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Nanotechnologies — Characterization of multiwall carbon nanotube (MWCNT) samples

Nanotechnologies — Caractérisation des échantillons de nanotubes en carbone multifeuillets (MWCNTs)

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In exceptional circumstances, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example), it may decide by a simple majority vote of its participating members to publish a Technical Report. A Technical Report is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.

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ISO/TR 10929 was prepared by Technical Committee ISO/TC 229, *Nanotechnologies*.

Introduction

Multiwall carbon nanotubes (MWCNTs) are nanomaterials for use in many industrial fields. They are beneficial because of their unique electronic, electromagnetic, thermal, optical and mechanical properties. The feasibility of using them in a variety of applications, such as field-emission based display panels, reinforced composite materials, multifunctional sensors and elements of new nanoscale logic circuits have been explored. In all cases, appropriate characterization of the MWCNT samples is necessary so that the desired products can be manufactured.

Nanotechnologies — Characterization of multiwall carbon nanotube (MWCNT) samples

1 Scope

This Technical Report identifies the basic properties of multiwall carbon nanotubes (MWCNTs) and the content of impurities, which characterize bulk samples of MWCNTs, and highlights the major measurement methods available to industry for the determination of these parameters.

This Technical Report provides a sound basis for the research, development and commercialization of these materials. Sample preparation and measurement protocol are not contained within this Technical Report.

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 27687, *Nanotechnologies — Terminology and definitions for nano-objects — Nanoparticle, nanofibre and nanoplate*

ISO/TS 80004-1, *Nanotechnologies — Vocabulary — Part 1: Core terms*

ISO/TS 80004-3, *Nanotechnologies — Vocabulary — Part 3: Carbon nano-objects*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/TS 27687, ISO/TS 80004-1 and ISO/TS 80004-3 apply.

4 Abbreviated terms

AAS	Atomic absorption spectrometry
DTA	Differential thermal analysis
EDS	Energy dispersive X-ray spectrometry
EGA-GCMS	Evolved gas analysis-gas chromatograph mass spectrometry
GC-MS	Gas chromatography-mass spectrometry
HPLC-MS	High performance liquid chromatography-mass spectrometry
ICP-AES/OES	Inductively coupled plasma-atomic emission spectroscopy/optical emission spectroscopy
ICP-MS	Inductively coupled plasma-mass spectrometry
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
XRD	X-ray diffractometry
XRF	X-ray fluorescence analysis

5 Basic MWCNT properties and impurity contents and their measurement methods

Basic properties of MWCNTs and contents of impurities for the characterization of bulk samples of MWCNTs are identified in Table 1. The properties and contents are associated with an industrially available measurement method, or methods.

Sampling and sample homogeneity should be considered, but they are not described here.

Table 1 — Basic MWCNT properties and impurity contents and their measurement methods

Category	Property/Content	Method
MWCNTs	Outer diameter	TEM, SEM
	Inner diameter	TEM
	Interlayer distance	XRD, TEM
	Length	SEM, TEM
	Disorder of crystal structure	Raman spectroscopy, TEM
	Oxidation temperature	TGA /DTA
Impurities	Carbon material content not in the form of MWCNT	SEM, TEM, XRD, TGA
	Metal content	ICP-AES/OES, AAS, ICP-MS, XRF, SEM/EDS
	Polyaromatic hydrocarbon content	HPLC-MS , GC-MS
	Volatile content to approximately 100 °C	Weight loss method, TGA, EGA-GCMS
	Volatile content for temperature higher than 100 °C	Weight loss method, TGA, EGA-GCMS
	Ash content	Weight loss method, TGA

6 Measurement methods for MWCNT properties

6.1 General

Industrially available measurement methods for determining the properties of MWCNTs in bulk samples are set out below. Sample preparation and measurement protocol are not contained with this Technical Report.

