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

Nanotechnologies — Caractérisation des nanotubes en carbone monofeuillet par analyse thermogravimétrique

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Foreword

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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.).