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# Nanotechnologies — Characterization of carbon nanotube samples using thermogravimetric analysis

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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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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.

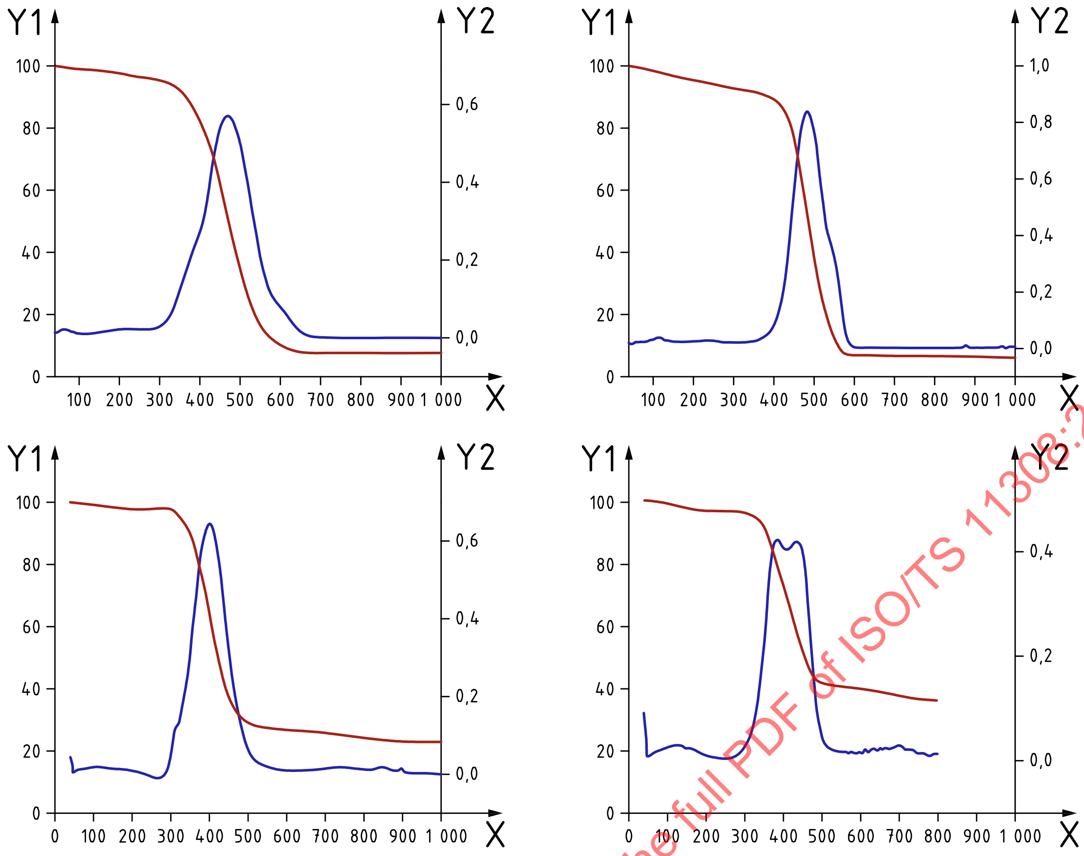
g) After completion of the measurement, record the residual mass ($W_{\text{res}}$) value for each scan at room temperature on a microbalance.

h) Record the oxidation temperature ($T_{\text{ox}}$) for each peak within a scan. The overall $T_{\text{ox}}$ for each species attributing to the TGA curve is determined from the mean value of the three runs. $T_{\text{ox}}$ 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.

## 8.3 Constituents

Most production methods for CNTs are not 100 % efficient in the conversion of the source carbon to a single species. Single-wall production methods do not eliminate multi-wall tubes and vice versa. Additional forms of carbon such as fullerenes or amorphous carbon also cannot be fully eliminated at the time of production. The presence of multiple constituents can be qualitatively determined from TGA data by determining the number of oxidation peaks present in the DTG curve[34]. While it is difficult to assign any particular carbon form to a specific oxidation peak, especially as the number of constituents in the sample increases, it is commonly agreed upon that multiple peaks arise due to the presence of different carbon types (see A.3).

NOTE TGA data from relatively pristine samples have shown that single, double and multi-wall CNTs have unique ranges of oxidation temperatures, which can be used to distinguish between the different CNT constituents if it is known that there is minimal overlap with any non-CNT carbon constituents[34].

## 8.4 Thermal stability

The thermal stability of a sample of CNT material is the dimensional stability of a solid material heated under specified conditions. Thermal stability of a sample of CNT material can be affected by the relative fraction of material constituents in the sample as well as physical characteristics of the nanotube materials, such as diameter, length, defect state or surface treatment. The parameter used to assess thermal stability is the primary oxidation temperature, which is the temperature at which the highest fraction of carbon content oxidizes (see A.4 and Reference [30]).

## 8.5 Homogeneity

The homogeneity of CNT materials is established in TGA by the constituency, thermal stability and scatter in the $T_{ox}$ and $W_{res}$ values of multiple runs (see A.5 and Reference [30]). A material is considered sufficiently homogeneous if it meets pre-defined quantitative limits for the following criteria.

The TGA data from a minimum of three runs:

- should produce the same set of oxidation peaks (same constituency);
- should have a similar primary $T_{ox}$ (thermal stability) from run to run;
- should have $T_{ox}$ and $W_{res}$ values with a narrow standard deviation (see Annex A).

