TECHNICAL SPECIFICATION

ISO/TS 11308

Second edition
2020-04

Nanotechnologies — Characterization of carbon nanotube samples using thermogravimetric analysis

Reference number
ISO/TS 11308:2020(E)

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

Published in Switzerland

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Foreword

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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).

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For an explanation of 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 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 11308:2011), which has been technically revised. The main change compared with the previous edition is as follows:

— a generalization has been made from single-walled carbon nanotubes to all forms of carbon nanotubes (including multi-wall).

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Carbon nanotubes (CNTs) are allotropic forms of carbon with cylindrical nanostructures. As a result of their geometric structures, these materials exhibit unique mechanical, thermal and electrical properties[1][2][3][4][5]. CNTs are synthesized by several different methods, including pulsed laser vaporization, arc discharge, high pressure disproportionation of carbon monoxide and chemical vapour deposition (CVD)[6][7][8]. These processes typically yield a heterogeneous mixture of CNTs and impurities, often requiring post-synthesis purification. Commonly observed impurities include other forms of carbon [e.g. fullerenes, amorphous carbon, graphitic carbon, single-wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes (MWCNTs) outside the desired size or chirality range], as well as residual metallic catalyst nanoparticles. Purification can be accomplished using gaseous, chemical or thermal oxidation processes[9][10][11][12].

Thermogravimetric analysis (TGA) measures changes in the mass of a material as a function of temperature and time, which provides an indication of the reaction kinetics associated with structural decomposition, oxidation, pyrolysis, corrosion, moisture adsorption/desorption and gas evolution. By examining the reaction kinetics for a given sample, the relative fraction of different constituents present can be either quantitatively or qualitatively determined.

TGA is one of a number of analytical techniques that can be used to assess impurity levels in samples containing CNTs[14][15][16][17][18][19][20][21][22]. For CNT-containing samples, TGA is typically used to quantify the level of non-volatile impurities present (e.g. metal catalyst particles). TGA is also used to assess thermal stability of a given sample, providing an indication of the type(s) of carbon materials present. Recent advances in TGA instrumentation enable better resolution during analysis. However, TGA alone is not specific enough to conclusively quantify the relative fractions of carbonaceous products within the material. Therefore, the information obtained from TGA should be used to supplement information gathered from other analytical techniques in order to achieve an overall assessment of the composition of a CNT sample[23][24][25][26][27][28][29].

Nanotechnologies — Characterization of carbon nanotube samples using thermogravimetric analysis

1 Scope

This document gives guidelines for the characterization of carbon nanotube (CNT)-containing samples by thermogravimetric analysis (TGA), performed in either an inert or oxidizing environment. Guidance is provided on the purity assessment of the CNT samples through a quantitative measure of the types of carbon species present as well as the non-carbon impurities (e.g. metal catalyst particles) within the material.

In addition, this technique provides a qualitative assessment of the thermal stability and homogeneity of the CNT-containing sample. Additional characterization techniques are required to confirm the presence of specific types of CNT and to verify the composition of the metallic impurities present.

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 80004-3, *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 80004-3 and the following 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 http://www.electropedia.org/

3.1
primary oxidation temperature
$T_{ox'}$
temperature at which the most intense peak occurs in the first derivative thermogravimetric curve

3.2
thermal stability
dimensional stability of a solid material heated under specified conditions

Note 1 to entry: Thermal stability can be affected by the relative fraction of material *constituents* (3.4) in the sample as well as physical characteristics of the nanotube materials, such as diameter, length, defect state or surface treatment.

3.3
homogeneity
degree to which a property or a *constituent* (3.4) is uniformly distributed throughout a quantity of material

EXAMPLE Primary oxidation temperature.

3.4
constituent
component present in a carbon-nanotube-containing sample

Note 1 to entry: A carbon-nanotube-containing sample is often comprised of different carbon and non-carbon materials and is identified by oxidation peaks in the thermogravimetric analysis curve and by residual weight.

3.5
monotypic
material consisting of only one type of carbon nanomaterial

Note 1 to entry: When multi-walled carbon nanotubes are present, monotypic samples may contain a narrow range of diameters and lengths.

Note 2 to entry: A typical carbon nanotube sample comprises several types of carbon nanomaterials, including amorphous carbon, fullerenes, single-wall carbon nanotubes and multi-wall carbon nanotubes.

