# TECHNICAL SPECIFICATION

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# 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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# Foreword

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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*

## 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 dodecylbezene 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 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, $\lambda$, 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
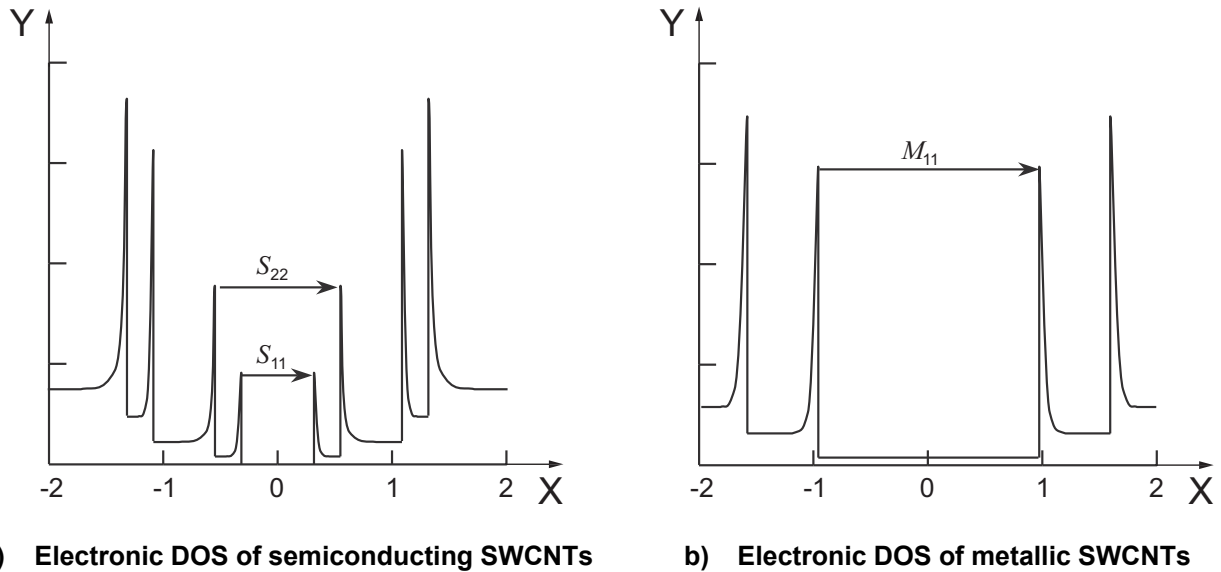
**Key**

X    Energy (eV)

Y    Electronic DOS (arbitrary unit)

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

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

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

NOTE    See Reference[2].

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

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].

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

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;

$\gamma$        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.

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

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

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

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 $\pi$ electron systems ($\pi$-plasmons) and can also be observed in most graphitic compounds[5]. Therefore, the $\pi$-plasmon absorption observed in most SWCNT samples is due to both SWCNTs and carbonaceous impurities. The $\pi$-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 $\pi$-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 $\pi$-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:

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

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.
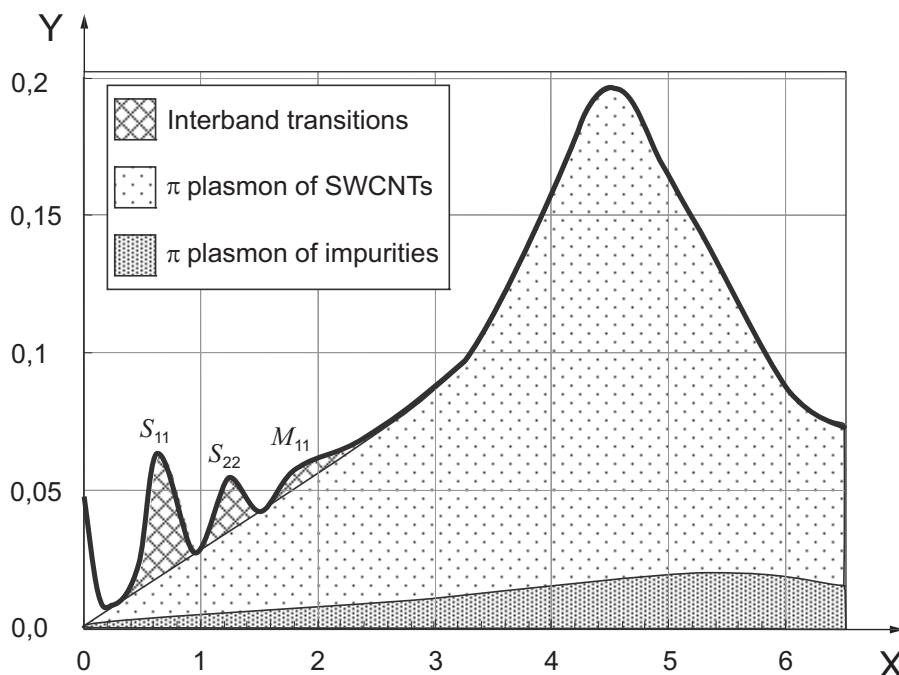
**Key**