If all three conditions are not met, the material cannot be considered homogeneous.

## 8.6 Purity

The purity of a either a SWCNT or a MWCNT sample is established by the mass fraction of the desired CNTs relative to both the carbon and non-carbon impurities within the material. TGA alone can only reliably provide purity assessment relative to the non-carbon impurities through the $W_{res}$ value. A material with lower residual values is therefore considered a material with better purity relative to the non-carbon impurity content. To clearly define the overall purity of a material, TGA results must be coupled with information from other techniques (see A.6).

## 8.7 Quality

As with purity assessment, the quality assessment of a CNT sample cannot be completely determined by TGA. However, two of the material characteristics (purity and homogeneity) required to establish the quality of a material can be identified by TGA, and are particularly useful when describing CNT materials[30].

A CNT sample that produces TGA data showing a low $W_{res}$ value and high homogeneity (reproducible TGA data from run to run) can be considered to have uniform quality relative to TGA. The actual quality of the CNT sample can only be established by coupling information from other analytical techniques such as elemental analysis for the composition or Raman spectroscopy for the level of defects in the material.

## 9 Uncertainties

Uncertainty can occur in the exact measurement of the non-carbon content present within a CNT sample. The non-carbon elements typically found in as-produced materials might react at elevated temperatures to form non-volatile oxides or carbides. In this case, the measure of $W_{\mathrm{res}}$ will be higher than the actual weight of the non-carbon content.

On the other hand, some non-carbon elements might react to form volatile oxides, in which case the measured $W_{\mathrm{res}}$ may be lower than the actual non-carbon content. As recommended in 8.3, the response of the catalyst to heating can be determined by running it under the same conditions used for the samples. The $W_{\mathrm{res}}$ value can then be used to calculate the amount of catalyst in the material.

Finally, in TGA runs on highly pure nanotubes [minimal (less than 10 %) content of ash remaining after the completion of the TGA run], the $W_{\mathrm{res}}$ is sometimes negative, mainly because of drift of the TGA balance. This can happen even with regular calibration of the instrument. The long-term stability of the instrument (during a run of more than 3 h) is generally within 20 µg to 40 µg, which is equivalent to 2 % to 4 % of a 1 mg sample. The stability of the instrument can be quantified by running an empty sample pan under the same conditions used for the samples. Alternatively, the larger the amount of sample that can be used, the more negligible the 20 µg to 40 µg drift becomes.

Determination of the measurement uncertainty value may be done by following ISO/IEC Guide 98-3:2008.

## 10 Test report

In addition to the information required for reporting test results from ISO/IEC 17025, the following data should be included in the test report:

a) sample information:
   1) lot number;
   2) manufacturer and production method used to synthesize CNT sample, if known (e.g. CVD from manufacturer A);
   3) weight of sample used:
      i) weight from microbalance (run1: weight1, run2: weight2, run3: weight3, etc.);
      ii) weight from TGA balance (run1: weight1, run2: weight2, run3: weight3, etc.);

b) TGA curve analysis that is to be recorded for evaluation of material (report the actual curves as well):
   1) number of peaks in individual DTG curves (run1: 3 peaks, run2: 1 peak, run3: 2 peaks);
   2) primary oxidation temperature from individual DTG curves (run1: x °C, run2: y °C, run3: z °C);
   3) weight of the remaining ash from individual runs from the microbalance (run1: x mg, run2: y mg, run3: z mg);
   4) weight of the remaining ash from individual runs from the TGA balance (run1: x mg, run2: y mg, run3: z mg);
   5) residual weight from individual TGA curves (run1: x%, run2: y%, run3: z%);
   6) calculation of the average residual weight with standard deviation (x% ± y%);
   7) heating ramp;

   8) temperature range;
   9) flow rate and type of gas used;

c) TGA data interpretation and results:

   1) constituency: monotypic or multiple constituents;
   2) thermal stability: when definable, list the average $T_{ox}$, with standard deviation, otherwise list as undefinable;
   3) homogeneity: state when the material can be considered sufficiently homogeneous if it meets pre-defined homogeneity criteria, otherwise state that it cannot be considered homogeneous;

d) additional information:

   1) brand and model of the TGA equipment used.

# Annex A
(informative)

# Case studies

## A.1 General

This annex gives examples on the use of $W_{res}$ and $T_{ox}$ values for the assessment of constituency, homogeneity, non-carbon content, purity, quality and thermal stability. TGA data were obtained on various CNT materials produced by arc discharge, CVD, high pressure disproportionation of carbon monoxide and pulsed laser vaporization.