3.6
purity
measure of the fraction (percentage weight or mass fraction) of impurities within a given sample

Note 1 to entry: Thermogravimetric analysis alone cannot conclusively quantify the relative fractions of any and all carbonaceous products within the material. It can, however, quantify the level of non-volatile (e.g. metal catalyst) impurities, which is one measure of purity.

3.7
quality
overall assessment of the carbon nanotube sample

Note 1 to entry: A high quality carbon nanotube material is taken as a material with *high purity* (3.6), structural integrity and *homogeneity* (3.3).

Note 2 to entry: Thermogravimetric analysis can partly contribute to the quality assessment of carbon-nanotube-containing material by providing its residual weight and oxidation temperature.

Note 3 to entry: A carbon nanotube material may have a high purity level (i.e. a net mass fraction of 100 %) but it may have a considerable amount of damage, which can alter or destroy its physical properties, thereby deteriorating the quality of the material.

4 Symbols and abbreviated terms

CNT	carbon nanotube
CVD	chemical vapour deposition
DSC	differential scanning calorimetry
DTGC	derivative thermogravimetric curve (sometimes known as the “derivative weight loss curve”)
HiPco	high pressure CO conversion
MWCNT	multi-wall carbon nanotube
SWCNT	single-wall carbon nanotube
TGA	thermogravimetric analysis
T_{ox}	oxidation temperature
W_{res}	residual mass of the sample after heating

5 Principles of TGA

5.1 Measurement

At the basic functional level, TGA measures the change in mass of a material as a function of temperature as it is heated at a specified rate. In order to accomplish this, TGA requires the precise measurements of mass, temperature and temperature change. The change in mass of a material is related to the composition of the material and its thermal reactivity with the atmospheric conditions of the measurement. TGA analysis of CNT samples is most commonly performed in an oxidizing atmosphere, but can also be done with inert, reducing or other atmospheric conditions to probe different thermal reaction kinetics. Mass loss relative to an increase in temperature can result from the removal of absorbed moisture, solvent residues, chemically bound moieties and/or the thermal or oxidative decomposition of product.

TGA alone cannot identify the volatile materials released during heating; analytical techniques such as mass spectrometry (MS), gas chromatography (GC) and Fourier-transform infrared spectroscopy (FTIR) can be combined with TGA in order to identify volatile materials by coupling the appropriate instrumentation to the exhaust. Similarly, with respect to CNT-containing materials, TGA cannot by itself identify the different carbon forms present within the material. What it does do is determine the temperature at which the carbon species oxidize, which can be indicative of the identity of the species, as well as provide a quantitative measure of the non-volatile component.

When a CNT-containing sample is subjected to elevated temperatures in the presence of air, the carbon species present will oxidize into gaseous compounds such as CO or CO_2. The residue comprises non-volatile materials, which for the most part are metal impurities.

5.2 Exothermic and endothermic reactions

Some CNT-containing samples have been observed to undergo combustive reactions during TGA analysis, resulting in rapid burning of material, possibly catalysed by residual metals in the sample. Such events are distinguished by a difference in temperature between the sample and the reference, but also a rapid change in sample mass with little or no change in reference temperature[30].

6 Sampling

6.1 Sample pan selection

Sample pan size and type will vary depending on the instrument being used and the temperature range of interest. There is no restriction on the sample pan size so long as it is compatible with the instrument and it is capable of accommodating the required amount of CNT sample with minimal compaction (see 6.3 and the references within for a discussion of sample compaction). Aluminium, ceramic or platinum pans may be used depending on the experimental temperature range. Aluminium pans are the least likely to catalytically oxidize the CNT material, but they do not cover as wide of a temperature range. Ceramic and platinum pans are more likely to have adsorbed contaminants that can lead to inconsistent or even erroneous data. Table 1 provides guidance to some of the available pans. Standard manufacturer recommended procedures should be followed to remove any residual material from previous samples prior to conditioning. To remove adsorbed moisture, it is recommended that the pans be conditioned by heating to at least 300 °C in an air environment prior to introduction of the CNT sample. If the pans are not used immediately after conditioning, they should be stored in a dry box or desiccator until loading to prevent the reintroduction of moisture.

Table 1 — Sample pan selection guidance for TGA of CNTs

Pan material	Temperature range	Comments
Aluminium	Ambient to 600 °C	Aluminium pans are considered disposable by manufacturers, which is beneficial in eliminating contamination. However, the low maximum temperature means they can only be used when it is certain that all the CNT material will burn off before 600 °C.
Ceramic	Ambient to 1 200 °C and above	Porous ceramic will easily pick up moisture from the atmosphere, so it is especially important to condition the pans for consistent results. Ceramic pans are capable of use above 1 200 °C; however, most TGA instruments are limited to an upper temperature of 1 200 °C.
Platinum	Ambient to 1 000 °C	It is important that the platinum pan is rated for high temperature use otherwise the maximum temperature is only 750 °C.