X    Photon energy (eV)

Y    Absorbance (absorbance unit)

NOTE 1    The relative contribution from each component is arbitrary.

NOTE 2    See Reference [6].

**Figure 2 — Typical UV-Vis-NIR absorption spectrum of a SWCNT sample**

## 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:

$$R_{\text{Metal}} = \frac{AA(\text{M}_{11})}{AA(\text{S}_{11}) + AA(\text{M}_{11})} \tag{6}$$

Furthermore, Equation (6) can be converted into the following Equation (7) for $R_{\text{Metal}}$ as the function of $AA(\text{S}_{22})$ and $AA(\text{M}_{11})$:

$$R_{\text{Metal}} = \frac{AA(\text{M}_{11})}{1,2\,AA(\text{S}_{22}) + AA(\text{M}_{11})} \tag{7}$$

Use of Equation (7) is frequently more favourable than use of Equation (6) because $AA(\text{S}_{11})$ is sensitive to the charge transfer[8].

$R_{\text{Metal}}$ does not literally represent the ratio of metallic SWCNTs, because integrated molar extinction coefficients in the $\text{M}_{11}$ and $\text{S}_{11}$ 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 homogenously 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 $D_2O$ 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 $\times$ $g$ to 150 000 $\times$ $g$ 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 $H_2O$ 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 $H_2O$ 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 homogenously 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 $H_2O$ 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 onto 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 3    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 $P_i$, perform the following procedure.

a)  Use dimethylformamide (DMF) alone as a solvent, which can disperse SWCNT in a relatively efficient way without any dispersant.

NOTE    This method does not have the necessary dispersing ability to sufficiently isolate individual SWCNTs and to ensure 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 using an ultrasonic bath for 10 min to 20 min. Mechanical stirring facilitates homogenization during this step, which should result in a homogenous concentrated slurry of SWCNTs in DMF.

d)  Collect a few drops of the concentrated SWCNT slurry by pipette from different regions of the sample and dilute to 10 ml with fresh DMF and sonicate it for 10 min. By using 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:

a)  Pick the peak wavelengths of maximum $S_{11}$, $S_{22}$, or $M_{11}$ absorptions.

b)  Convert these wavelengths into photon energies (eV) and substitute them into the following formula (8).

c) Calculate the value of $d$ as the mean diameter from the formula (8)[13].

$$E_g(S_{11}) = \frac{0,96}{d}$$
$$E_g(S_{22}) = \frac{1,7}{d} \tag{8}$$
$$E_g(M_{11}) = \frac{2,6}{d}$$

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:

a) If the spectrum data are a function of wavelength (nm), convert the data to be a function of photon energy (eV) or wavenumber (cm$^{-1}$).

b) Integrate the total area under the absorption spectrum as $AA_t$.

c) 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).

d) Calculate purity indicator, $P_i$ by using Equation (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:

a) Convert the spectrum data to be a function of energy (eV) or wavenumber (cm$^{-1}$).

b) Draw a tangent line between the minima of the absorption curve at the low and high energy sides of $S_{nn}$ or $_{M11}$ transition and calculate the areas between the spectrum curve and the straight line as $AA(S_{nn})$ and $AA(M_{11})$.

c) Calculate $R_{Metal}$ as an indicator of the ratio of metallic SWCNTs to the total SWCNTs in the sample using Equation (6) or (7).

