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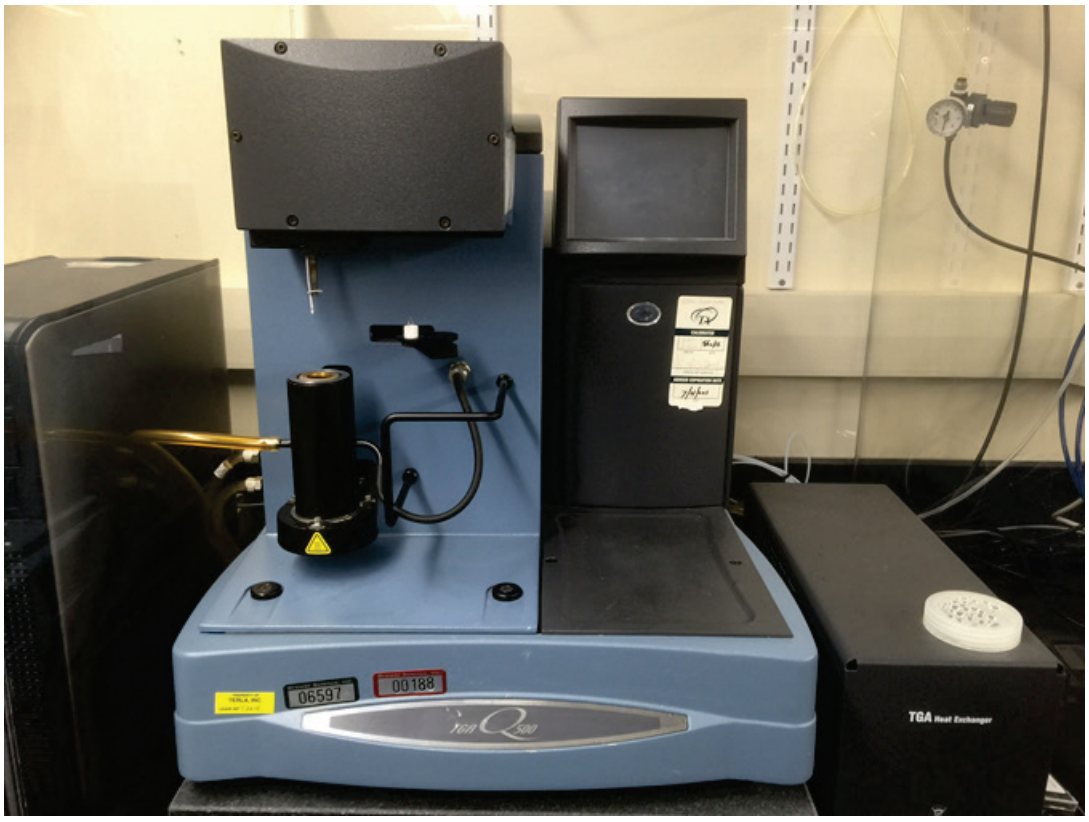
Environmental Consequences of Nanotechnologies

Characterization of Carbon Nanomaterials Using the Thermogravimetric Analyzer

Standard Operating Procedure Series: Characterization (C)

Qihua Wu, Kathryn Kremer, Yongqing Jiang, Stephen Gibbons,
and Alan J. Kennedy.

July 2018



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Abstract

Thermal stability and compositional analysis are important characterization for nanomaterials, especially for carbon-based nanomaterials. The general composition of carbon nanomaterials can be determined from the weight loss curve. Multiple decomposition peaks could indicate low purity or low quality of the carbon nanomaterials. The residual mass obtained after thermogravimetric analysis represents the metal content in the sample. In this standard operating procedure (SOP), thermogravimetric analysis (TGA) protocol was developed for characterization of nanomaterial thermal decomposition characteristics as well as metal catalyst content in carbon-based nanomaterials. Procedures and recommendations of sample preparation, instrument preparation, analysis, and results are included. This procedure was tested on a variety of carbon-based nanomaterials.