6.2 Sample size

The controlling factor in the selection of sample size is the bulk density of the CNT material. As-produced samples can be more difficult to accommodate in TGA pans because of their lower bulk density, whereas purified materials are condensed during the purification processes. If the minimum recommended amount of the sample is too fluffy for the available TGA pan, slight compacting with a spatula may be used to contain the sample within the pan.

Additional details on sampling can be found in Reference [31].

For dry powder samples:

a) use a minimum of 1 mg of sample or the amount recommended for the instrument by the manufacturer for the specific pan size being used, whichever is greater;

b) load samples into pan and store in a dry environment for at least 48 h prior to measurement; if possible, load samples in a controlled environment such as a glove box or nano-hood to prevent the airborne release of nanotubes;

c) weigh samples at an ambient temperature on a microbalance.

6.3 Sample compaction

Compaction of a powder using a press is a common method of preparation for TGA and DSC measurements of powder samples. The effects of high pressure compaction of SWCNT samples have been investigated[31] and it has been found that compaction in a KBr pellet die (such as those commonly used for the preparation of samples for infrared spectroscopy) can influence the observed oxidation temperatures, though no effect was found on the residual mass values. Details of necessary provisions concerning compaction are described further in B.3.

The following rules regarding sample compaction apply:

a) do not use high pressure sample compaction (e.g. with a pellet die);

b) slight compaction by low pressure pressing with a spatula is acceptable to contain the full sample within the pan.

7 Test method

The following procedure outlines the minimum requirements for obtaining TGA data that will allow for a reliable characterization of CNT samples. At a minimum, this procedure should be repeated three times for each sample. A typical run usually takes approximately 2 h, depending on the ramp rates used.

a) Calibrate the TGA instrument according to the manufacturer's protocols to ensure the proper temperature and weight measurement.

b) Prepare the TGA instrument by first taring an empty sample pan in the TGA balance. On a microbalance, weigh and record a minimum of 1 mg of sample and transfer into the pan. If possible, perform all weighing and transfer operations in a dry environment. The samples should be kept in a desiccator for 48 h to remove any retained moisture. If the equipment allows it, store the loaded pan in the same way. Alternatively, if the tare function is not available in the instrument (as may be the case with older instrumentation), weighing the sample in a dry environment is acceptable.

c) Transfer the sample, or the loaded pan, to the TGA instrument for analysis.

d) Set the maximum temperature for the scan based on the anticipated composition of the sample and the sample pan being used. If the sample is unknown, set the maximum temperature to 900 °C or the highest temperature that can be used with the sample pan selected.

e) Set the temperature ramp rate to a constant rate between 1 °C/min and 10 °C/min for the entire temperature range. Slower heating rates allow more time for reactions to occur.

NOTE 1 If there are known or suspected organic impurities in the sample, the sample can first be heated to 120 °C with an inert gas flow and held at this temperature for 30 min prior to heating over the entire temperature range. This additional heating step can also be used if the sample is unknown to ensure that there is sufficient time for evolution of any organic impurities.

f) Set the gas flow rate based on the manufacturer's recommendation for the particular TGA instrument. If no recommendation is given, set the flow rate to no less than 100 ml/min.

NOTE 2 The flow rate needed for successful operation will be dependent on the instrument geometry. If no flow rate is recommended by the manufacturer, the most important consideration is that the flow rate provides an optimal burn rate of the sample while minimizing any buoyancy effects on the sample weight determination.

NOTE 3 Air or oxygen is used as the gas for oxidative decomposition studies while an inert gas such as nitrogen or argon is used for pyrolytic decomposition studies. Other gases can be used for different situations.

NOTE 4 Cooling rate is instrument dependent.

