3 Data analysis for characterization of the ratio of metallic SWCNTs

The procedure for determining the ratio of metallic SWCNTs to the total SWCNT content in the sample is as follows.

- Convert the spectrum data to be as a function of energy (eV) or wavenumber (cm^{-1}).
- Draw a tangent line between the minima of the absorption curve at the low and high energy sides of S_{nn} or M_{11} transition and calculate the areas between the spectrum curve and the straight line as $AA(S_{nn})$ and $AA(M_{11})$.
- Calculate R_{Metal} as an indicator of the ratio of metallic SWCNTs to the total SWCNTs in the sample by using [Formula \(6\)](#) or [Formula \(7\)](#).

9 Measurement uncertainties

Currently, the uncertainties in the optical absorption characterizations for SWCNTs should be estimated from various origins as listed below:

- a broadening effect originated from bundling of SWCNTs in the sample;
- optical absorption by impurities including multiwall CNTs and amorphous carbon contained in the sample;

- c) the statistical uncertainty associated with the diameter distribution of SWCNTs in the sample;
- d) the systematic and statistical uncertainties associated with deducing [Formula \(5\)](#) to [Formula \(8\)](#);
- e) additional uncertainties stemming from the dependence of nanotube length and surface defect density on the optical properties;
- f) traces of water in the solvent that cause spurious absorbance in the NIR;
- g) uncertainties due to change from NIR detector to UV-Vis detector that occurs in commercial spectrophotometers, introducing uncertainties into spectrum and the linear baseline correction.

10 Test report

The test report shall include the following information:

- a) the results:
 - 1) the mean diameter;
 - 2) the purity indicator, $P_i(S_{nn})$ or $P_i(M_{11})$;
 - 3) the indicator of the ratio of metallic SWCNTs, R_{Metal} ;
- b) all information necessary for the identification of the sample tested:
 - 1) the sample name;
 - 2) the lot number;
- c) all information necessary for the specimen preparation:
 - 1) the dispersant used;
 - 2) the solvent used;
 - 3) the sonication power;
 - 4) the sonication time;
 - 5) the centrifugal force;
 - 6) the centrifugation time;
 - 7) the type of sonicator (tip, horn, bath, etc.);
- d) the type of apparatus used;
- e) details regarding the analysis procedure:
 - 1) the type of interband transition (S_{11} , S_{22} or M_{11}) used in the each analyses;
 - 2) calculated energy range of spectrum for deducing P_i and R_{Metal} .

Annex A

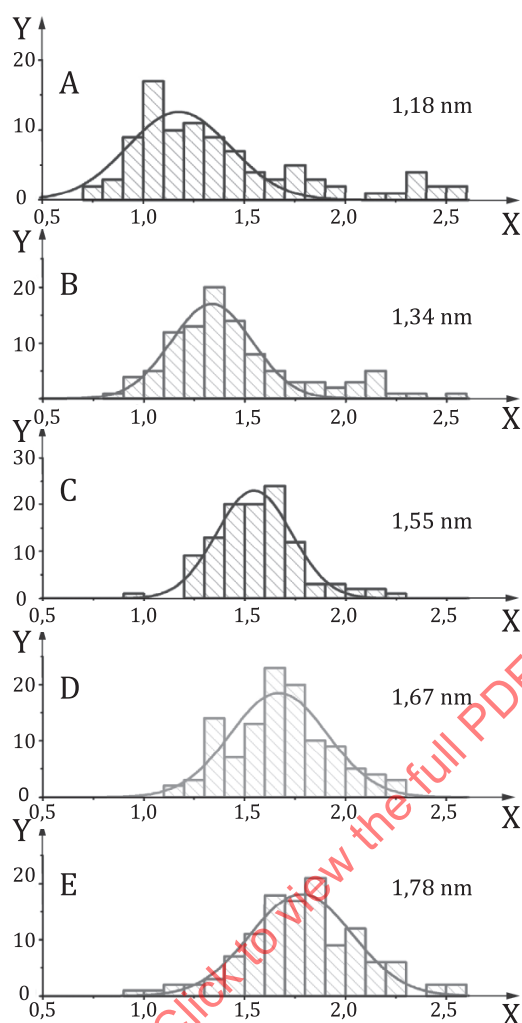
(informative)

Case study for derivation of the relation between optical absorption peaks of SWCNTs and their mean diameter

NOTE See Reference [\[14\]](#).

