
**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*

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Published in Switzerland

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Foreword

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In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of normative document:

— an ISO Publicly Available Specification (ISO/PAS) represents an agreement between technical experts in an ISO working group and is accepted for publication if it is approved by more than 50 % of the members of the parent committee casting a vote;

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ISO/TS 10868 was prepared by Technical Committee ISO/TC 229, *Nanotechnologies*.

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

1 Scope

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

The purpose of this Technical Specification is to describe a measurement method for establishing the diameter, purity, and ratio of metallic SWCNTs to the total SWCNT content in the sample.

The analysis of the diameter is applicable to a diameter range of 1 nm to 2 nm.

2 Normative references

The following referenced documents are indispensable for the application 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 80004-3, *Nanotechnologies — Vocabulary — Part 3: Carbon nano-objects*
<http://www.iso.org/standards/std/80004-3/16450008505c9c6765ecc/iso-ts-10868-2011>

3 Terms, definitions and abbreviated terms

For the purposes of this document, the terms and definitions given in ISO/TS 80004-3 and the following apply.

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 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, see ISO/TS 11308, which addresses thermogravimetric analysis.

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

CMC	sodium carboxymethylcellulose
DMF	dimethylformamide
DOS	density of states
NIR	near infrared
SC	sodium cholate
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

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4 Principle

4.1 General

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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 semi-quantitative information important for the characterization of SWCNT samples, such as mean diameter, purity, and the ratio of metallic SWCNTs to the total SWCNT content.

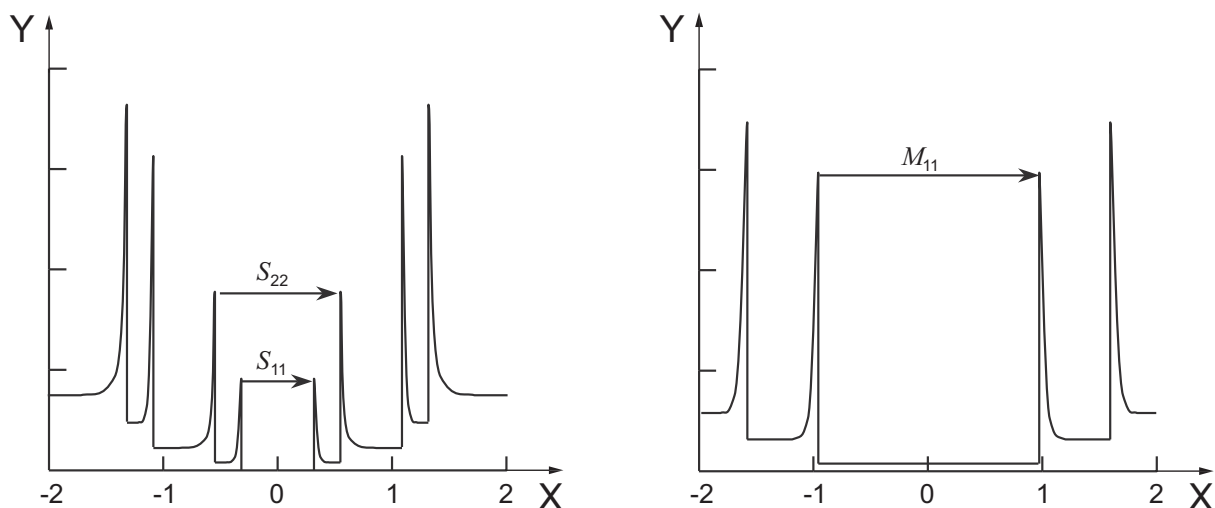
4.2 UV-Vis-NIR absorption spectroscopy

The intensity of light, I , passing at a specified wavelength, λ , through a specimen is measured and 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.

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



a) Electronic DOS of semiconducting SWCNTs

b) Electronic DOS of metallic SWCNTs

Key

X Energy (eV)

Y Electronic DOS (arbitrary unit)

S₁₁ The first interband optical transition attributed to semiconducting SWCNTsS₂₂ The second interband optical transition attributed to semiconducting SWCNTsM₁₁ The first interband optical transition attributed to metallic SWCNTsNOTE See Reference^[2].**Figure 1 — Electronic DOS diagram of SWCNTs near the Fermi level**

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To interpret absorption spectra of SWCNTs, band structures calculated using the zone-folding method are frequently used. The electronic structure of a SWCNT is generally given by that of a two-dimensional graphite sheet expressed by the tight binding approximation as shown in Equation (1)^[3].

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

where

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

a is the lattice parameter;

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 the following equations.

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

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

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

where

$E_g(S_{11})$, $E_g(S_{22})$ and $E_g(M_{11})$ are the energy gaps corresponding to the transitions of S_{11} , S_{22} and M_{11} , respectively; d is the diameter of SWCNTs^[4].

Equations (2) to (4) show a simple relationship between the diameter and the optical transition energies (and thus the peak wavelengths). This enables the mean diameter of a SWCNT sample to be estimated by the analysis of the absorption spectra originating from the optical transitions between VHSs.