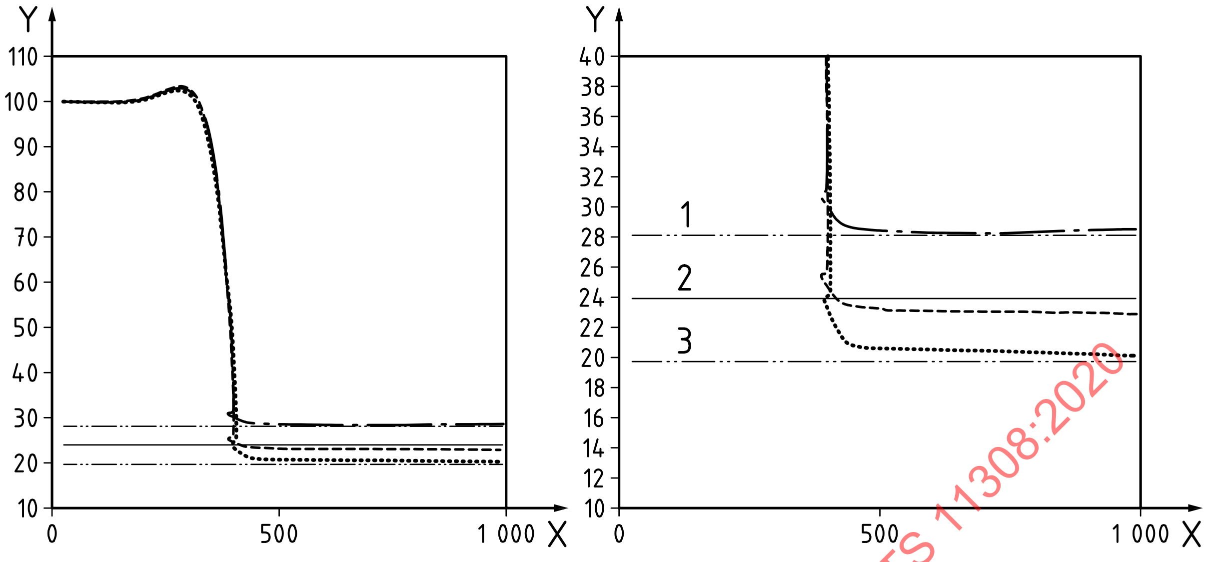
## A.2 Evaluation of non-carbon content

### A.2.1 Determination of non-carbon content

The non-carbon content is determined from weight measurements obtained from both the TGA apparatus and a microbalance before and after the run. The reason for this is to identify any possible sources of measurement error. Discrepancies may arise from buoyancy effects, thermal expansion of balance arms, loss of sample during transfer or moisture adsorption of the sample. Furthermore, the long-term stability of the instrument zero (during a run of more than 3 h) is generally within 20 µg to 40 µg, which is equivalent to 2 % to 4 % of a 1 mg sample. Weighing independently allows for greater confidence in the data.

The most representative measure of the $W_{res}$ of a sample is taken as the lowest point in the TG curve. The mean value of the $W_{res}$ and the standard deviation from multiple runs are to be calculated and used to report the non-carbon content (see Figures A.1 and A.2). Similar calculations for the $W_{res}$ as determined by the microbalance measurements are to be compared (see Tables A.1 and A.2). Large differences between the two determinations would merit additional runs or re-calibration of the system.

Two factors which may influence the $W_{res}$ determination are adsorbed water content and oxygen uptake from the non-carbon components. The water content can be easily accounted for by measuring the mass difference between the starting weight and the weight at which the TG curve first levels off, typically around 150 °C. Oxygen uptake due to the oxidation of non-carbon impurities is addressed in more detail in A.2.2.



a) actual TG curve

b) $W_{\text{res}}$ average and standard deviations

**Key**

—·— run 1
······ run 2
---- run 3
—··— std. dev
—··— average

X temperature (in °C)
Y percentage weight (in %)
1 std. dev. = +4,2
2 average =
3 std. dev. = −4,2

NOTE $W_{\text{res}}$ average and standard deviations are calculated in Table A.1

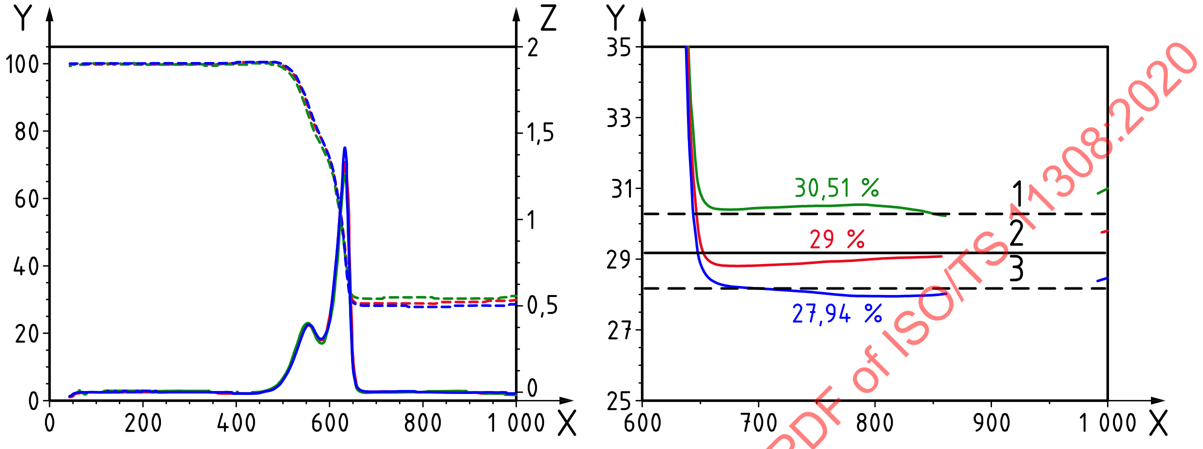
Figure A.1 — TGA results for a CNT sample