## 9   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[14],

b) optical absorption by impurities including multiwall CNTs contained in the sample,

c) statistical uncertainty associated with the diameter distribution of SWCNTs in the sample,

d) systematic and statistical uncertainties associated with deducing Equations (5) to (8),

e) additional uncertainties stemming from the dependence of nanotube length 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)   mean diameter

   2)   purity indicator, $P_i$ ($S_{nn}$) or $P_i$ ($M_{11}$)

   3)   indicator of the ratio of metallic SWCNTs, $R_{Metal}$

b)   all information necessary for the identification of the sample tested;

   1)   sample name

   2)   lot number

c)   all information necessary for the specimen preparation;

   1)   dispersant used

   2)   solvent used

   3)   sonication power

   4)   sonication time

   5)   centrifugal force

   6)   centrifugation time

   7)   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 each analysis

   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

### A.1 SWCNT samples

Following the procedure described in this International Standard, five SWCNTs samples, A to E, with different mean diameters, i.e. 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 below:
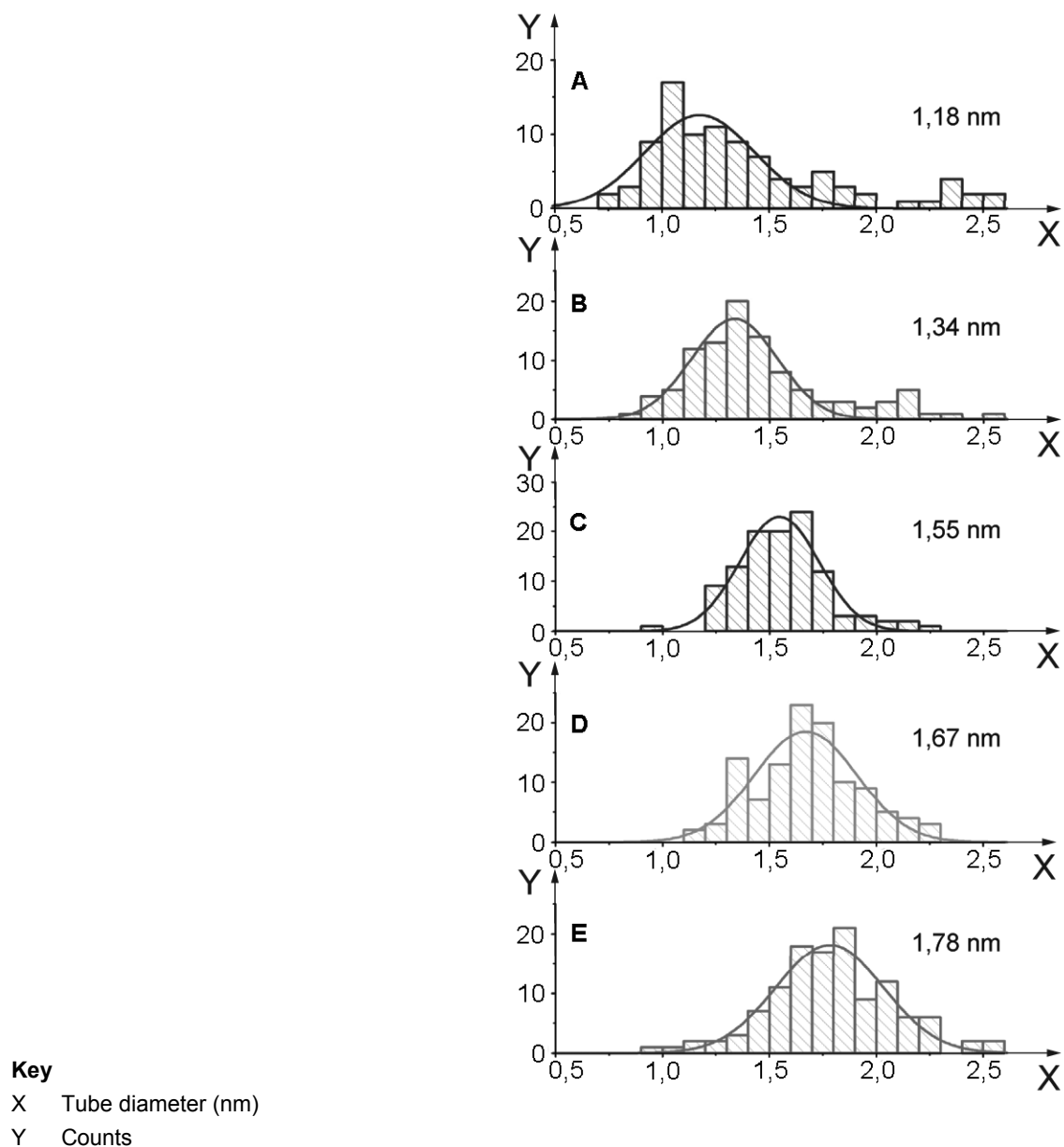


