TECHNICAL SPECIFICATION

ISO/TS 23690

First edition
2023-07

Nanotechnologies — Multiwall carbon nanotubes — Determination of carbon impurity content by thermogravimetric analysis

Nanotechnologies – Nanotubes de carbone multicouches – Détermination de la teneur en impureté de carbone par analyse thermogravimetrique

Reference number
ISO/TS 23690:2023(E)

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Published in Switzerland

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Foreword

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

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Introduction

Multiwall carbon nanotubes (MWCNTs) are quasi-one-dimensional tubular carbon nanomaterials rolled up or coaxial nested by three or more graphene sheets. The production of carbon nanotubes (CNT) generally results in significant amounts of carbon impurities (carbon material content not in the form of CNT, including amorphous carbon and trace amounts of other types of structured carbon), which influence the physical and chemical properties of the nanomaterial. Therefore, the measurement of carbon impurities content in MWCNT samples is highly desirable for the determination of their purity.

Several methods have been reported to characterize carbon impurities in MWCNT samples, including transmission electron microscopy (TEM), temperature programmed oxidation (TPO) and thermogravimetric analysis (TGA), etc., among which TGA can provide quantitative results.[1][2][3][4][5][6] This technique makes use of the fact that MWCNTs are more stable than the majority of carbon impurities, so carbon impurities less stable than MWCNTs will react firstly with carbon dioxide in carbon dioxide atmosphere. The oxidation of carbon impurities with carbon dioxide is an endothermal process, which prevents overheating in certain areas and restrains the reaction of MWCNTs at the same time. Therefore, the separation between the oxidation of carbon impurities and those of MWCNTs is enhanced,[7][8][9][10] allowing the amount of carbon impurities less stable than MWCNTs to be calculated from the mass loss in thermogravimetric analysis.

Nanotechnologies — Multiwall carbon nanotubes — Determination of carbon impurity content by thermogravimetric analysis

1 Scope

This document specifies a mild oxidation method to determine the content of carbon impurities (carbon material content not in the form of CNT, including amorphous carbon and trace amountd of other types of structured carbon) less stable than multiwall carbon nanotubes (MWCNTs) by thermogravimetric analysis (TGA) under carbon dioxide atmosphere.

This document is applicable to the characterization of carbon impurities content in MWCNT samples prepared by chemical vapour deposition (CVD). Measurement of carbon impurities in MWCNT samples prepared by other methods can refer to this document. This method is not applicable to functionalized MWCNT samples or MWCNT samples with encapsulant species.

NOTE This method is applicable for the case of TG curves with a single-stage.

2 Normative references

There are no normative references in this document.

3 Terms, definitions and abbreviated terms

3.1 Terms and definitions

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

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

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1.1
multiwall carbon nanotube
MWCNT
multi-walled carbon nanotube
carbon nanotube composed of nested, concentric or near-concentric graphene layers with interlayer distances similar to those of graphite

Note 1 to entry: The structure is normally considered to be many single-walled carbon nanotubes nesting each other and would be cylindrical for small diameters but tends to have a polygonal cross-section as the diameter increases.

[SOURCE: ISO/TS 80004-3:2020, 3.3.6[11]]

3.1.2
amorphous carbon
carbon material without long-range crystalline order

[SOURCE: IUPAC, Compendium of Chemical Terminology[12]]

3.2 Symbols

T_o	temperature of the peak on DTG curve (°C)
w_{300}	mass percentage (%) of the sample at 300 °C
w_e	mass percentage (%) of the sample at temperature T_e
ΔH	is the enthalpy change

3.3 Abbreviated terms

CO_2	carbon dioxide
CVD	chemical vapour deposition
DTG	derivative thermogravimetric
MWCNT	multiwall carbon nanotube
TG	thermogravimetric
TGA	thermogravimetric analysis

4 Principle

Thermogravimetric analysis measures the change in mass of a material as a function of temperature. In order to accomplish this, TGA requires the precise measurements of mass, temperature and temperature change. The change in mass of a material relates to change in composition and structure of the material. Observed mass changes with temperature increases may result from the removal of absorbed moisture, solvent residues, chemically bound moieties and/or the thermal or oxidative decomposition of product.[13] The experiments are carried out in an inert or oxidising atmosphere. The recorded mass change as a function of temperature is a thermogravimetric (TG) curve. Mass change and the extent of these changes of a material in a TG curve are indicators of the thermal stability of the material.[14] Derivative thermogravimetric (DTG) curve is a display of the first derivative of thermogravimetry data with respect to temperature or time[15].