### Table A.1 — Calculations of $W_{\text{res}}$ average and standard deviations from three HiPco SWCNT runs

| Parameter | Run 1 | Run 2 | Run 3 | Average | Standard deviation |
|---|---|---|---|---|---|
| Sample weight: microbalance (in mg) | 3,09 | 3,20 | 3,00 | — | — |
| Sample weight: TGA (in mg) | 3,22 | 2,98 | 2,84 | — | — |
| Residual weight: microbalance (in mg) | 0,63 | 0,65 | 0,65 | 0,64 | 0,01 |
| Residual weight: TGA at 1 000 °C (in mg) | 0,91 | 0,60 | 0,65 | 0,72 | 0,17 |
| Residual weight: TGA at room temperature (in mg) | 0,90 | 0,59 | 0,61 | 0,70 | 0,17 |
| Amount of oxygen uptake (in mg) | 0,09 | 0,07 | 0,10 | — | — |
| Amount of $H_2O$ desorption (in mg) | — | — | — | — | — |
| % residual weight: microbalance (uncorrected) | 20,36 | 20,32 | 21,73 | 20,80 | 0,80 |

**Table A.1** *(continued)*

| Parameter | Run 1 | Run 2 | Run 3 | Average | Standard deviation |
|---|---|---|---|---|---|
| % residual weight: TGA at 1 000 °C (uncorrected) | 28,22 | 20,22 | 23,01 | 23,82 | 4,06 |



a) actual TG and DTG curves

b) $W_{res}$ average and standard deviations

**Key**

| | | | |
|---|---|---|---|
| 🟥 | Run 1 | X | temperature (°C) |
| 🟩 | Run 2 | Y | percentage weight (%) |
| 🟦 | Run 3 | Z | derivative percentage weight (%/°C) |

NOTE $W_{res}$ average and standard deviations are calculated in Table A.2.

**Figure A.2 — Weight loss and derivative curves for as-produced CVD material**

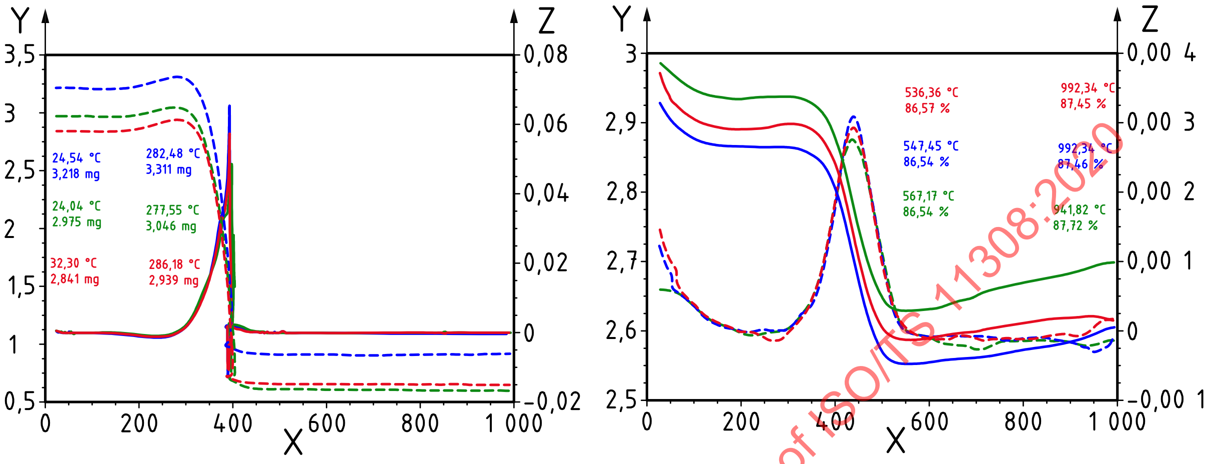
**Table A.2 — Calculations of $W_{res}$ and $T_{ox}$ average and standard deviations from three repeat runs**

| Parameter | Run 1 | Run 2 | Run 3 | Average | Standard deviation |
|---|---|---|---|---|---|
| Sample weight: microbalance (in mg) | 1,37 | 1,23 | 1,37 | — | — |
| Sample weight: TGA (in mg) | 1,35 | 1,22 | 1,41 | — | — |
| Residual weight: microbalance (in mg) | 0,43 | 0,41 | 0,40 | — | — |
| Residual weight: TGA at 800 °C (in mg) | 0,39 | 0,37 | 0,39 | — | — |
| % residual weight: microbalance (uncorrected) | 31,39 | 33,33 | 29,20 | 31,31 | 1,69 |
| % residual weight: TGA at 800 °C (uncorrected) | 29,00 | 30,51 | 27,94 | 29,15 | 1,05 |
| Primary $T_{ox}$ (in °C) | 632,55 | 631,73 | 633,43 | 632,57 | 0,69 |
| Additional peak $T_{ox}$ (in °C) | 556,39 | 554,81 | 555,34 | 555,51 | 0,66 |

### A.2.2 Oxidation of non-carbon content

The non-carbon content consists primarily of metal catalyst used in CNT synthesis, which can itself become oxidized under the TGA run conditions and influence the non-carbon content determination. Oxidation of the non-carbon is observed as weight increase in the TG curve and may occur before or after the oxidation of carbon species (see Figure A.3). In either case, it is difficult to quantify the extent of oxidation to the non-carbon components since TGA cannot identify the type of oxides formed.