**Key**

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:

a)   SWCNTs ($\approx$ 1 mg) were dispersed in $\approx$ 20 g of $D_2O$ containing 1 % (mass fraction) of SC or CMC using a tip ultrasonic homogenizer equipped with a titanium alloy tip. Pulsed sonication was applied (on for 1 s, off for 2 s) with a power of 200 W for 30 min.

b)   Each dispersed solution was then centrifuged at 127 600 $\times$ $g$ for 2,5 h using a swing rotor and the supernatant of $\approx$ the upper two thirds of the volume was collected and subjected to UV-Vis-NIR absorption measurements.

c)   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

The absorption spectra of the samples dispersed in 1% (mass fraction) SC-$D_2O$ 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, i.e. 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 $D_2O$. In that case, a film sample should be used for characterization.

Key
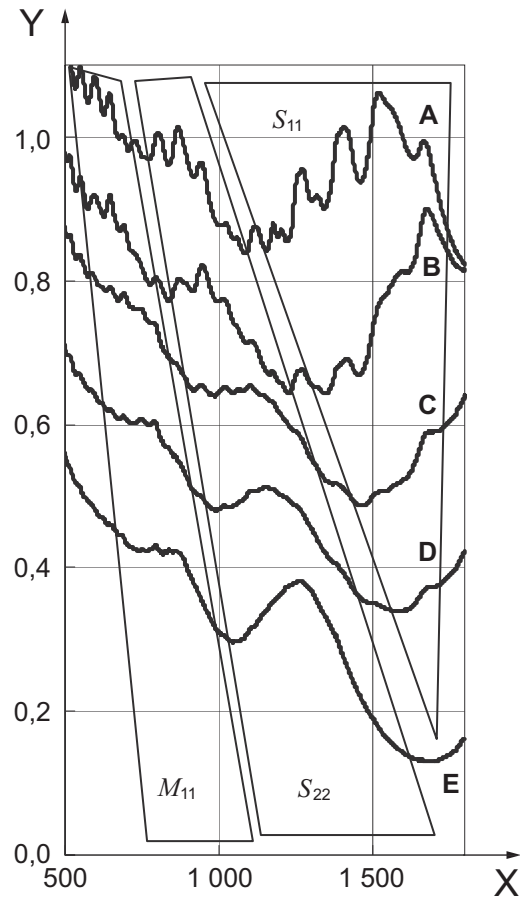
X    Wavelength (nm)

Y    Absorbance (absorbance unit)

**Figure A.2 — Absorption spectra of SWCNT samples dispersed in 1 % (mass fraction) SC-D$_2$O solvent**

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**
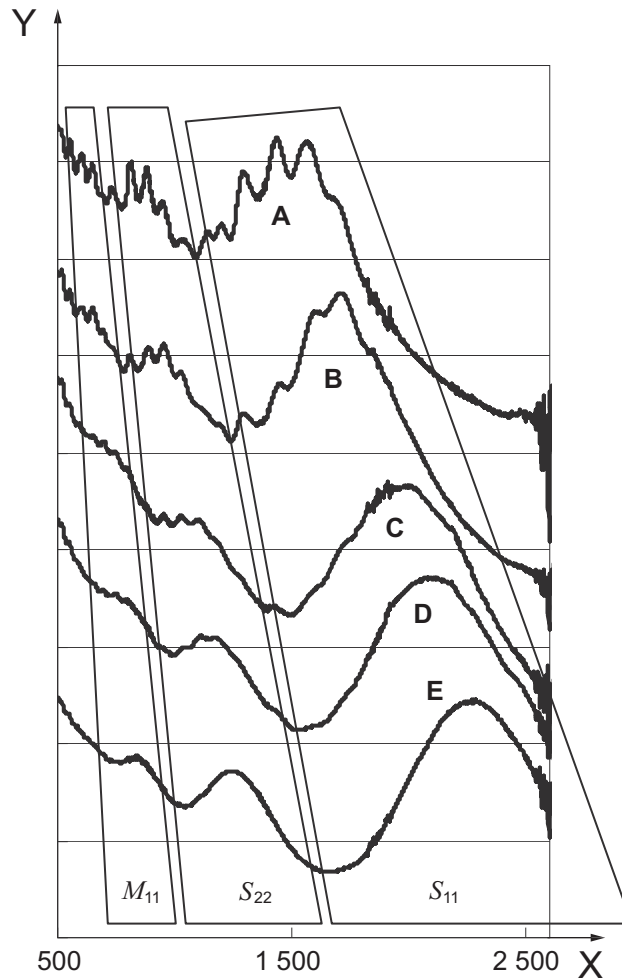
X    Wavelength (nm)