A.1 SWCNT samples

Following the procedures in this document, five SWCNTs samples A to E with different mean diameters, which are, 1,2 nm, 1,3 nm, 1,6 nm, 1,7 nm, and 1,8 nm, were tested. Each sample was observed with TEM in advance, yielding histograms and mean diameters as shown in [Figure A.1](#):



Key

X tube diameter (nm)
Y counts

Figure A.1 — Histogram and mean diameter of each sample as observed with TEM

A.2 Sample preparation

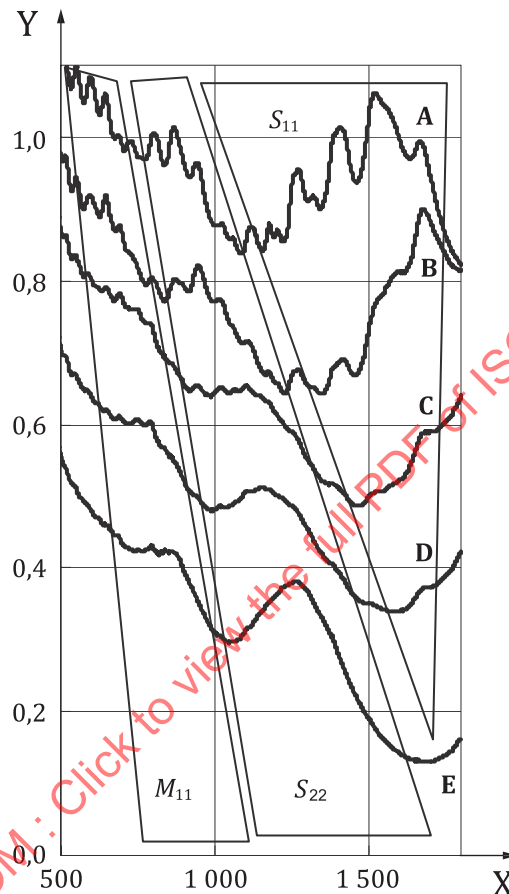
Dispersed solutions of SWCNTs were prepared as follows.

- SWCNTs (ca. 1 mg) were dispersed in ca. 20 g of D₂O containing 1 % (mass fraction) of SC or CMC using a tip ultrasonic homogenizer equipped with a titanium alloy tip. Pulsed sonication was applied (on: 1 s, off: 2 s) with a power of 200 W for 30 min.
- Each dispersed solution was then centrifuged at $127\,600 \times g$ for 2,5 h by using a swing rotor and the supernatant of the upper ca. two thirds of the volume was collected and subjected to UV-Vis-NIR absorption measurements.
- The supernatant solution prepared using CMC as a dispersant was cast on a glass substrate and dried to obtain a film sample for UV-Vis-NIR measurement.

A.3 Apparatus and measurement parameters

The absorption was measured with a standard spectrophotometer covering a broad, ultraviolet to NIR wavelength range from 190 nm to 3 200 nm. The spectrophotometer was turned on 1 h prior to the measurement to allow the baseline to stabilize.

A.4 Results



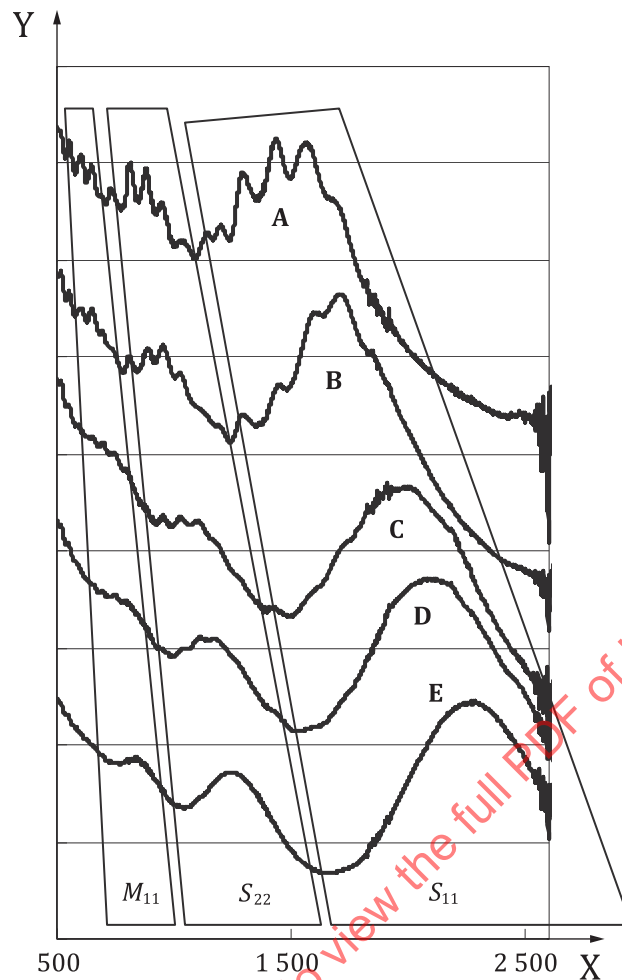
Key

X wavelength (nm)
Y absorbance (absorbance unit)

Figure A.2 — Absorption spectra of SWCNT samples dispersed in 1 % (mass fraction) SC-D₂O solvent

The absorption spectra of the samples dispersed in 1 % (mass fraction) SC-D₂O solvent are shown in [Figure A.2](#). S_{11} , S_{22} and M_{11} peaks resolved as indicated in [Figure A.2](#) are clearly correlated with their mean diameters, that is, the peak shift generally scales with the mean diameter.