However, the amount of oxygen uptake is to be recorded in order to provide a measure of uncertainty in the $W_{res}$ determination. Furthermore, some oxides that form during a TGA run can be volatile, which adds additional complication into the $W_{res}$ determination. This is difficult to measure in a stand-alone TGA. Without knowledge of this type of oxide formation, the $W_{res}$ is taken as representative of the non-carbon content. Whether oxidation of the non-carbon content results in a volatile or non-volatile oxide, the variation in reactivity introduces uncertainty in the determination of the true non-carbon content.



a) **before carbon decomposition**

b) **after carbon decomposition**

**Key**

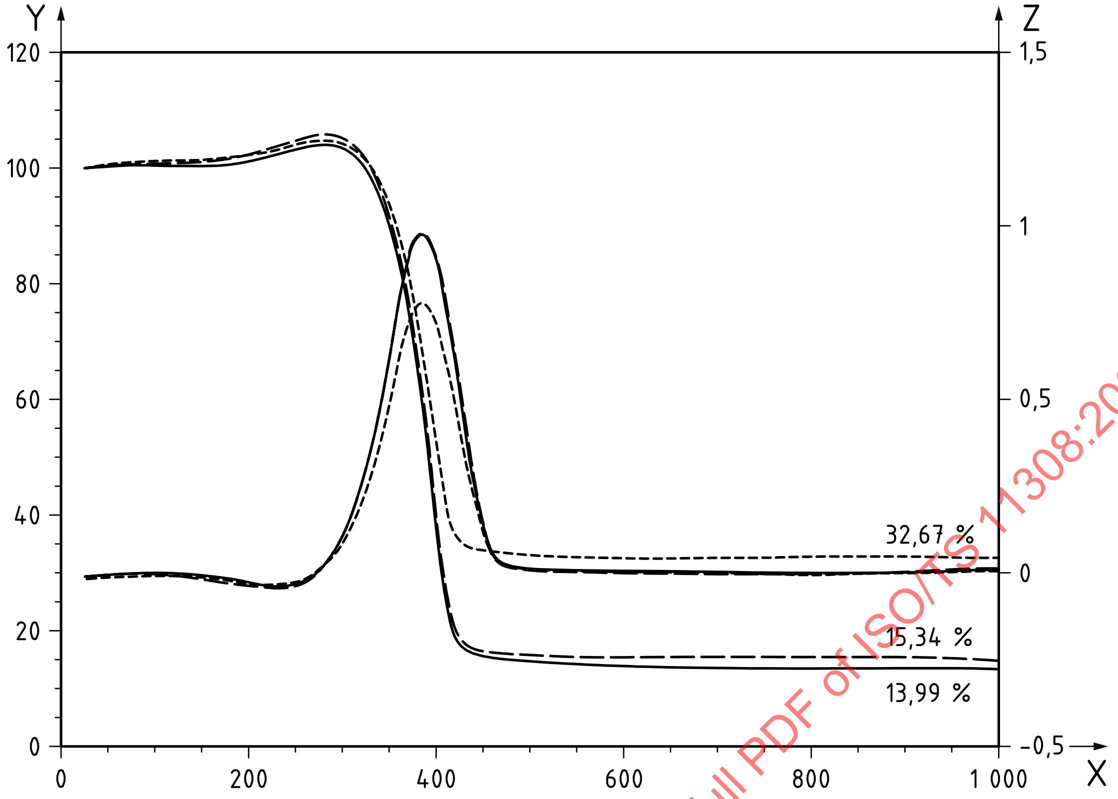
| | |
|---|---|
| X | temperature (in °C) |
| Y | percentage weight (in %) |
| Z | derivative weight (in mg/°C) |

**Figure A.3 — Oxidation of non-carbon content before and after carbon decomposition**

## A.3 Constituency

The constituency of a CNT material is described as arising from the different carbon forms present within the material, as is observed in TGA by multiple peaks in the DTG curve (see Figures A.2 and A.5). The presence of multiple peaks in the DTG curve represents a material with higher constituency. While it is difficult to assign any individual peak to a particular form of carbon, it is agreed upon that multiple peaks arise from different carbon species. These multiple peaks in the DTG curve may be attributed to isolated amorphous carbon[3][4][5], amorphous coated CNTs[4], defective tubes, chemically derivatized tubes[6], tubes of varying diameters or crystallinity[4][6], graphitic carbon, and the dispersion of the residual metal catalyst after purification.

Uncertainty in the constituency can arise in CNT materials that exhibit combustive behaviour, which are marked in TGA by an abrupt drop-off in the DTG curve as well as a backwards trace in the TG curve [see Figure A.3 a)]. This behaviour is more often observed in unpurified CNT materials that have fluffy morphology and greater metal content, and it is more probable with increased heating rate. This behaviour is explained by a rapid burning of the sample, resulting in a very quick release of a considerable amount of heat, causing a sharp increase in temperature followed by heat dissipation and a subsequent temperature drop. Combustion can complicate the constituency assessment since components with higher oxidation temperatures might be burned or blown out of the sample pan during the combustion.



