TECHNICAL SPECIFICATION

ISO/TS 11308

First edition
2011-11-15

Nanotechnologies — Characterization of single-wall carbon nanotubes using thermogravimetric analysis

Nanotechnologies — Caractérisation des nanotubes en carbone monofeuillet par analyse thermogravimétrique

Reference number
ISO/TS 11308:2011(E)

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of document:

— an ISO Publicly Available Specification (ISO/PAS) represents an agreement between technical experts in an ISO working group and is accepted for publication if it is approved by more than 50 % of the members of the parent committee casting a vote;

— an ISO Technical Specification (ISO/TS) represents an agreement between the members of a technical committee and is accepted for publication if it is approved by 2/3 of the members of the committee casting a vote.

An ISO/PAS or ISO/TS is reviewed after three years in order to decide whether it will be confirmed for a further three years, revised to become an International Standard, or withdrawn. If the ISO/PAS or ISO/TS is confirmed, it is reviewed again after a further three years, at which time it must either be transformed into an International Standard or be withdrawn.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO/TS 11308 was prepared by Technical Committee ISO/TC 229, *Nanotechnologies*.

Introduction

Single-wall carbon nanotubes (SWCNTs) are an allotropic form of carbon which exhibit unique mechanical, thermal and electronic properties respective to the geometric structure[1][2][3][4][5]. SWCNTs can be synthesized by several different methods, including pulsed laser vaporization, arc discharge, high pressure disproportionation of carbon monoxide, and chemical vapor deposition[6][7][8]. These processes often yield a heterogeneous mixture of SWCNTs and impurities, requiring post-synthesis purification. Commonly observed impurities include other forms of carbon [e.g. fullerenes, amorphous carbon, graphitic carbon and multiwall carbon nanotubes (MWCNTs)], as well as residual metallic catalyst nanoparticles. Purification can be accomplished using gaseous, chemical and/or thermal oxidation processes[9][10][11][12].

Thermogravimetric analysis (TGA) is one of a number of techniques that can be used to assess impurity levels in as-produced and purified samples containing SWCNTs[14] to [22]. TGA measures changes in mass as a function of temperature and is widely used to assess reaction kinetics associated with structural decomposition, oxidation, corrosion, moisture adsorption/desorption, and gas evolution. By evaluating the reaction kinetics for a given sample, the relative fraction of different constituents present can be either quantitatively or qualitatively determined. For SWCNT-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 (a measure of the type or types of carbon present). However, TGA alone cannot conclusively quantify the relative fractions of carbonaceous products within the material. Therefore, the information obtained from TGA is used to supplement information gathered from other analytical techniques in order to achieve an overall purity and quality assessment of a SWCNT-containing sample.

Additional uses of TGA include process and quality control[23] and the characterization of MWCNTs[24][25][26][27][28] and few-walled carbon nanotubes[29].

Nanotechnologies — Characterization of single-wall carbon nanotubes using thermogravimetric analysis

1 Scope

This Technical Specification provides guidelines for the characterization of SWCNT-containing samples by the use of TGA, performed in an air environment. Guidance is provided on purity assessment of SWCNT samples through a quantitative measure of the non-carbon impurity (i.e. metal catalyst) level within the material.

In addition, this technique can provide a qualitative assessment of the thermal stability and homogeneity of the SWCNT-containing sample. Additional characterization techniques are required to confirm the presence of SWCNTs and to verify the composition of the metallic impurities present.

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 and definitions

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

3.1
primary oxidation temperature
temperature at which the most intense peak occurs in the derivative thermogravimetric curve

3.2
thermal stability
temperature at which the major carbon component oxidizes in an air (i.e. oxygen-containing) environment, represented by the primary oxidation temperature

3.3
homogeneity
measure of how uniformly distributed all constituents (nanotubes as well as impurities) of SWCNT material are throughout a larger sample, as determined by measuring repeated smaller samples using TGA

3.4
constituents
different components present in a SWCNT-containing sample

NOTE A SWCNT-containing sample is often comprised of different carbon and non-carbon materials and is identified by oxidation peaks in the TGA curve and by residual weight.

3.5
monotypic
material consisting of only one type of carbon nanomaterial

NOTE A typical SWCNT sample is comprised of several types of carbon nanomaterials, including amorphous carbon, fullerenes, SWCNTs and MWCNTs.

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

NOTE TGA 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 (i.e. metal catalyst) impurities, which is one measure of purity.

3.7
quality
measure of the overall degree of excellence of SWCNT material, established by the level of impurities and the level of structural imperfections or defects to the crystal structure (structural integrity)

NOTE 1 TGA can partly contribute to the quality assessment of SWCNT material by providing its residual weight and oxidation temperature.

NOTE 2 A SWCNT 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 SWCNT material.

4 Abbreviated terms

TGA thermogravimetric analysis

TGC thermogravimetric curve (sometimes known as weight loss curve)

DTGC derivative thermogravimetric curve (sometimes known as derivative weight loss curve)

T_{ox} oxidation temperature

$T_{ox'}$ primary oxidation temperature

W_{res} residual weight of sample after heating

DTA differential thermal analysis

DSC differential scanning calorimetry

CVD chemical vapor deposition

HiPco high pressure CO conversion

5 Principles of TGA

5.1 Measurement

When a SWCNT-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 is comprised of non-volatile materials, which for the most part are metal impurities.

In principle TGA measures the weight loss of a material as a function of temperature as it is heated. TGA requires the precise measurements of weight, temperature and temperature change. The weight loss of a material is related to the composition of the material. Weight loss relative to an increase in temperature can result from the removal of absorbed moisture, solvent residues, chemically bound moieties and/or decomposition of product.