Y    Absorbance (absorbance unit)

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

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 $\approx 1 < d_m < \approx 2$ nm. The approximate relations between energy gaps ($y$) and reciprocal mean diameters ($x$) were obtained as follows:

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

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

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

NOTE    See Reference[13].
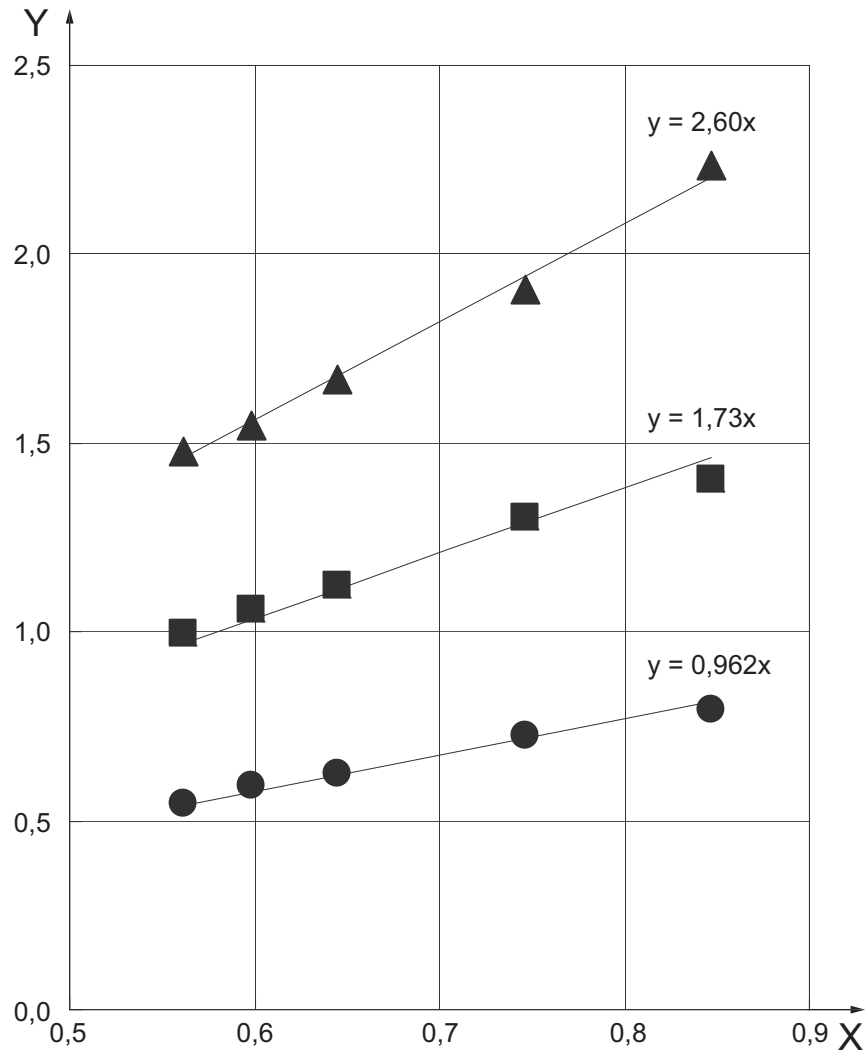
**Key**

X     $1/d_m$ (nm$^{-1}$)

Y     Energy (eV)

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

# Annex B
## (informative)

# Case study for determination of the purity indicator

## B.1  An example of purity indicator analysis

Following the procedure described in this International Standard, a sample produced by the electric arc method was tested to determine the purity indicator. Spectra were taken in the range 7 000 to 17 000 cm$^{-1}$ in order to visualize both the $S_{22}$ and $M_{11}$ interband transitions for this material. The data were processed in the frequency (energy) range as opposed to the wavelength range, as shown in Figure B.1, because the absorption spectra as a function of wavelength (proportional to inverse energy) showed significantly more curvature and were more difficult to analyse.