The method specified in this document is based on different reactivity of MWCNTs and carbon impurities under carbon dioxide (CO_2) atmosphere during heating. Carbon dioxide works as a mild oxidant to first oxidize carbon impurities less stable than MWCNTs. Moreover, the reaction between carbon impurities and CO_2 absorbs heat from environment,[7][8][9] which prevents local overheating, and thus enhances the separation of carbon impurities and MWCNTs. The amount of carbon impurities in MWCNT samples can be calculated from the mass loss in thermogravimetric analyser. See the reaction formula below.

$$C_{(s)} + CO_{2(g)} \rightarrow 2\ CO_{(g)}\ ;\ \Delta H > 0$$

where

$C_{(s)}$	is the carbon impurities in solid state;
$CO_{2(g)}$	is the carbon dioxide in gaseous state;
$CO_{(g)}$	is the carbon monoxide in gaseous state;
ΔH	is the enthalpy change.

5 Sample preparation

MWCNT sample should be of good quality. MWCNT sample is first placed in a thermostatic vacuum drying furnace for 2 h at 150 °C to remove unwanted volatile components.[16] Then the sample is transferred to a desiccator to cool down to room temperature and it is stored there until used.

6 Measurement

6.1 Apparatus

6.1.1 Thermogravimetric analyser

Thermogravimetric analyser should consist of a furnace, which is capable of heating from room temperature to 1 000 °C or above. Heating rate during experiment should be controlled by temperature programme set in software[14].

The linear heating rate should be controllable in the range from 1 °C min^{-1} to 50 °C min^{-1}. The balance sensitivity should be at least 1 µg, and the temperature controller sensitivity less than or equal to 0,01 °C.

A crucible should be used as a sample container. The crucible is generally made of alumina, platinum, quartz or other materials, which does not change or react under the measurement conditions.

6.1.2 Drying furnace

A drying furnace capable of controlled heating to at least 150 °C is used.

6.1.3 Analytical balance

An analytical balance capable of weighing 0,1 mg or lower is used.

6.1.4 Desiccator

A dessicator containing a desiccant such as dried silica gel impregnated with cobalt chloride is used. The drying agent shall not react with MWCNT samples.

6.2 Reagents

6.2.1 Inert gas

Dry, commercially available inert gas, such as nitrogen gas or argon gas, with minimum volume fraction of 99,999 % should be used in the measurement.

6.2.2 Carbon dioxide

Dry, commercially available carbon dioxide gas with minimum volume fraction of 99,999 % should be used in the measurement.

6.3 Measurement procedures

The thermogravimetric analyser should be calibrated according to the manufacturer's protocol to ensure proper temperature and mass measurement.

a) Turn on the thermogravimetric analyser and wait until equilibrium is reached. Then inert gas and carbon dioxide gas are introduced.

b) Obtain a baseline correction file using empty crucibles at the same experiment conditions to be used for the MWCNT sample. Specifically, set the flow rate of gas to the furnace according to the instrument type. The recommended inert gas flow is 10 ml min^{-1} to 20 ml min^{-1} and carbon dioxide gas flow is 20 ml min^{-1} to 40 ml min^{-1}; set the heating rate as 10 °C min^{-1} within the temperature range from room temperature to 1 000 °C.

c) Weigh an appropriate amount of MWCNT sample (3 mg to 5 mg) using an analytical balance and transfer the sample into the crucible.