TGA alone cannot identify the volatile materials; however, if other analytical equipment such as a mass spectrometer or infrared spectrometer is employed, such information can be obtained. With respect to SWCNT materials, TGA cannot by itself identify the different carbon forms present within the material. However, it can provide a quantitative measure of the non-volatile products and the temperature at which the carbon species oxidize.

5.2 Exothermic and endothermic reactions

Many materials can undergo transitions in which heat is absorbed or given off without a change in weight. Such events will result in differences in temperature between the sample and a reference. Many TGA systems are equipped to operate in a DTA or DSC mode, which can provide information on these transitions. SWCNT-containing samples of particular morphologies have been observed to undergo combustive reactions resulting in rapid burning of material, which may be catalyzed by residual metals.

6 Sampling

6.1 Sample pan selection

Sample pan size and type will vary depending on the type of instrument being used. Other than equipment limitations, there is no restriction on the sample pan size so long as it is capable of accommodating the required amount of SWCNT material. Larger pan sizes can accommodate SWCNT without need for compaction, which is desirable but might not be accessible for all instruments. Either aluminium or platinum pans can be used under the experimental temperature range. Aluminium pans are recommended since they are less likely to catalytically oxidize SWCNTs, which can lead to erroneous data. It is recommended that the pans be conditioned by prior heating to at least 1 000 °C in an air environment in order to prevent errors due to oxidation of the pan material during sample analysis.

6.2 Sample size

The type of SWCNTs (as-produced versus purified) is the controlling factor in the selection of sample size. As-produced materials can be more difficult to accommodate in TGA pans because of their lower apparent density, whereas purified materials are denser due to compaction associated with the purification processes. If the sample is too fluffy for the TGA pan, slight compacting with a spatula may be used to fill the pan with 3 mg of sample.

See 6.3 for more information on sample compaction. Further details on sampling can be found in Reference[30].

The following are requirements for sampling:

a) use a minimum of 3 mg;

b) weigh samples at ambient temperature on a microbalance.

6.3 Sample compaction

Sample compaction using a press is a common method of sample preparation for TGA and DSC measurements. 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 (commonly used for preparation of samples for infrared spectroscopy) can influence the oxidation temperatures while having no influence on the residual mass values. Details of necessary provisions concerning compaction are described in B.3.

The following rules regarding compaction apply:

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

b) slight compaction by low pressure pressing with a spatula is acceptable.

7 Test method

Performing the following procedure is the minimum requirement for obtaining TGA data which will allow reliable characterization of SWCNT materials.

a) Prior to TGA measurement, calibrate the TGA instrument for temperature and mass according to the manufacturer's instructions. The separate microbalance should also be calibrated for mass according to the manufacturer's instructions.

b) Measure out an appropriate amount of SWCNT material. First tare an empty sample pan on both the TGA balance and a microbalance at room temperature. Weigh and record a minimum of 3 mg of SWCNT material on the microbalance. Transfer the material to the TGA balance and record the mass after closing the furnace. Tare and sample weights shall be recorded with air flowing through the instrument.

NOTE By locating the microbalance close to the TGA instrument, loss of material during transfer can be minimized.

c) Set the temperature range of the TGA scan from room temperature to 900 °C.

NOTE The maximum temperature of 900 °C is to ensure the complete combustion of all carbon materials in the sample, as MWCNTs and graphitic carbon can oxidize above 800 °C.

d) Set the temperature ramp for the TGA scan at a continuous rate of 5 °C/min up to the maximum temperature of 900 °C.

NOTE The heating rate can have a pronounced effect on the measured values of the oxidation temperature and residual weight as well as their standard deviations. This ramp rate of 5 °C/min has been observed to produce consistent and reliable measurements in addition to a reasonable experiment duration. See Annex B for more details.

e) Set the air flow rate into the furnace at $1{,}67 \times 10^{-3}$ l/s (100 ml/min or 100 sccm).

NOTE 1 The conventional terminology for TGA flow rate is the standard cubic centimeter per minute (sccm) which is equivalent to 1 ml/min.

NOTE 2 This is the recommended flow rate but it can be changed according to the best rate in relation to the instrument structure. The most important consideration is that the flow rate provides an optimal burn rate while reducing any buoyancy effects.

f) Run TGA scans for a minimum of three separate samples.

NOTE While a larger data set will minimize scatter in data points, three runs will still produce reliable data in an affordable time.

g) Record the residual weight (W_{res}) value for each scan at room temperature, as determined on both the TGA apparatus and independently on a microbalance after completion of the TGA run.

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. Additional details on determining the oxidation temperature can be found in Annex A.

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 SWCNT materials.

8.2 Non-carbon content

The non-carbon content of the SWCNT-containing sample is assessed through the W_{res} values. These values are acquired from both the TGA data and a microbalance. From the TG curve, W_{res} is recorded as the mass at 800 °C. This value is compared to the microbalance weight to make assessment on any variance in measurements, which might be due to buoyancy effects caused by air flow. The W_{res} can be expressed as either the actual weight or as a percentage of the original weight that remains. For the determination of non-carbon content, the W_{res} will be expressed as a percentage weight. The W_{res} shall be reported as the mean value together with the standard deviation from at least three TGA measurements.

NOTE The determination of non-carbon content from the W_{res} may be inaccurate as some components oxidize, resulting in either a decrease or increase in weight. It will, however, still provide a good approximation to the overall non-carbon impurity contribution to the SWCNT material (see A.2.2).