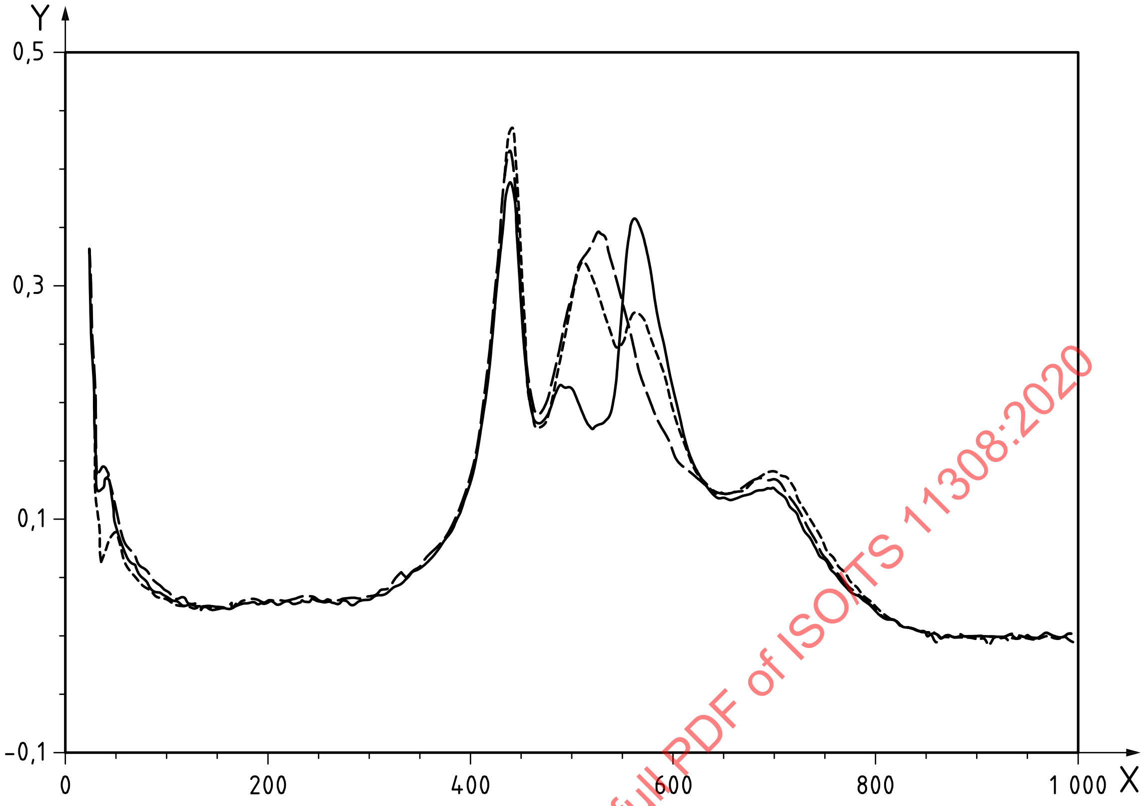
**Key**

X temperature (in °C)

Y percentage weight (in %)

Z derivative weight (in mg/°C)

Figure A.4 — Material with well-defined constituency and thermal stability but large deviation in the residual weight value resulting in low homogeneity



**Key**

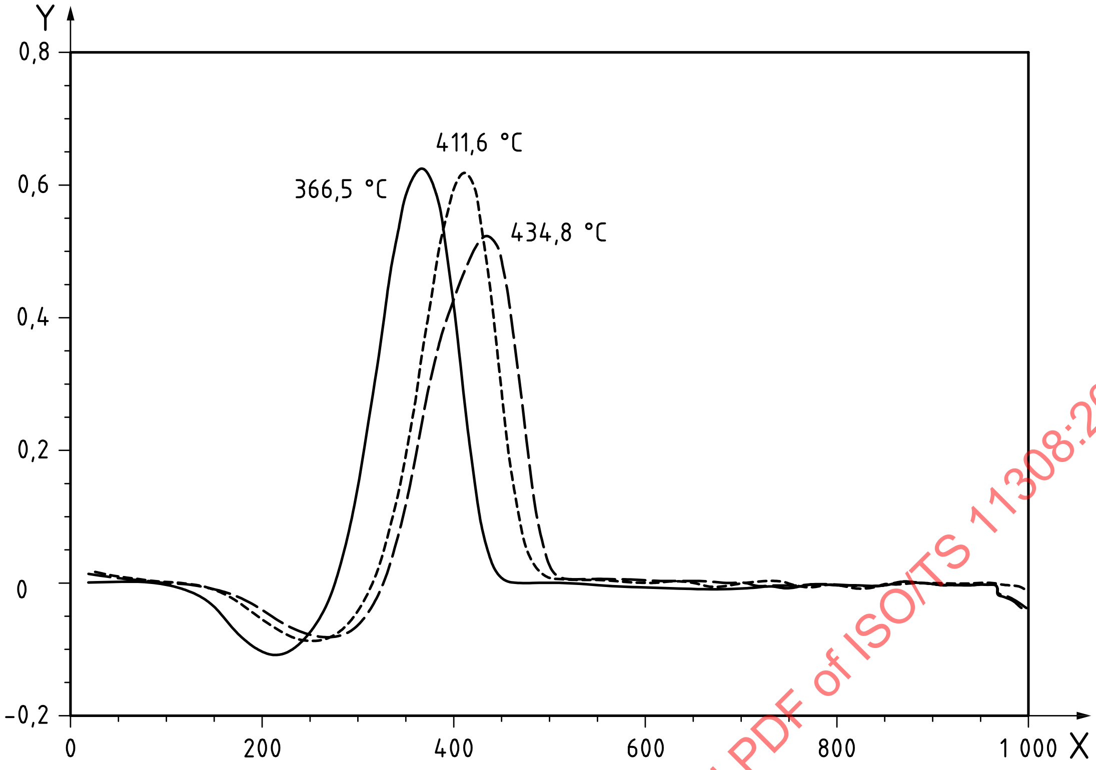
X temperature (in °C)