Equations (2) to (4) can give information related to the diameter within some limitations. One of the limitations is that the analysed peak(s) need(s) to be clearly resolved.

4.5 Derivation of the purity indicator from optical absorption peak areas

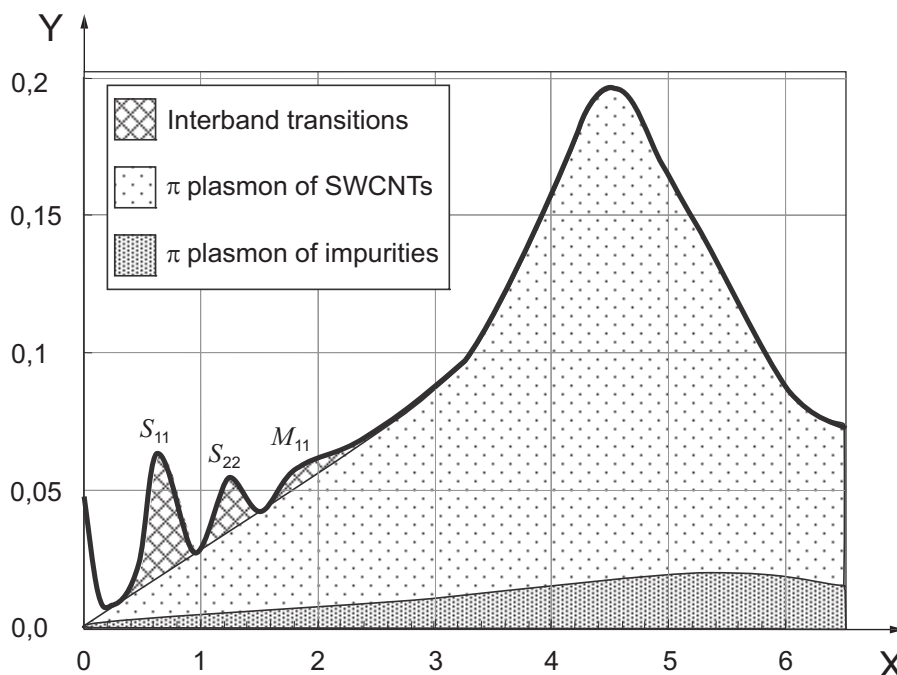
As mentioned in 4.3, there are the specific absorptions of SWCNTs originating from interband transition between VHSs. These absorption peaks are typically observed in the Vis-NIR region. On the other hand, in the UV region, most SWCNT samples present optical absorption with the peak at 200 nm to 300 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^[6]. 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).

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 $P_i(M_{11})$ ^{[6][7]}, which is given by:

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

Equation (5) gives information related to purity within some limitations. One of the limitations is that the analysed peak(s) need 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.

**Key**

X Photon energy (eV)

Y Absorbance (absorbance unit)

NOTE 1 The relative contribution from each component is arbitrary.

NOTE 2 See Reference [6].

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Figure 2 — Typical UV-Vis-NIR absorption spectrum of a SWCNT sample
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4.6 Derivation of ratio of metallic SWCNTs from optical absorption peak areas

On the basis of the analogy in 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:

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

Furthermore, Equation (6) can be converted into the following Equation (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 Equation (7) is frequently more favourable than use of Equation (6) because $AA(S_{11})$ is sensitive to the charge transfer^[8].

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 to 1,3 nm, Equations (6) and (7) provide the actual ratio of metallic SWCNTs, because these coefficients have been determined to be equal experimentally^[9].

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^[10], or the ratio of 1 in the sample treated by the special separation process^[9], 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 a SWCNT diameter of 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 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 its high dispersing ability. Furthermore, for measurement in 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.

For the preparation of D_2O dispersion of SWCNT, see 6.2; 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 D_2O dispersion for measurement of mean diameter and the ratio of metallic SWCNTs

For the preparation of D_2O dispersion of SWCNTs for measurements of mean diameter and the ratio of metallic SWCNTs, the following procedure shall be performed.

- a) Use D_2O as the solvent, which transmits light in the broad range from UV-Vis to 1 800 nm.

NOTE 1 H_2O is unsuitable above 1 400 nm because it strongly absorbs light.

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

NOTE 2 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.

NOTE 3 Even after ultrasonic homogenization, some SWCNTs still remain bundled, broadening the 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 × *g* to 150 000 × *g* for 2 h to 5 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 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 onto a quartz substrate and leave it still for 10 h or longer until it dries.

NOTE 1 This results in the formation of an optically uniform film in which SWCNTs are homogeneously dispersed^[11]. 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 mean diameter and the ratio of metallic SWCNTs without using surfactants.

NOTE 2 CMC itself works both as a dispersant and as a film-forming agent^[12], simplifying the sample preparation process.

For the preparation of CMC film dispersion of SWCNTs, perform the following procedure 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.