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

8.3 Constituents

SWCNT-containing samples can be comprised of multiple constituents, including different forms of carbon such as fullerenes, amorphous carbon and MWCNTs. The presence of multiple constituents can be qualitatively determined from TGA data by determining the number of oxidation peaks present in the DTG curve[32]. While it is difficult to assign any particular carbon form to a specific oxidation peak, it is commonly agreed upon that multiple peaks arise due to presence of different carbon types (see A.3).

NOTE TGA has also been used to distinguish between SWCNTs, double-wall carbon nanotubes and MWCNTs, where each sample was relatively pristine[33].

8.4 Thermal stability

The thermal stability of a sample of SWCNT material is the temperature at which the highest fraction of carbon content oxidizes and is established by the primary T_{ox} (see A.4). The thermal stability is the mean value of the primary T_{ox} values of at least three TGA runs, together with the standard deviation. If the primary T_{ox} has a large inconsistency or scatter between different TGA runs it shall be labelled “not definable”.

8.5 Homogeneity

The homogeneity of SWCNT 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). A material is considered homogeneous only if all the following conditions are met.

The TGA data from multiple runs:

— shall produce the same set of oxidation peaks (same constituency),

— shall have a similar primary T_{ox} (thermal stability) from run to run,

— shall have T_{ox} and W_{res} values with a narrow standard deviation (see Annex A).

A material which meets all the above requirements is considered to have good homogeneity. If none of the above requirements is met, the material is described as having poor homogeneity. If at least one requirement is met, the material's homogeneity is labelled as “fair”.

8.6 Purity

The purity of SWCNT material is established by the mass fraction of SWCNTs within the material. TGA can only 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 shall be coupled with information from other techniques (see A.6).

8.7 Quality

As with purity assessment, the quality assessment by SWCNT is also limited by TGA. However, some of the material characteristics (such as purity and homogeneity) required to establish the quality can be identified by TGA.

A material which produces TGA data showing low W_{res} values and high homogeneity (reproducible TGA data from run to run) is indicative of a material of good quality relative to TGA. A material which meets none of these requirements is of poor quality relative to TGA. The actual quality can only be established by coupling information from other analytical techniques.

9 Uncertainties

Uncertainty can occur in the exact measurement of the non-carbon content present within an SWCNT 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_{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_{res} may be lower than the actual non-carbon content.

Finally, in TGA runs on clean nanotubes [minimal (less than 10 %) content of ash remaining after the completion of the TGA run], the W_{res} is sometimes negative, mainly because of low accuracy of the TGA balance. This can happen even after calibration of the instrument. The long-term stability of the instrument (over a run of more than 3 h) might be within 20 to 40 µg, which constitutes 1 to 2 % of an initial 3 mg sample.

10 Test report

It is recommended that the following data be collected and presented in a test report.

a) Sample information:

   1) lot number;

   2) manufacturer and production method used to synthesize SWCNT 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:

   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 both microbalance and TGA balance (run1:x mg, run2:y mg, run3:z mg);

   4) residual weight from individual TGA curves (run1:x %, run2:y %, run3:z %);

   5) calculation of the average residual weight with standard deviation (x % $\pm$ y %).

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 indefinable);

   3) homogeneity — good, fair or poor.

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 SWCNT 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

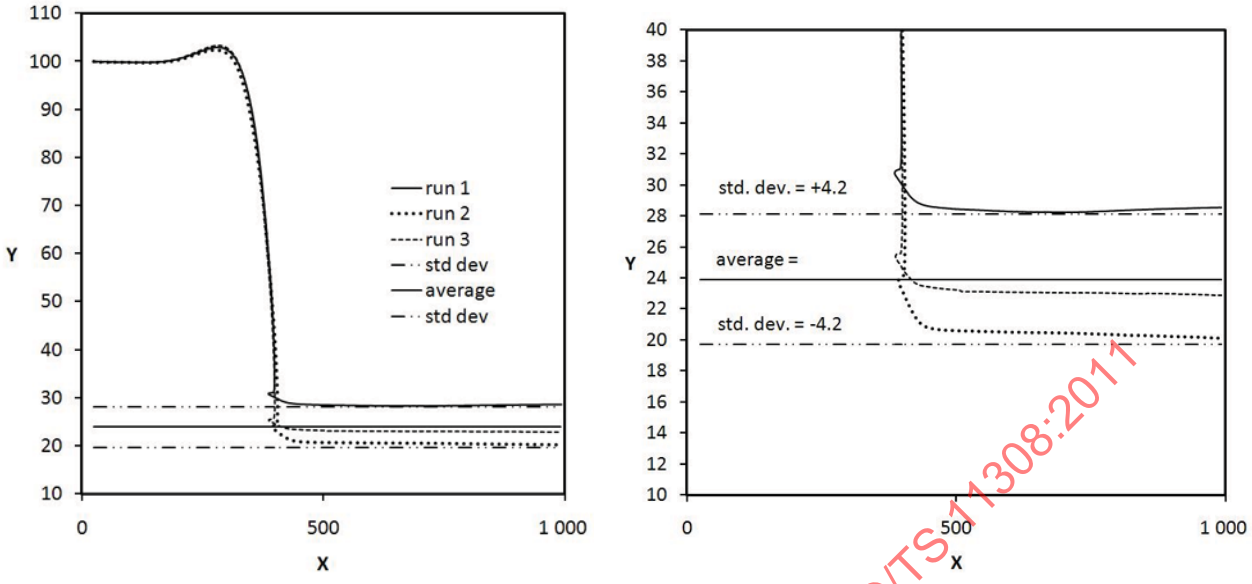
The non-carbon content is determined from weight measurements obtained from both the TGA apparatus and a microbalance before and after the run. The reason for this is to identify any possible sources of measurement error. Discrepancies may arise from buoyancy effects, thermal expansion of balance arms, loss of sample during transfer or moisture absorption of the sample. Furthermore, the long-term stability of the instrument zero (over a run of 3 h) is within 20 to 40 µg, which constitutes 1 to 2 % of the initial 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 Figure A.1). Similar calculations for the W_{res} as determined by the microbalance measurements are to be compared (Table A.1). Large differences should merit additional runs or re-calibration of the system.