Contents

Preface

This standard operating procedure (SOP) was developed under Task 1: "Materials evaluation and characterization" of project "Advancing Carbon Nanomaterials-Based Device Manufacturing through Life Cycle Analysis, Risk Assessment and Mitigation." This program was funded by the Engineer Research and Development Center (ERDC) of the U.S. Army Corps of Engineers (USACE), contract number W912HZ-15·2-0032. This work was directed by Mr. Rishi J. Patel, Senior Research Scientist at Missouri State University's Jordan Valley Innovation Center. This task was under the direct supervision of Dr. Wu-Sheng Shih of Brewer Science, Inc. The technical monitor was Dr. Elizabeth Ferguson.

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The Commander of ERDC was COL Bryan S. Green and the Director was Dr. David W. Pittman.

Acronyms and Abbreviations

CNT	Carbon Nanotube
DoD	Department of Defense
EL	Environmental Laboratory
ERDC	Engineer Research and Development Center
ISO	International Organization for Standards
µg	microgram
µl	microliter
µ-TGA	microscale TGA
mg	milligram
ml	milliliter
M_{res}	Residual mass
MWCNT	multi-walled carbon nanotube
ng	nanogram
QA	Quality Assurance
QC	Quality Control
SOP	Standard Operating Procedure
SWCNT	single-walled carbon nanotube
T_o	Oxidation temperature
T_{onset}	Onset temperature
TS	Tuning Solution
TG	Thermogravimetry
TGA	Thermogravimetric Analysis
USACE	US Army Corps of Engineers
wt%	weight percentage

Unit Conversion Factors

Multiply	By	To Obtain
degrees Fahrenheit	(F-32)/1.8	degrees Celsius
pints (U.S. liquid)	0.473176	liters

1 Introduction

This standard operating procedure (SOP) describes how to determine the metal catalyst content and thermal decomposition characteristics of carbon-based nanomaterials using a thermogravimetric analysis (TGA) technique. The primary goal of this task was to develop a SOP for evaluating properties of nanomaterials and products incorporating nanomaterials. This SOP provides general guidance for testing carbon-based nanomaterials, including both solid materials and liquid materials.

1.1 Background

TGA is a thermal technique in which changes of material weights are measured as a function of increasing temperature (Coats and Redfern 1963). The weight changes represent changes in physical and/or chemical properties of the materials, such as decomposition, oxidation and volatilization. TGA is commonly used in the study of polymeric materials (International Organization for Standards [ISO] 1997).

TGA is one of the most straightforward techniques for characterization of nanomaterials, especially carbon-based nanomaterials. TGA typically requires no special sample preparation, other than drying of specimens. During the thermogravimetric analysis, samples are heated in a given atmosphere while the mass loss of the sample is monitored as temperature increases. Previously, TGA has been frequently reported as a reliable method for the evaluation of thermal stability, purity and composition of carbon nanomaterials (Mansfield et al. 2010; Freiman et al. 2008; Arepalli et al. 2004; ASTM E1131 2008).

For carbon-based nanomaterials, such as carbon nanotubes (CNT), TGA can be used to evaluate the percentage of amorphous carbon, metal catalyst content, and purity of samples (Freiman et al. 2008; Trigueiro et al. 2007; Dillon et al. 1999).