6.2 Outer diameter

The outer diameter of MWCNTs is the diameter of the outermost graphene layer from which the tube is constructed. The outer diameter of MWCNT may be measured by TEM and SEM with the aid of image analysis techniques. The applicability of SEM depends on the resolution of the SEM instrument. Appropriate procedures for sampling, statistics and calibration are needed for the TEM and SEM measurements.

ISO/TS 10797 and ISO/TS 10798 provide guidance on SWCNT (single wall carbon nanotube) characterization and include reference to outer diameter measurements by TEM and SEM.

6.3 Inner diameter

The inner diameter of MWCNTs is the diameter of the innermost graphene layer from which the tube is constructed. The inner diameter may be measured by TEM with the aid of image analysis techniques. Appropriate procedures for sampling, statistics and calibration are needed for the TEM measurements.

ISO/TS 10797 provides guidance on SWCNT characterization and includes reference to inner diameter measurements by TEM.

6.4 Interlayer distance

The stacking nature of MWCNTs is represented by the distance between the graphene layers that make up adjacent walls in a MWCNT. The interlayer distance of MWCNTs may be measured by the X-ray diffraction method[8] and by TEM employing appropriate sampling and statistical procedures for the bulk sample of MWCNTs.

ISO/TS 10797 provides guidance on SWCNT characterization and includes reference to interlayer distance measurements by TEM.

6.5 Length

The length of a MWCNT is the longitudinal distance between its two ends, or the distance from the root of a branch to its tip for ramified structures. The lengths of MWCNTs may be measured by SEM with the aid of image analysis techniques. TEM can also be used for thin, short tubes, if they fall within the maximum image size of the TEM. Appropriate procedures for sampling, statistics and calibration are needed for the SEM measurements as well as TEM. The measurement of MWCNT length can be extremely challenging as capturing both ends of a MWCNT in a single image, using either SEM or TEM, is unlikely.

ISO/TS 10797 and ISO/TS 10798 provide guidance on SWCNT characterization and include reference to length measurements by TEM and SEM.

6.6 Disorder in crystal structure

Disorder in the crystal structure of MWCNTs comes from geometrical and chemical deviations of the atomic arrangement in a well-ordered MWCNT. Typical disorders are defects in the graphitic structure and disordered regions of amorphous carbons. Such disorders may affect properties of the MWCNT such as electrical, thermal, mechanical and chemical properties. The degree of disorder can be qualitatively assessed from the Raman spectrum of MWCNTs. The intensity ratio of the D band (at approximately 1 360 cm^{-1}) to the G band (at approximately 1 540 cm^{-1}) (D/G ratio) obtained from a Raman spectrum using a visible laser gives information about the degree of disorder in the MWCNTs. The D band indicates defects in the graphitic structure and disordered structures, e.g. amorphous carbons. The G band originates from the well-ordered graphitic structure. Lower values for the D/G ratio indicate less disorder in the crystal structure of MWCNTs. Appropriate procedures for sampling, statistics and calibration are needed for the measurements.

The degree of disorder can also be qualitatively assessed from TEM observation with atomic resolution.

6.7 Oxidation temperature

The oxidation temperature of MWCNTs gives information about defect content. Lower oxidation temperatures imply more defects of the crystal structure in the MWCNTs. To measure the oxidation temperature, a bulk sample of MWCNTs is heated in an oxidizing environment from room temperature to a defined high temperature, e.g. 900 °C or above, using a combined TGA and DTA apparatus. The oxidation temperature is determined from the exothermic inflection point in the DTA profiles and at the maximum in the derivative weight loss profiles of TGA. When the sample contains a lot of impurities, there can be multiple possible oxidation temperatures in the measured profiles that originate from the different impurities. The full set of results should be reported as described in Clause 7 without determination of the oxidation temperature. A dynamic temperature program is preferred to a linear one.

ISO/TS 11308 provides guidance on SWCNT characterization and includes reference to oxidation temperature measurements by TGA.

7 Measurement methods for impurity contents of bulk samples of MWCNTs

7.1 General

Industrially available measurement methods are identified to determine the content of impurities in bulk samples of MWCNTs. Sample preparation and measurement protocol are not contained with this Technical Report.