**Key**
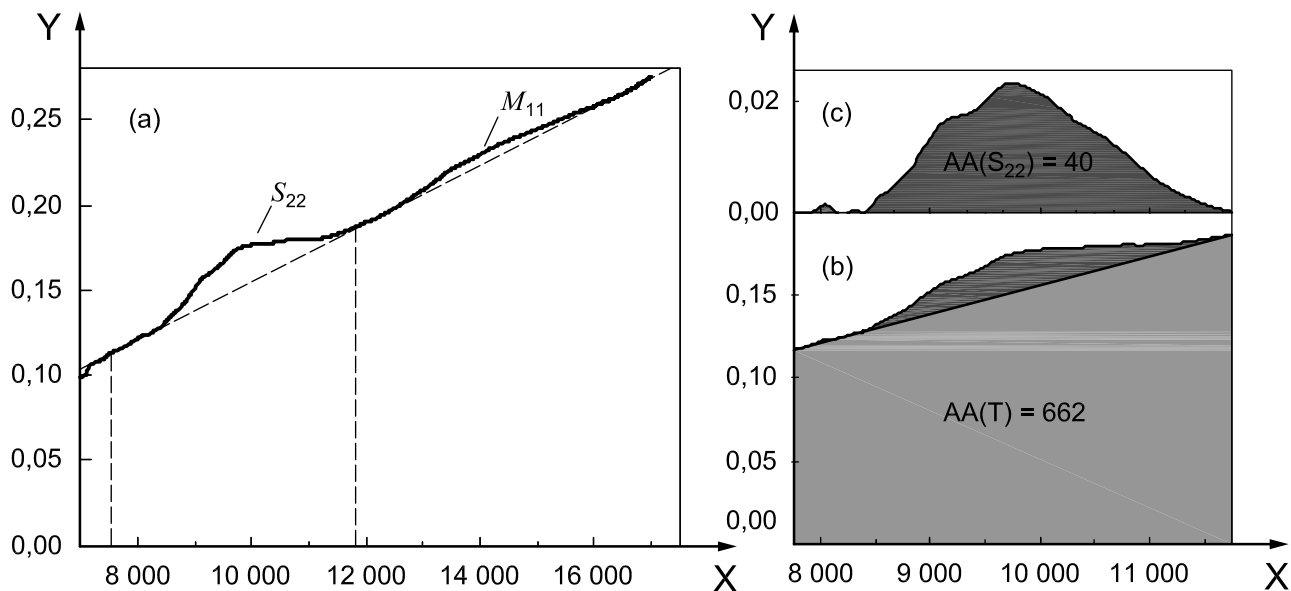
X    Wavenumber (cm$^{-1}$)

Y    Absorbance (absorbance unit)

**Figure B.1 — Absorption spectra of SWCNT samples dispersed in DMF**

While the $S_{11}$ transition was the most prominent, the second semiconducting transition, $S_{22}$, for the purity evaluation was chosen for the following reasons:

a)  its amplitude,

b)  its lower susceptibility to incidental doping[6],

c)  it matched the transmission window for dimethylformamide (DMF), which was utilized for the solution (dispersion) phase NIR.

In order to establish the baseline, a tangent line was drawn to the minima of the absorption curve at the low and high energy sides of the $S_{22}$ transition. In practice it is best to use 5 data points on each side of the chosen $S_{22}$ spectral window (7 750 to 11 750 cm$^{-1}$) for the linear fitting routine. The absorption spectrum within the cutoffs was presented separately in Figure B.1 (b) with calculated total area $AA_t$ = 662. Figure B.1 (c) shows the spectrum of the $S_{22}$ feature after linear baseline correction with integrated area $AA(S_{22})$ = 40, yielding a purity indicator value of $P_i$ = 0,060. The value of $P_i$ can be directly compared with that from other samples.

NOTE      The value of $P_i$ for a sample with no carbonaceous impurities is not known. If a pure SWCNT sample (or a SWCNT sample with known purity) becomes available, the purity indicator $P_i(S_{nn})$ or $P_i(M_{11})$ of a sample can be measured relative to the purity of the sample with no (or known) carbonaceous impurities.