This TGA test requires around 5 to 10 mg of sample, no special sample preparation is needed. During the TGA run, amorphous carbon in the sample decomposes between 200 and 400°C, which is lower than that for graphitic structured carbons (i.e., graphene, graphite, carbon nanofibers, single-walled carbon nanotube [SWCNT] and multi-walled carbon

nanotube [MWCNT]). Thus, the amount of amorphous carbon in the sample can be quantified from the decomposition curve (Trigueiro et al. 2007; Murakami et al. 2003). For SWCNTs, the oxidation temperature is normally below 600°C, however, some MWCNTs have higher oxidation temperatures (Murakami et al. 2003). The residual mass after 700°C is considered as metal catalysts and oxidation products of the metal catalysts (Rinzler et al. 1998; Bahr and Tour 2002; Hennrich et al. 2003). This information can be used to (1) determine the effectiveness of the purification process of CNTs, (2) monitor the changes in the manufacturing of CNTs, and (3) characterize manufactured CNTs for quality control (QC). As an example, Mansfield, et al. (2014), utilized TGA for (1) comparison of nanoparticle materials produced by different manufacturing processes, (2) identifying variability within a single batch, and (3) determining variability from batch to batch. Their results suggested that TGA is sufficiently sensitive to enable QC at both micro-scale and nano-scale structures (SWCNT to MWCNT). Recently μ-TGA, with the capability of detecting mass change of less than one nanogram, has been introduced for the characterization of nanomaterials (Mansfield, et al. 2014). This greatly improves the sensitivity of conventional TGA.

1.2 Objective

The objective of this SOP is to define the operating procedure for characterizing thermal stability and metal content of carbon-based nanomaterial samples by using TGA.

1.3 Scope

Thermal stability and metal catalyst content are good measures of overall quality of carbon-based nanomaterials. This procedure applies to most carbon-based nanomaterials including raw materials, intermediates, final products, and experimental samples. Based on the properties of samples, sample pretreatment may apply. The operation procedure of TA Instruments Q500 TGA is included as an example.

2 Terminology

2.1 Related documents

- ASTM E1131 (2008): *Standard Test Method for Compositional Analysis for Thermogravimetry*.
- ASTM E1582-93 (2000): *Standard Practice for Calibration of Temperature Scale for Thermogravimetry*.
- ASTM E2040-08 (2014) *Standard Test Method for Mass Scale Calibration of Thermogravimetric Analyzers*.
- ISO 11358 Plastics (1997): *Thermogravimetry (TG) of polymers – General Principles*.
- NIST SP 960-19 (2008): *Practice Guide: Measurement Issues in Single Wall Carbon Nanotubes*.
- Instrument operating manual provided by instrument manufacturer (e.g., TA Instruments Q500 operation manual).

2.2 Definitions

- Oxidation temperature (T_o): When samples are analyzed in reactive atmosphere (oxygen or air), the temperature of the maximum in the mass loss rate. The oxidation temperature indicates the temperature of the maximum rate of oxidation. It provides an indirect measure of the purity, structure and composition of nanomaterials.
- Onset temperature (T_{onset}): The temperature when weight loss begins. The onset temperature provides information on the material's decomposition in the experimental atmosphere.
- Residual mass (M_{res}), (also known as ash content): For nanomaterials, residual mass could be due to inorganic nanomaterials, residual metal catalysts, or impurities.

3 Materials and Apparatus

3.1 Materials

- Nanomaterial samples (solid or liquid).
- Inert compressed gas, such as nitrogen or argon, with ≥99.99% purity.
- Reactive compressed gas, such as air or oxygen, with ≤1.0 µg/g water impurity and ≤1.0 µg/g hydrocarbon impurity.
- Weight calibration standard (according to ASTM E2040-08 [2014]).
- Temperature calibration standard (according to ASTM E1582-93 [2000]).
- TGA sample pans that are available from various suppliers (e.g., 500-µl ceramic sample pans).
- Tweezers used for handling TGA sample pans.

3.2 Apparatus

- Thermogravimetric analyzer: the TGA instrument is required to have a thermo-balance with accuracy of ± 0.1 µg and *tare* function, a furnace with the ability to control the heating rate in the temperature range of 25 to 1000°C, a temperature sensor with the accuracy of ±1°C, and repeatability of 0.2°C. (e.g., TA Instruments Q500 TGA).
- A purge gas system for both inert and reactive gas should have the capability of sustaining the furnace and specimen with a constant rate of approximately 10 to 100 ml/min, ± 5 ml/min.
- A balance with sensitivity of a minimum of 0.001 g for specimen preparation.