7.2 Carbon material content not in the form of MWCNTs

Carbon materials not in the form of MWCNTs that are present in a bulk sample, such as amorphous carbons and graphitic flakes, can be identified by SEM, TEM, XRD and TGA. The content of carbon materials not in the form of MWCNTs is qualitatively estimated through the SEM, TEM, XRD and TGA by employing appropriate sampling and statistical procedures.

ISO/TS 10798 provides guidance on SWCNT characterization and includes reference to measurements of carbon material content different from MWCNT by SEM and EDS.

7.3 Metal content

Metal constituents are most likely introduced from catalysts and substrates used in manufacturing MWCNTs. The metal content is described as the identity of the metal type and its amount present in a bulk sample of MWCNTs. The metal content can be measured by ICP-AES/OES, AAS, ICP-MS, XRF and SEM/EDS with the aid of relevant reference materials. These methods are applicable to a variety of metallic constituents.

ISO/TS 13278 provides guidance on SWCNT characterization and includes reference to metal content measurements by ICP-MS.

7.4 Polyaromatic hydrocarbon content

Polyaromatic hydrocarbons are typical non-volatile constituents that are most likely to be introduced into the bulk sample during manufacture of MWCNTs. Chromatographic methods are applicable to the measurement of polyaromatic hydrocarbon content. Polyaromatic hydrocarbons may be extracted from bulk samples of MWCNTs by the Soxhlet extraction method. HPLC-MS and liquid injection GC-MS may be used to separate polyaromatic hydrocarbons and analyse the contents with the aid of relevant reference materials.

7.5 Volatile content to approximately 100 °C

A bulk sample of MWCNTs is heated in an inert environment from room temperature to approximately 100 °C and held at that temperature until volatile constituents are fully released. Assuming that no chemical reaction takes place within the sample, the volatile content is given by the weight lost from the sample during the heating. TGA can be used to measure volatile content. The volatile content is usually expressed as the percentage weight loss resulting from the heating. It is often called moisture content when the major species released is water. Also, it is possible to use an EGA-GCMS combined instrument to analyse the evolved gas.

ISO/TS 11308 and ISO/TS 11251 provide guidance on SWCNT characterization and include reference to volatile content measurements by TGA and EGA-GCMS respectively.

7.6 Volatile content for temperatures higher than 100 °C

A bulk sample of MWCNTs is heated in an inert environment from room temperature to the temperature of interest, e.g. 900 °C, and is held at that temperature until volatile constituents are fully released. Assuming that no chemical reaction takes place within the bulk sample, the volatile content is given by the weight lost from the sample during the heating. TGA can be used to measure volatile content. The volatile content is usually expressed as the percentage weight loss resulting from the heating. Also, it is possible to use an EGA-GCMS combined instrument to analyse the evolved gas.

ISO/TS 11308 and ISO/TS 11251 provide guidance on SWCNT characterization and include reference to volatile content measurements by TGA and EGA-GCMS respectively.

7.7 Ash content

A bulk sample of MWCNTs is heated in an oxidizing environment from room temperature to well above the combustion temperature (around 1 000 °C or higher) and is held at that temperature until combustion is complete. The ash content is the weight of the residue remaining after heating. TGA can be used as a method to measure the ash content. The ash content is usually expressed as the percentage of the original weight of the sample remaining after heating.

NOTE Typically, the metal catalyst used to grow MWCNTs is oxidised at these temperatures, which could lead to weight gain and is a major component of the ash content.

8 Reporting

The reporting of characterizations should include the following:

a) properties and contents evaluated as listed in Table 1;

b) measurement methods for the individual properties and contents;

c) quantitative and/or qualitative results of measurements;

d) identification of the sample tested, e.g. sample name and lot number;

e) information on the reliability of the data;

f) additional information, e.g. variations from methods given in this Technical Report.

NOTE ISO/TS 11888 provides guidance on SWCNT characterization and includes references for the determination of mesoscopic shape factors by SEM and TEM.