Y derivative weight (in mg/°C)

**Figure A.5 — Material with low homogeneity as a result of variable constituency**

## A.4 Thermal stability

Thermal stability is a straightforward assessment as it is simply the most intense DTG peak for each run, which signifies the most abundant carbon species present in the sample. The intensity of the peak is used instead of the area under the peak (determining areas is not straightforward since this requires deconvolution of the DTG curve into multiple peaks). In addition, the background subtraction and curve shape may be cumbersome. On the other hand, the peak intensity is easy to identify and is indicative of a greater rate of mass loss. The thermal stability is also reported as the mean value of $T_{ox}$ from the multiple TGA runs along with its standard deviation. If $T_{ox}$ has large scatter in value (see Figure A.6) or is inconsistent in assignment (see Figure A.7), then the thermal stability cannot be defined.

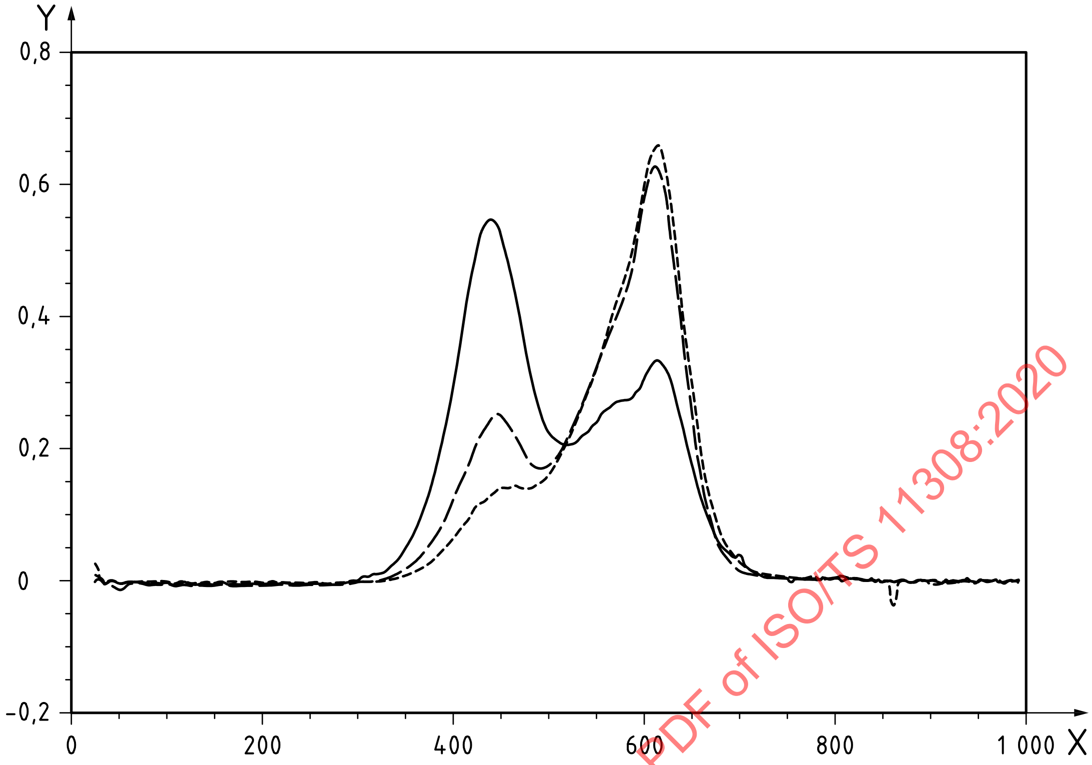


**Key**

X temperature (in °C)

Y derivative weight (in mg/°C)

**Figure A.6 — Material with essentially one constituent but large scatter in primary oxidation temperature resulting in an undefined primary oxidation and low homogeneity**



**Key**

X temperature (in °C)

Y derivative weight (in mg/°C)

**Figure A.7 — Material with variable constituency and thermal stability**

## A.5 Homogeneity

### A.5.1 General

In this subclause, several examples are presented to help explain the assessment of homogeneity through variations in the non-carbon content, constituency and thermal stability. The determination of homogeneity is influenced by several parameters, which will be described individually. Examples of TGA features not consistent with a homogeneous material are shown in Figures A.4 to A.7.

### A.5.2 Variation in non-carbon content

The homogeneity of a batch of CNT material is in part established by the uniform distribution of non-carbon content throughout the batch. If there is not a uniform distribution of the non-carbon component in the material, there will be large scatter of the $W_{res}$ values from multiple runs. This in turn will result in $W_{res}$ values with a standard deviation greater than 2,0 %, the acceptable limit (see Figure A.4). In this case, the material will not be considered homogeneous. On the other hand, if the standard deviation of the $W_{res}$ values is less than or equal to 2,0 %, the material may be considered homogeneous with respect to the quantity of the non-carbon content.