4 Procedure

4.1 Experiment preparation

4.1.1 Specimen preparation

Most specimens can be directly tested as is, with no sample preparation. Ensure the selected part of the sample is representative of the entire specimen. If the specimen needs to be pretreated (e.g., heat or mechanical treatment) prior to testing, record the treatment in the proper notebook.

4.1.2 Instrument preparation

4.1.2.1 Calibration

Check to determine if the instrument needs to be calibrated. Refer to the instrument operation manual or ASTM E2040-08 (2014) for weight calibration. Temperature calibration should be performed following the instrument operation manual or ASTM E1582-93 (2000).

4.1.2.2 Instrument parameters

Switch on the instrument power and open the control software. Ensure the instrument is functioning and that the inert and reactive gases are at desired flow rate and pressure. Select or setup the desired instrument parameters in the software. Suggested parameters are as follows:

Method: TGA protocol for nanomaterials in air

- Purge gas switch to nitrogen
- Equilibrate at 40.00°C
- Ramp at 20.00°C/min to 110.00°C
- Isothermal hold for 40.00 min at 110.00°C
- Switch purge gas to air (or oxygen)
- Ramp at 5.00°C/min to 800.00°C
- Isothermal hold for 30.00 min at 800.00°C

Method: TGA protocol for nanomaterials in nitrogen

- Purge gas switch to nitrogen
- Equilibrate at 40.00°C
- Ramp at 20.00°C/min to 110.00°C

- Isothermal hold for 40.00 min at 110.00°C
- Ramp at 5.00°C/min to 800.00°C
- Isothermal hold for 30.00 min at 800.00°C

4.2 Sample analysis

Sample analysis can be executed after proper method has been selected. This section describes the general operation procedure of TA Instruments Q500 TGA as an example. These instructions may apply to any TGA instrument with an auto-sample stage and control software.

4.2.1 Tare the balance

Place a clean sample pan on the sample platform of instrument using tweezers. Be sure to align the ridge along the bottom of the pan with the indent on the platform. Load the clean sample pan on the sample hang-down wire. Zero the mass signal and tare the balance. When the tare is completed, unload the empty sample pan.

4.2.2 Load sample

After the balance is tared, load the nanomaterial sample into the sample pan. The sample size is dependent on the instrument and the sample itself. For dry nanomaterials, a sample size of approximately 2 to 4 mg is recommended but can be more than 4 mg. For liquid samples, depending on the percentage of solid and sample pan size, the sample size can be as large as 100 mg.

After the sample is loaded, position the loaded sample pan onto the sample platform by using tweezers (after the sample pan has been removed to load the sample). Be sure to align the ridge along the bottom of the pan with the indent on the platform.

4.2.3 Start the experiment

Load the sample pan with loaded sample into the TGA, ensuring the operator name and data file name have been correctly added. Start the experiment, wait to be sure the sample pan loaded properly and the furnace temperature increased without any issues. After completion of the experiment, save the residual mass for further analysis (energy-dispersive X-ray spectroscopy, etc.)