Two factors which may influence the W_{res} determination are absorbed 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 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.2.2 Oxidation of non-carbon content

The non-carbon content consists primarily of metal catalyst used in SWCNT synthesis, which can itself become oxidized under the TGA run conditions, thus influencing 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.2). 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, this possible reactivity introduces some uncertainty in the true determination of the non-carbon content.



a) Actual TG curve

b) W_{res} average and standard deviations

Key

X Temperature (°C)

Y Percentage weight (%)

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

Figure A.1 — Weight loss curves for as-produced HiPco material

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

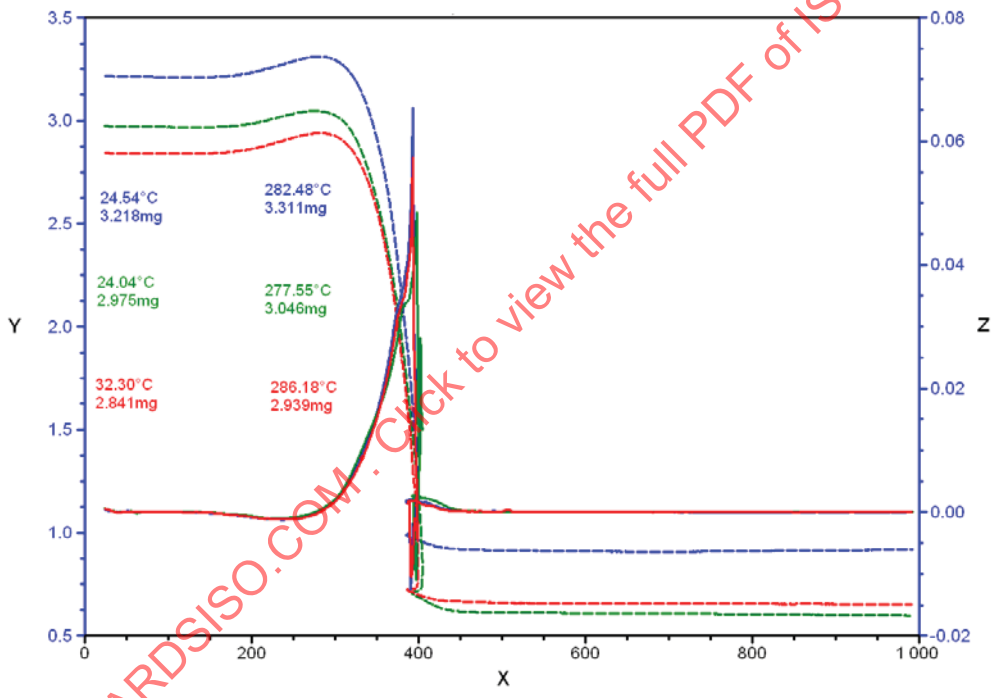
Weight in milligrams

	Run 1	Run 2	Run 3	Average	Standard deviation
Sample weight (microbalance)	3,09	3,20	3,00	—	—
Sample weight (TGA)	3,22	2,98	2,84	—	—
Residual weight (microbalance)	0,63	0,65	0,65	0,64	0,01
Residual weight (TGA at 1 000 °C)	0,91	0,60	0,65	0,72	0,17
Residual weight (TGA at room temperature)	0,90	0,59	0,61	0,70	0,17
Amount of oxygen uptake	0,09	0,07	0,10	—	—
Amount of H_2O desorption	—	—	—	—	—
% residual weight (microbalance-uncorrected)	20,36	20,32	21,73	20,80	0,80
% residual weight (TGA 1 000 °C-uncorrected)	28,22	20,22	23,01	23,82	4,06