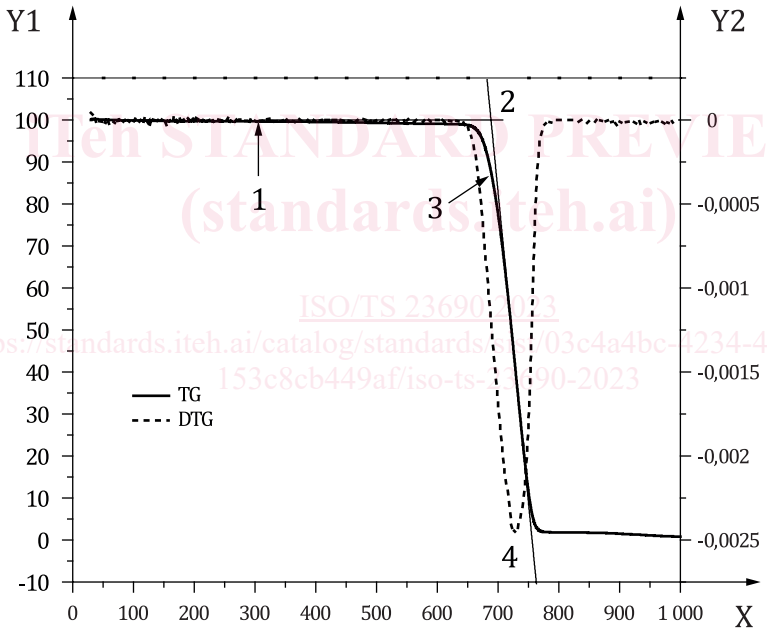
d) Before starting the measurement, keep the MWCNT sample in a closed thermogravimetric analyser under a gas flow for at least 15 min and wait until the signal (mass, temperature, gas flow) is stable.

e) Test the sample under the same conditions as in b). Thermogravimetric analyser will automatically record the mass change of MWCNT sample with temperature.

Repeat the measurement at least three times for one MWCNT sample.

7 Data analysis and interpretation of results

TG and DTG curves of one MWCNT sample are shown in Figure 1.



Key

X temperature (°C)

Y_1 mass percentage (%)

Y_2 derivative mass percentage (%/ °C)

1 mass percentage of the MWCNT sample at 300 °C, w_{300} (%)

2 extrapolated initial temperature of MWCNT component oxidation in one MWCNT sample, T_e (°C)

3 mass percentage of the sample at T_e, w_e (%)

4 temperature of the peak on DTG curve, T_o (°C)

Figure 1 — TG and DTG curves of one MWCNT sample

The mass loss below 300 °C is due to the loss of volatile components[16].

T_e is the intersection point between the base line and the tangent line at the maximum mass loss rate point, where the maximum mass loss rate point is provided in the DTG curve and the tangent line is obtained by ordinary analysis software.

Calculate the content of carbon impurities in MWCNT sample by Formula (1),

$$w = w_{300} - w_e \tag{1}$$

where w is the mass percentage (%) of the carbon impurities.

Conduct three independent TGA measurements for one MWCNT sample. The three measurements results are referred as w_1, w_2 and w_3, respectively. Calculate mass percentage of carbon impurities in MWCNT sample according to Formula (1). Calculate the average value of the three measurements by Formula (2):

$$\bar{w} = \frac{w_1 + w_2 + w_3}{3} \tag{2}$$

where $\bar{w}$ is the average mass percentage (%) of the carbon impurities in one MWCNT sample.

Annex A and Annex B provide the case studies of repeatability and reproducibility, respectively. Annex C provides the detailed procedures for the analysis of the TG curve.

NOTE This method is applicable for the case of a TG curve with a single-stage.

Sample homogeneity should be considered. The homogeneity of MWCNT samples can be evaluated by the constituency, thermal stability and scatter in the oxidation temperature and the residual material content in several separate TGA runs.[13] Errors in result calculation can be introduced if the sample is non-homogeneous.

8 Measurement uncertainty

8.1 Type A uncertainty

8.1.1 The uncertainty is introduced by the measuring method, such as measurement precision, and method bias. It is calculated by measuring repetitive standard deviation of the reference material, which is used for instrument calibration.

8.1.2 The uncertainty is introduced by aspects of sample measurement, such as the uniformity of samples, weighing, drying and gridding. It is calculated by measuring repetitive standard deviation of the sample.

8.2 Type B uncertainty

The uncertainty is introduced by instrument calibration, such as mass calibration, and temperature calibration[15].

9 Test report

The test report shall include the following information:

a) refer to this document (i.e. ISO/TS 23690:2023);

b) sample type and name;

c) tester;

d) organization, contact address and telephone number;

e) type of thermogravimetric analyser and model;