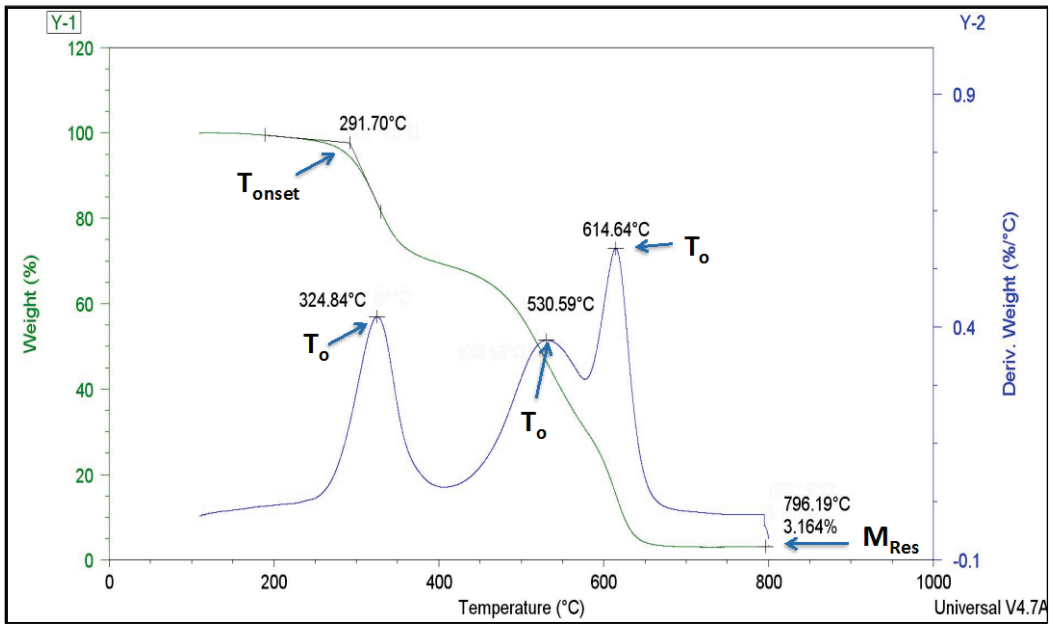
5 Reporting

5.1 Analysis of results

After the run is completed and data is recorded, raw data should be processed by the data analysis program (normally provided by the vendor). Open a raw data file using the analysis program. When a data file is opened, verify the data file information, including the sample name, sample size, method used and run time. An example of processed data file of nanomaterials is showed in Figure 1. The data file should be plotted with desired parameters for *X*-axis and *Y*-axis. Generally, it is recommended to use wt % for Y1 axis, derivative wt % for Y2 axis, and temperature for X-axis.

Once the data file is correctly plotted, data limits should to be selected prior to analysis. If a pre-isotherm step was utilized to remove extra solvents/moisture in samples, then data (both *X*- and *Y*-axis) during the pre-isotherm step should be excluded. After the desired data limits are set, measure onset temperatures by determining the temperature at which a change in the slope of the curve occurs. The onset point is defined as the intersection of an intimal tangent line with a final tangent line. The residue mass is measured at the end point where the weight loss stopped (Figure 1).

Figure 1. Example of processed TGA graph, with oxidation temperature (T_o), onset temperature (T_{onset}) and residual mass (M_{res}) are determined.



5.2 Key results provided

The most important results to report are: (1) oxidation temperature, which is a measure of the thermal stability of nanomaterials in air, and (2) residual mass, which is the amount of metal catalysts and metal impurities in the samples.

The report should also include the following information: (1) specimen information, including any pretreatment prior to analysis, and (2) description of the method used for sample analysis, including heating rate, temperature range, purge time, flow rate, sample size, sample pan type, and original thermal curve.

5.3 Quality Assurance/Quality Control (QA/QC) concerns

To ensure the quality of data, the instrument should be calibrated and NIST traceable standards should be measured routinely. Refer to the manufacturer's operation manual for calibration procedure. It is recommended to perform duplicated runs (approximately 2 to 3) for each sample and compare the difference in T_o, T_{onset} and M_{res}. Typically, the mean difference or standard deviation should be less than 5%.

6 Summary

This SOP describes the procedure of using TGA to characterize carbon-based nanomaterials on their thermal decomposition characteristics as well as metal catalyst content. It includes general procedures and recommendations of specimen preparation, instrument preparation, sample testing and results analysis. The operation procedure of TA Instruments Q500 TGA is included as an example. This SOP can be used as a guidance for testing thermal stability, impurities and other qualification factors of carbon-based nanomaterials and has been tested on a variety of carbon nanomaterial samples.

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14. ABSTRACT

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