A.3 Constituency

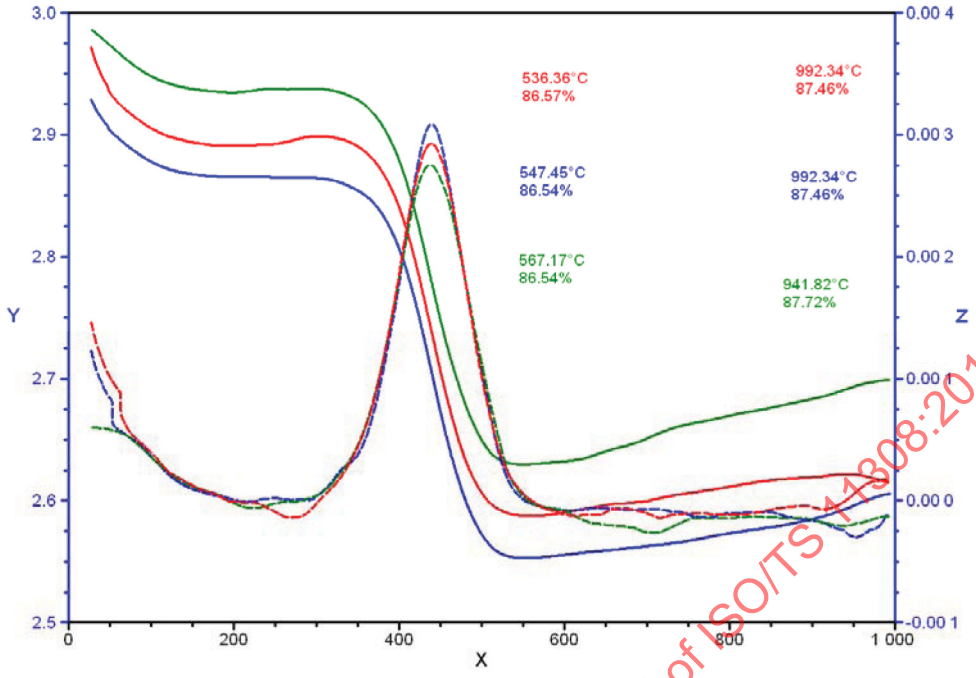
The constituency of a SWCNT material is described as arising from the different carbon forms present within the material, as is observed in TGA by multiple peaks in the DTG curve (see Figure A.4). The presence of multiple peaks in the DTG curve represents a material with higher constituency. While it 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 SWCNTs[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 SWCNT materials that exhibit combustive behaviour, which are marked in TGA by an abrupt steep drop-off in the DTG curve as well as a backwards trace in the TG curve (see Figure B.3). This behaviour is more often observed in unpurified SWCNT 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.



a) **Before carbon decomposition**

Figure A.2 (*continued*)



b) After carbon decomposition

Key

X Temperature (°C)

Y Percentage weight (%)

Z Derivative weight (mg/°C)

Figure A.2 — Oxidation of non-carbon content before (top figure) and after (bottom figure) carbon decomposition

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.5) or is inconsistent in assignment (see Figure A.6) then the thermal stability cannot be defined.

A.5 Homogeneity

A.5.1 General

In this clause, several examples will be 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.3 to A.6.

A.5.2 Variation in non-carbon content

The homogeneity of a batch of SWCNT material is in part established by the uniform distribution of non-carbon contents throughout the batch. If there is a large difference in the non-carbon concentration from run to run there will be large scatter of the W_{res} values. This in turn will result in W_{res} values which lie outside the acceptable standard deviation range (Figure A.3). In this case the material will not be considered homogeneous. On the other hand, if the W_{res} values lie within the acceptable standard deviation range, the material may be considered homogeneous with respect to the non-carbon content.

A.5.3 Variation in the constituency

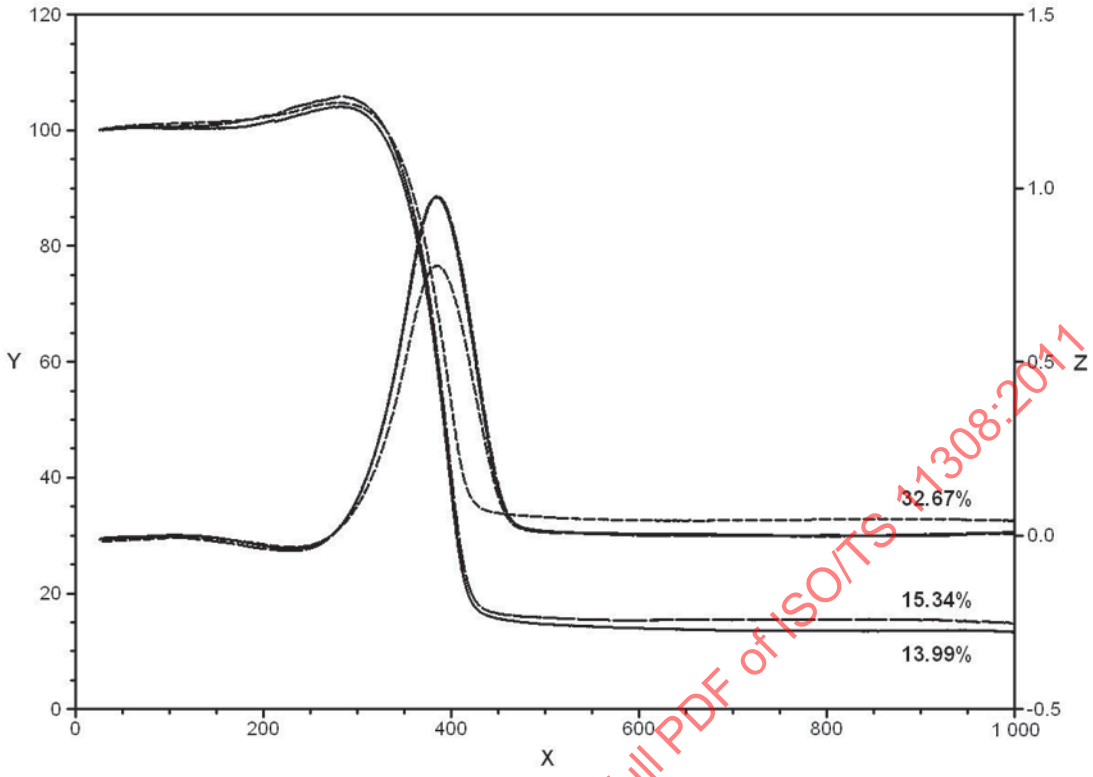
Constituency is another parameter which helps define the homogeneity as assessed through TGA. Uniform constituency from run to run is a trait of a homogeneous material. If the concentration of different carbon contents varies among the samples in the same batch, the relative intensities of the oxidation 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 intensity of the oxidation of peaks present (Figure A.4) or if the primary oxidation temperature shifts (Figure A.6) from run to run, 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 (Figure A.5).