### A.5.3 Variation in the constituency

Constituency is another parameter that helps define the homogeneity as assessed through TGA. Uniform constituency from run to run is a trait of a homogeneous material. If the concentration of different carbon components varies among the samples in the same batch, the relative intensities of the oxidation peaks in the DTG curves will also vary from run to run. Because morphology and catalyst content can influence the burn rates of carbon material, it is difficult to quantify the constituency;

however, the qualitative analysis can still be used to assess the homogeneity. If from run to run there are variations in the number or relative intensities of the oxidation peaks present (see Figure A.5) or if the primary oxidation temperature shifts (see Figure A.7) by more than an acceptable amount, then the material cannot be labelled as homogeneous as defined by TGA.

Combustion can complicate the assessment of homogeneity since sample material can be blown out of the pan when this occurs. If combustion occurs in one run but not the other two, the homogeneity cannot be defined. However, if all three runs display a combustive behaviour, the material is considered homogeneous as the morphology is the same throughout the batch.

### A.5.4 Variation in the thermal stability

Another factor used for the assessment of homogeneity is the variation in the thermal stability of multiple TGA runs. This variation is established by the value of the standard deviation of the primary $T_{ox}$. If the standard deviation in $T_{ox}$ is greater than the value of the heating rate (i.e. if the standard deviation exceeds 5 °C), the material may not be considered homogeneous (see Figure A.6).

NOTE The heating rate directly influences the kinetics of oxidation (see B.2). Therefore, the heating rate is chosen as the basis to discount any lag in the oxidation process due to variation in the activation energy, thermal conduction through the material in proper air flow or inaccuracy in the thermocouple measurements.

## A.6 Purity assessment

TGA by itself is unable to provide a measure of the overall purity of CNT material since it is limited in the information relative to the types of impurities which can be found in CNT material. TGA can only provide one piece of the puzzle regarding impurity levels with the material: the amount of non-carbon content through the $W_{res}$ value. Even if the oxidation temperatures of pure SWCNTs were known and accepted, for example, there are other carbon types that have a similar enough oxidation temperature to make them indistinguishable by TGA. A true purity assessment can be accomplished when TGA is coupled to other analytical techniques since TGA can provide the information on the non-carbon impurity levels with the material.

## A.7 Quality assessment

The quality of a CNT material cannot be clearly defined through the use of TGA. TGA can, however, indicate the likelihood for a material to have good quality. The quality of the CNT material is taken as a material with high purity, structural integrity and homogeneity. The high purity of the CNT material can be assessed partly by obtaining a low value of $W_{res}$ in the TGA runs. Another way that TGA can contribute to the quality assessment of the material is to compare the structural integrity between runs. While a CNT material could have a high degree of purity, it could have enough damage to its chemical structure that its physical properties can be altered. Defects[7], such as Stone-Wales defects[8][9][10], or severe oxidative damage in the form of vacancies or $sp^3$ hybridization, can destroy the structural integrity. The structural integrity can be evaluated by the primary $T_{ox}$ in the TGA. A good-quality CNT material should possess a low level of variation in the $W_{res}$, constituency and $T_{ox}$ values.

# Annex B
(informative)

# Effects of operating parameters on TGA analysis

## B.1 General

In this annex, the influence of operating parameters on TGA results is briefly explained, the effects of heating rate and sample compaction are presented, and a technical explanation of combustion is provided. For more in-depth information, refer to the relevant part of Reference [35].

## B.2 Influence of heating rate

TGA experiments were done with the following heating rates: 1 °C/min, 2,5 °C/min, 5 °C/min, 10 °C/min, 30 °C/min, and 100 °C /min. Figure B.1 shows that the mean value of $T_{ox}$ increases gradually from 360 °C to 430 °C as the heating rate increases from 1 °C/min to 30 °C/min. The origin of such a significant change in $T_{ox}$ (70 °C) is attributed to the kinetics of the oxidation reaction. Experimentally the change may be influenced by the limited rate of heat conduction into the sample under the high heating rate such as 100 °C/min. It is difficult to reliably determine $T_{ox}$ (and its standard deviation) for the experiment with a 100 °C/min heating rate due to the very broad transition with several peaks that are not reproducible.

The value of $W_{res}$ and its standard deviation are also dependent on the heating rate. Figure B.2 shows that $W_{res}$ for 1 °C/min, 2,5 °C/min and 5 °C/min heating rates are well within one standard deviation (which is nearly constant), while above 5 °C/min $W_{res}$ becomes smaller and its standard deviation sharply increases. This observation can be explained by spontaneous combustion of the SWCNT materials above the heating rate of 5 °C/min (i.e. the heat released in the exothermic reaction is enough to sustain rapid burning of the sample). Therefore, it is important to collect TGA data with heating rates that do not allow combustion.

Selection of the heating rate is also of practical importance. Usually a sample has to be heated to at least 1 000 °C, which requires 13,3 h at a rate of 1 °C/min, compared to 8 min at 100 °C/min. Heating quickly saves time, so the majority of researchers have used 10 °C/min to 20 °C/min rates. Based on the discussion above, 5 °C/min has been selected as a compromise, as each run takes less than 3 h and combustion is avoided for most types of samples.