In general, three absorption bands, S_{11} , S_{22} , and M_{11} , are observed for SWCNTs. For SWCNTs with relatively large diameters (over 1,6 nm), however, the S_{11} band cannot be observed because of the strong absorption by D₂O. In that case, a film sample should be used for characterization.

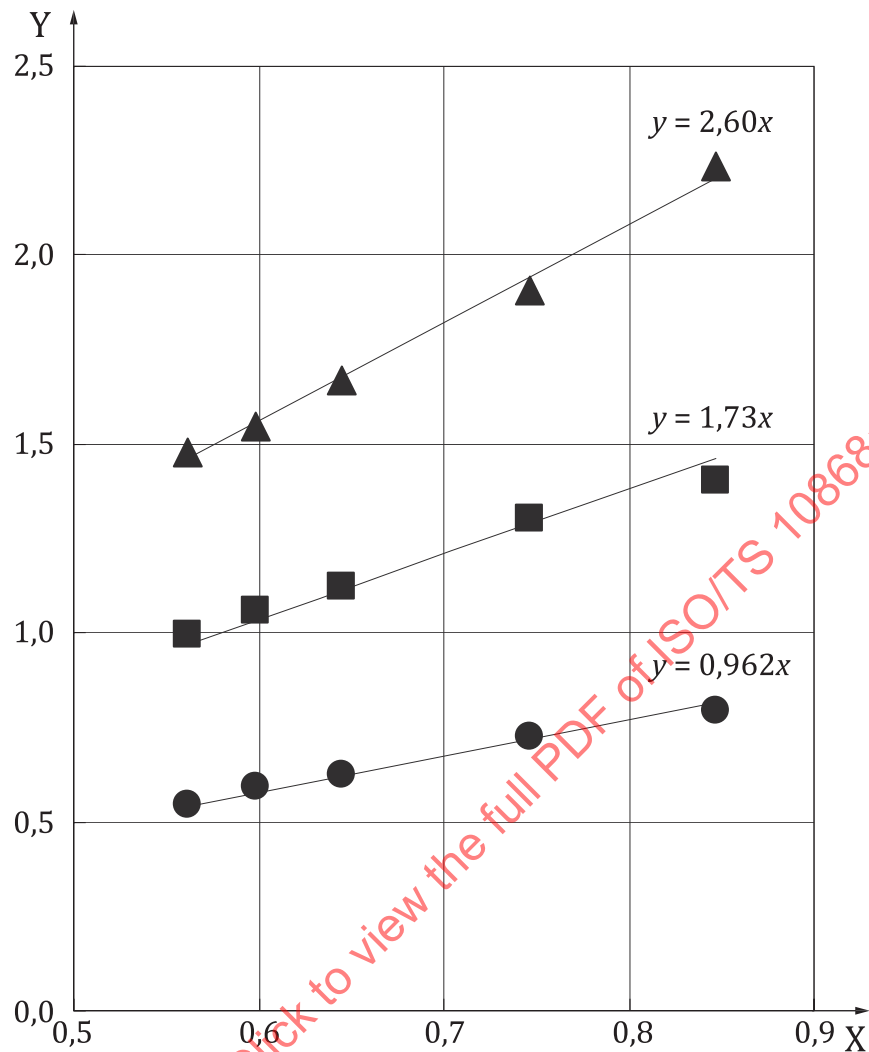
**Key**

X wavelength (nm)

Y absorbance (absorbance unit)

Figure A.3 — Absorption spectra of SWCNT samples dispersed in CMC film

The absorption spectra of the samples dispersed in CMC film are shown in [Figure A.3](#). Because of the transparency of CMC, S_{11} peaks can be detected for all the samples, thus enabling the characterization of SWCNTs with a greatly extended diameter range.

**Key**X $1/d_m$ (nm⁻¹)

Y energy (eV)

Figure A.4 — Energy gaps plotted against reciprocal mean diameters

To analyse the correlation between the diameter and absorption spectra, the energy gaps evaluated from the peak positions of S_{11} , S_{22} , and M_{11} are plotted against the reciprocal mean diameter as shown in Figure A.4. It is found that the energy gaps almost linearly scale with the reciprocal mean diameter for ca. $1 < d_m < \text{ca. } 2$ nm. The approximate relations between energy gaps (y) and reciprocal mean diameters (x) were obtained as follows:

$$S_{11} : y = 0,962x$$

$$S_{22} : y = 1,73x$$

$$M_{11} : y = 2,60x$$