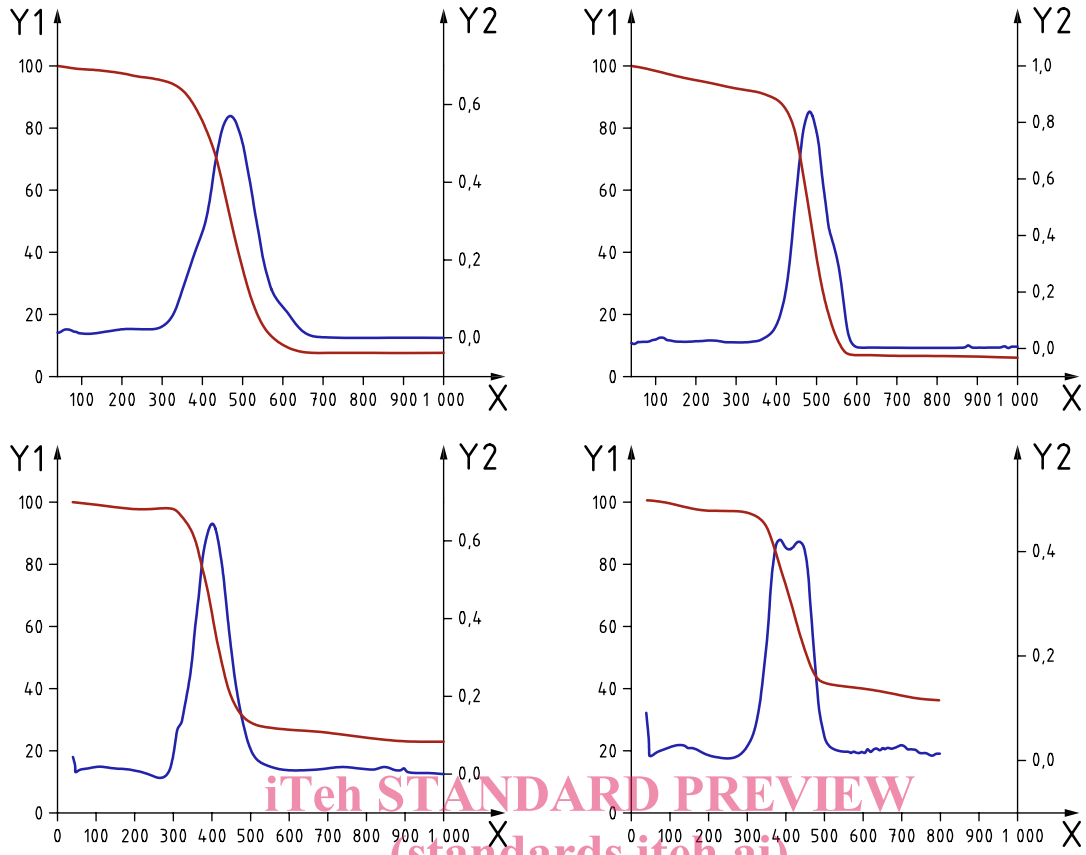
g) After completion of the measurement, record the residual mass (W_{res}) value for each scan at room temperature on a microbalance.

h) Record the oxidation temperature (T_{ox}) for each peak within a scan. The overall T_{ox} for each species attributing to the TGA curve is determined from the mean value of the three runs. T_{ox} for the particular species is then documented as the mean value plus and minus the standard deviation.

8 Data interpretation and results

8.1 General

The following are guidelines for the interpretation of the TGA curves and the type of information used to evaluate CNT-containing materials. An example of TGA curves for four different CNT samples (each produced by a different method) is shown in Figure 1.



Key

X temperature (in °C)
Y1 weight (in %)
Y2 deriv. weight (in %/°C)

Figure 1 — TGA curves for CNT samples produced by different methods[32]

8.2 Non-carbon content

The non-carbon content of the CNT-containing sample is assessed through the W_{res} value. This value is acquired from both the TGA data and a microbalance value. From the TG curve, W_{res} is recorded as the mass remaining above 800 °C. This value is compared to the microbalance weight in order to assess if there is a systematic error due to buoyancy effects caused by the air flow in the instrument. W_{res} can be expressed as either the actual weight that remains or as a percentage of the original weight of the sample. To report the non-carbon content of a CNT-containing sample, W_{res} will be expressed as the mean percentage weight together with the standard deviation from at least three TGA measurements.

NOTE The determination of non-carbon content in the original CNT sample from W_{res} can be inaccurate as some contributors to the residual will change oxidation state during heating, resulting in either a decrease or increase in weight. W_{res} will, however, still provide a good approximation to the overall non-carbon impurity component of the CNT material, especially when comparing samples from the same production method (see A.2) that will likely have the same impurities.

It is recommended that the user verify the oxidative stability of the metals used as catalysts by conducting TGA analysis of the catalyst at identical heating and air flow rates. These measurements will establish whether W_{res} measures metals, metal oxides or a mixture of the two. If the catalyst composition is unknown, the largest temperature range should be used.