## B.2  A common source of experimental uncertainty — distorted baseline

Figure B.2 represents a NIR spectrum of a SWCNT dispersion in DMF, exhibiting both of the two most common spectral distortions which occur in the vicinity of 8 000 and 12 000 cm$^{-1}$ (shown by the arrows in Figure B.2). The distortion just above 8 000 cm$^{-1}$ is due to the presence of traces of water in the solvent which gives very strong absorptions that in some cases cannot be properly subtracted from the baseline by the pure solvent in the reference channel.



**Key**
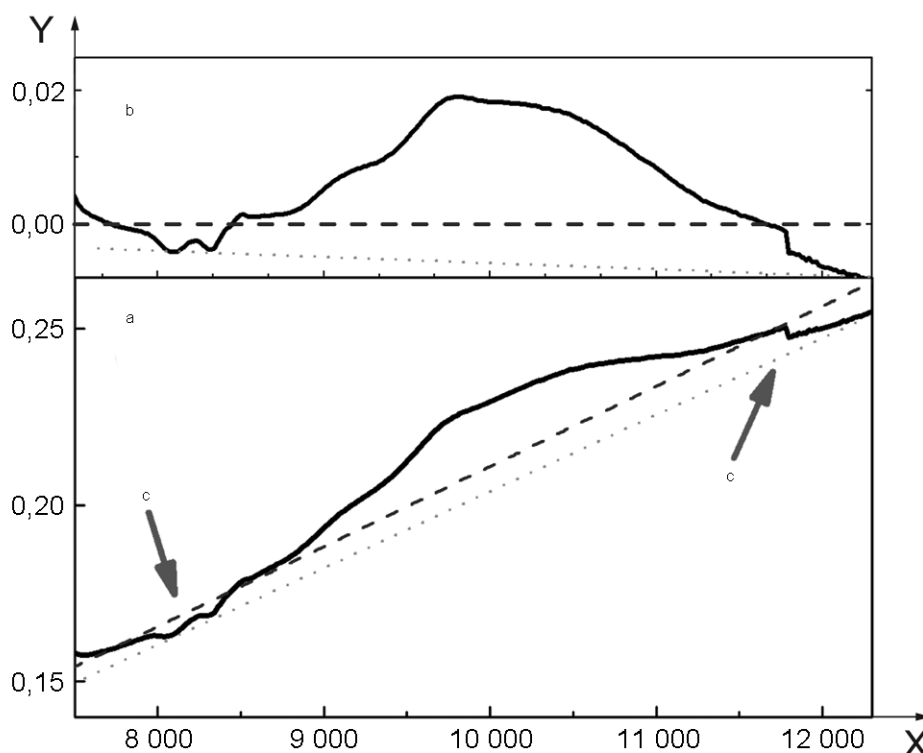
X    Wavenumber (cm$^{-1}$)

Y    Absorbance (absorbance unit)

a    Complete spectrum.

b    Spectrum of $S_{22}$ feature after linear baseline correction.

c    Distortions in NIR spectra.

**Figure B.2 — Example of distortions in NIR spectra due to the presence of traces of water in the DMF and the change of optical elements in the spectrophotometer**

In the example given in Figure B.2 this distortion produces a negative contribution to the integrated area, thus reducing the purity indicator because of the uncertainty in the baseline position at the low energy spectral cutoff. It is important to use dry solvent and to avoid admitting any traces of water to the solvent during the sample preparation procedure.

The step in the trace in the vicinity of 12 000 cm$^{-1}$ corresponds to the change from the NIR detector to the UV-Vis detector in the spectrophotometer and introduces uncertainties into the spectrum and the linear baseline correction near the high-energy spectral cutoff. Possible baseline choices are shown by dashed and dotted lines and this uncertainty serves to introduce uncertainties into the calculated $P_i$. The jumps in the spectrum result from the change of optical elements inside the spectrophotometer. They can be minimized in the following ways:

— careful alignment of spectrophotometer components by the manufacturer;

— optimum alignment of the sample positions in both optical channels;

— modifying the ratio of spectral resolutions in the NIR and UV-Vis spectral ranges;

— stabilization of the spectrometer by utilizing an extended warm-up time.

It is practically impossible to avoid such steps in the case of scattering samples such as poorly dispersed SWCNTs or inhomogenous or thick SWCNT films.

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1)   Under preparation.

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