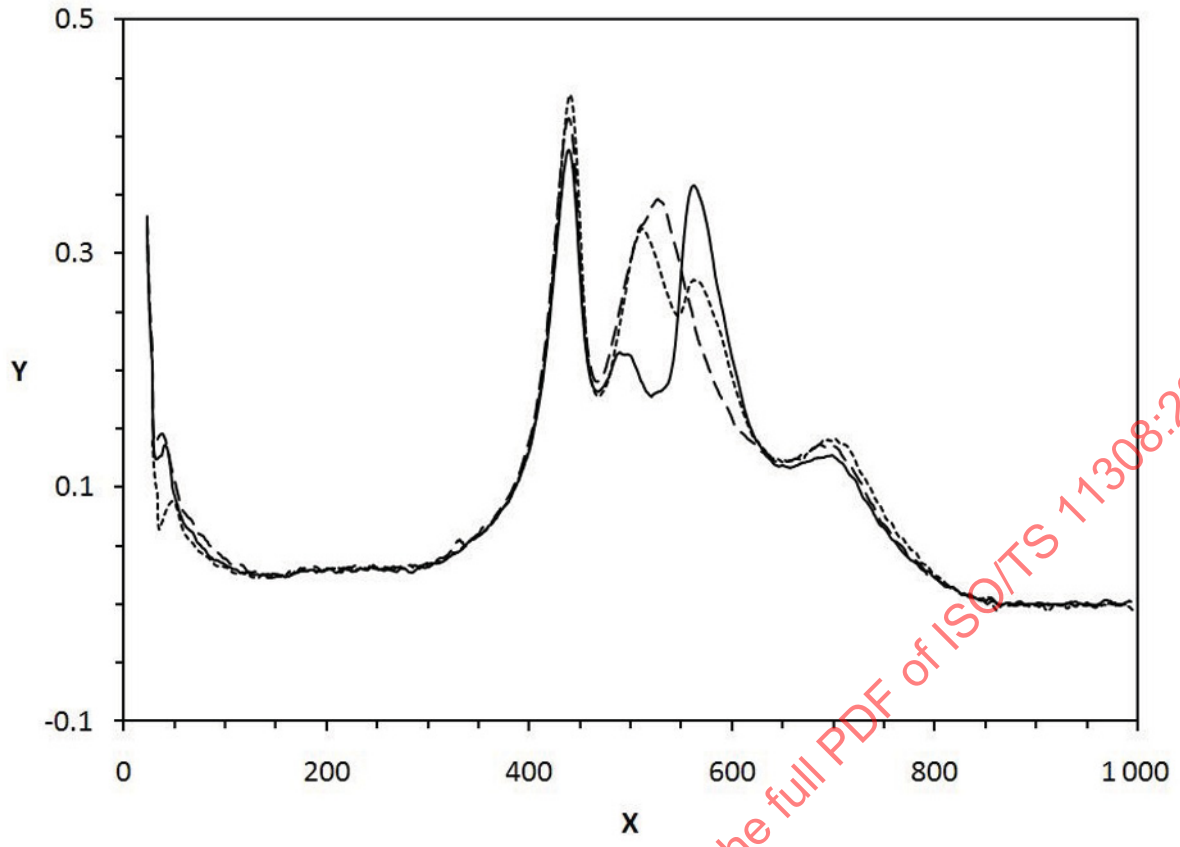
NOTE The heating rate directly influences the kinetics of oxidation (see B.2). Therefore the heating rate is chosen as the basis to discount any lag in the oxidation process due to variation in the activation energy, thermal conduction through the material in proper air flow or inaccuracy in the thermocouple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



Key

X Temperature (°C)
Y Percentage weight (%)
Z Derivative weight (mg/°C)

Figure A.3 — Material with well-defined constituency and thermal stability but large deviation in the residual weight value resulting in low homogeneity

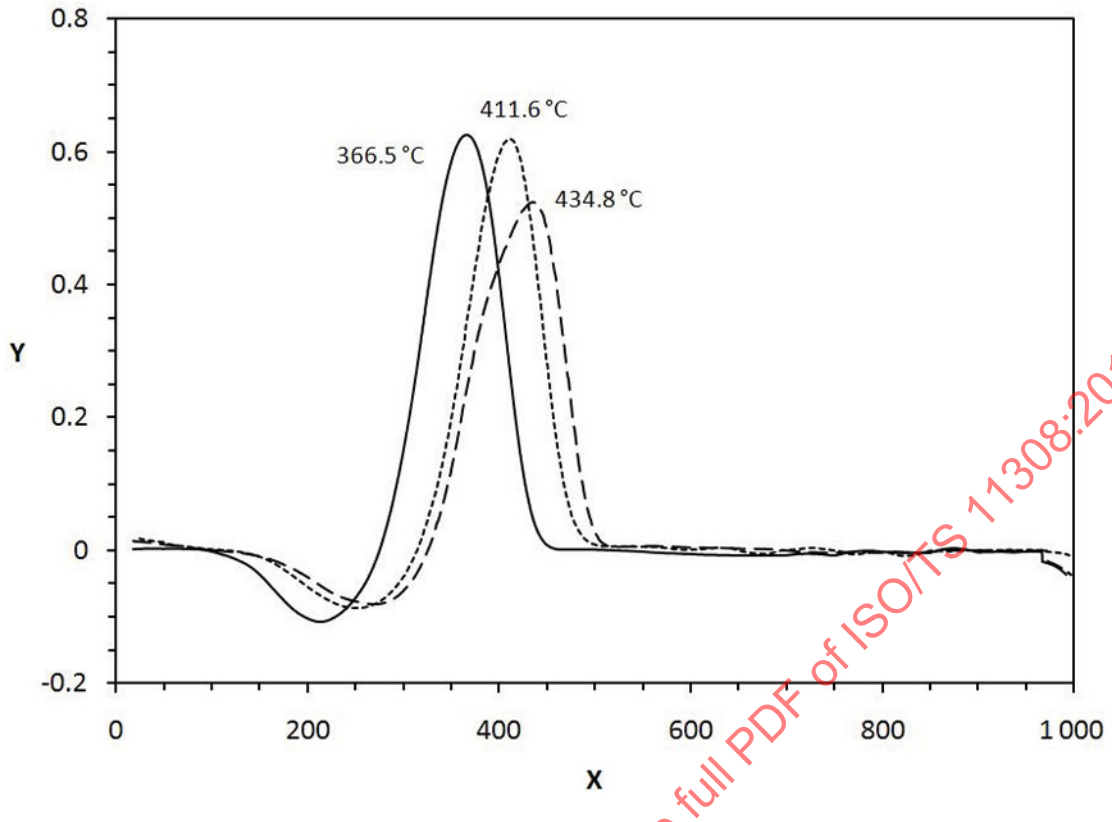


Key

X Temperature (°C)

Y Derivative weight (mg/°C)

Figure A.4 — Material with low homogeneity as a result of variable constituency

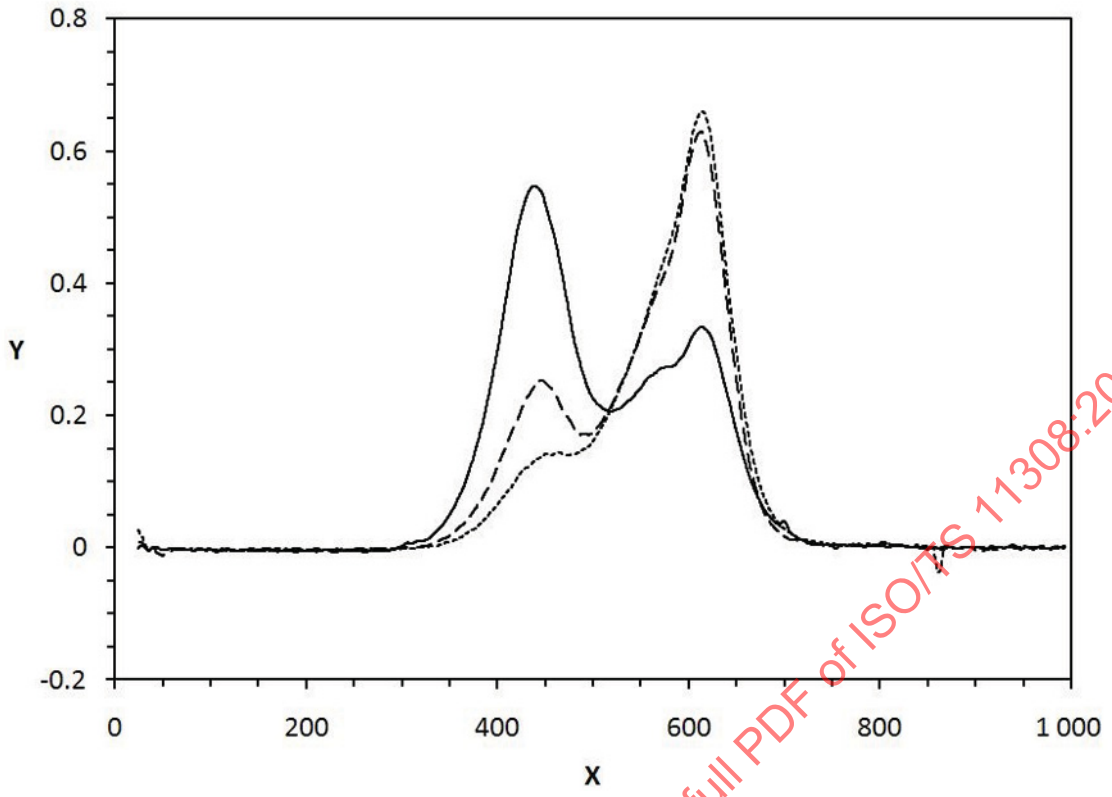


Key

X Temperature (°C)

Y Derivative weight (mg/°C)

Figure A.5 — Material with essentially one constituent but large scatter in primary oxidation temperature resulting in an undefined primary oxidation and low homogeneity



Key

X Temperature (°C)

Y Derivative weight (mg/°C)

Figure A.6 — Material with variable constituency and thermal stability

A.6 Purity assessment

TGA by itself is unable to provide a measure of the overall purity of SWCNT material since it is limited in the information relative to the types of impurities which can be found in SWCNT material. TGA can only provide one piece of the puzzle regarding impurity levels with the SWCNT: the amount of non-carbon content through the W_{res} values. Even if the oxidation temperature of pure SWCNTs were known and accepted, there are other carbon types which may have a similar oxidation temperature. TGA alone would not be able to distinguish these. 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 assessments

The quality of SWCNT material cannot be clearly defined through the use of TGA. TGA can, however, indicate the likelihood for a material having good quality. The quality of the SWCNT material is taken as a material with high purity, structural integrity and homogeneity. The high purity of the SWCNT material can be reached partly by lowering the W_{res} in the TGA run. While a SWCNT material may have a high degree of purity, it may 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. The good-quality SWCNT material should also possess the high level of homogeneity 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 are briefly explained, the effects of heating rate and sample compaction are presented and a technical explanation of combustion is also provided. For more in-depth information, refer to the relevant part of the NASA/NIST Practice Guide on Measurement Issues in Single Wall Carbon Nanotubes[34].

B.2 Influence of heating rate

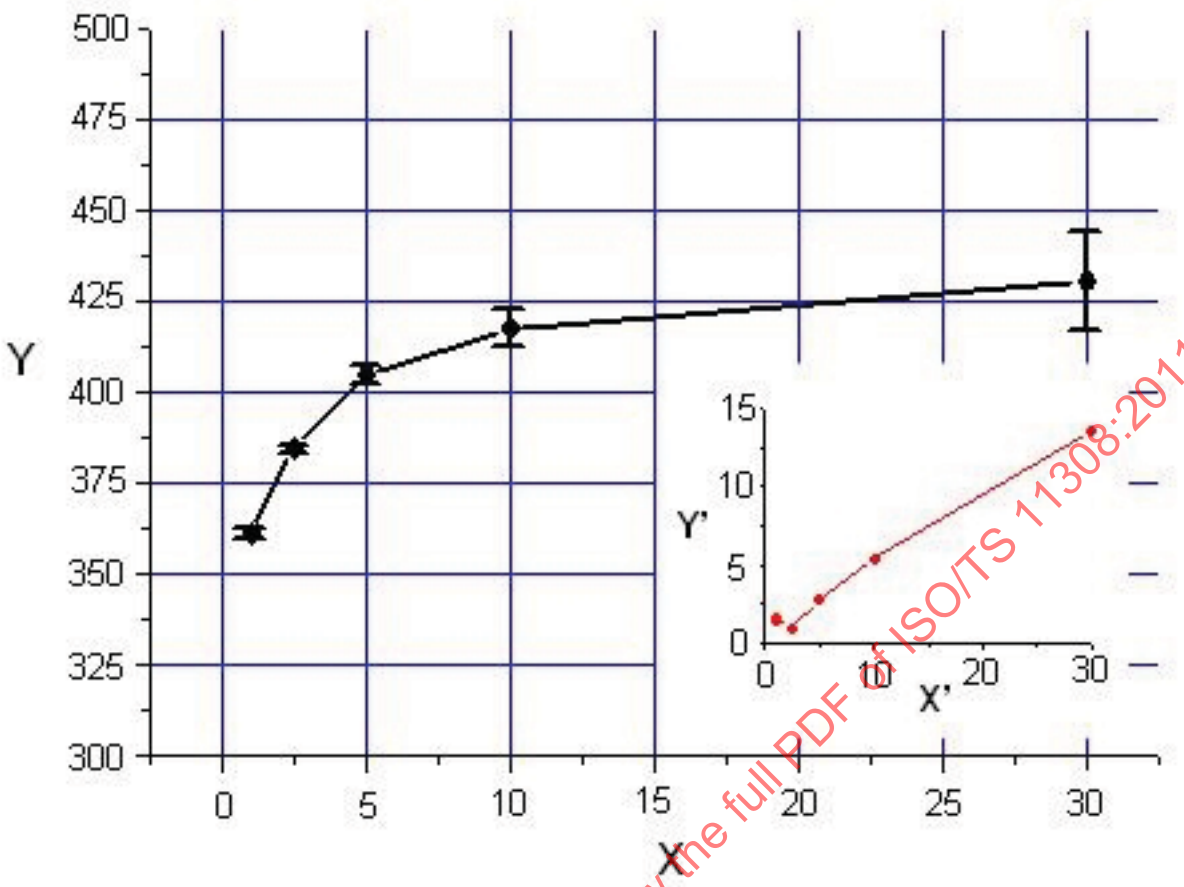
TGA experiments were done with the following heating rates: 1; 2,5; 5; 10; 30 and 100 °C/min, respectively. Figure B.1 shows that the mean value of T_{ox} increases gradually from 360 °C to 430 °C as the heating rate increases from 1 °C/min to 30 °C/min. The origin of such a significant change in T_{ox} (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, 2,5 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 fast saves time, so the majority of researchers have used 10 °C/min to 20 °C/min rates. Based on the discussion above, we have selected 5 °C/min as a compromise, as each run takes less than 3 h and we avoid combustion for most types of samples.

B.3 Sample compaction

TGA results of the “as-is” SWCNT material were compared with those of the material compacted in a standard KBr die by applying 2, 5 and 10 tons pressure in a hydraulic press. The values of W_{res} were essentially unaffected, while compacting at progressively higher pressure leads to a 10 °C to 20 °C decrease in the T_{ox} values. However, changes in T_{ox} do not follow a uniform trend. Compacting pressure does not affect the standard deviations of W_{res} and T_{ox}. The reason for this behaviour is not clear. It is concluded that it is better to avoid compaction, as results are difficult to predict.



Key

X Ramp rate (°C/min)
Y Oxidation temperature(°C)
X′ Ramp rate (°C/min)
Y′ Standard deviation of oxidation temperature

Figure B.1 — Heating rate dependence of oxidation temperature, T_{ox}, and its standard deviation σT_{ox} (inset)