IEC TS 62607-6-13

Edition 1.0 2020-07

TECHNICAL SPECIFICATION

colour inside

Nanomanufacturing – Key control characteristics –
Part 6-13: Graphene powder – Oxygen functional group content: Boehm titration method

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 6-13: Graphene powder – Oxygen functional group content: Boehm titration method

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- the subject is still under technical development or where, for any other reason, there is the future but no immediate possibility of an agreement on an International Standard.

Technical Specifications are subject to review within three years of publication to decide whether they can be transformed into International Standards.

IEC TS 62607-6-13, which is a Technical Specification, has been prepared by IEC technical committee 113: Nanotechnology for electrotechnical products and systems.

The text of this Technical Specification is based on the following documents:

Draft TS	Report on voting
113/455/DTS	113/486/RVDTS

Full information on the voting for the approval of this Technical Specification can be found in the report on voting indicated in the above table.

This document has been drafted in accordance with the ISO/IEC Directives, Part 2.

A list of all parts of the IEC 62607 series, published under the general title *Nanomanufacturing – Key control characteristics,* can be found on the IEC website.

The committee has decided that the contents of this document will remain unchanged until the stability date indicated on the IEC website under "http://webstore.iec.ch" in the data related to the specific document. At this date, the document will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

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INTRODUCTION

In recent years, graphene has attracted extensive attention from academia and industry, due to the extraordinary physical and chemical properties for promising applications in energy conversion and storage, electronics, composites and catalysis, etc. In the case of most graphene available in the laboratory or on the market, oxygen functional groups are inevitable, especially for the powder form products. These oxygen functionalities, which exist mainly in the form of carboxyl groups, lactones or lactols, phenolic hydroxyl groups, reactive carbonyl groups and epoxide groups, etc., are located on the surface or edge of the two-dimensional carbon lattice. They affect many crucial properties of graphene, including wettability, electrical and thermal conductivity, electron density, acidity and reactivity, etc. [1][2][3][4][1], and so determine the performance of graphene for downstream applications. For example, in an energy storage device such as lithium ion battery or supercapacitor, the oxygen heteroatoms will introduce irreversible reaction to exhaust the organic electrolyte and emit small molecules, which will reduce the cycling stability and even cause safety problems to the final products [5][6]. Besides, the oxygen functional groups will significantly decrease the electrical conductivity of graphene, which has a negative impact on the rate capacity of the cell, due to the increase of internal resistance for the electrode [7][8]. Furthermore, the different oxygen containing functional groups will play very different roles in affecting the properties of graphene. For example, in catalysis, graphene has been employed as an effective solid acid catalyst for hydrocarbon chemistry, as many oxygen functionalities show acidic properties [9][10][11]. However, the acidity strength of different oxygen species is distinct, as the acidity sequence is carboxyl, lactone, hydroxyl, and carbonyl. Besides, it is proved that ketonic carbonyl groups, with higher electron density, are the catalytic active sites for oxidative dehydrogenation reactions [12][13]. So, the type and proportion of oxygen groups will significantly influence the catalytic activity and selectivity of graphene. Therefore, the qualification of different oxygen functional groups on the surface of graphene is a key control characteristic for the production, application and trading of graphene and related products.

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The most common methods for identification and quantification of oxygen functional groups on graphene are FT-IR, XPS, EELS and Boehm titration. Moreover, other recent methods such as SAED, MS and FLOSS are springing up. However, some of these methods have difficulty quantifying oxygen functional groups on graphene, and there is no standard method to quantify the oxygen functional groups. Boehm titration, dating from 1962, is an efficient, repeatable and easy to operate method with low cost. More importantly, the Boehm titration method can provide absolute values of the surface concentration of oxygen functional groups and avoid the ambiguity and subjectivity brought by spectroscopies, which shows its unique advantage in quantification of many oxygen functional groups on graphene [14][15][16][17][18][19][20]. Note that Boehm titration cannot determine the total oxygen content of a powder, as it only measures those functional groups that can dissociate under the conditions of the test.

Boehm titration has been applied to determine the oxygen functional groups of many traditional carbonaceous materials for decades, such as activated carbon and carbon black. In recent years, it was applied to graphene [21][22]. Because the physical properties of graphene are very different from those of other carbonaceous materials, the operation-specific details in this document are suitable for powders of graphene oxide, reduced graphene oxide, graphene and related materials only. When applying Boehm titration to graphene dispersions, the dispersion medium needs to be removed. This document can be used as the reference for other carbonaceous materials.

This document focuses on the determination of oxygen functional groups and standardization of the operation method. Due to various steps such as agitation, end-point determination, etc. required in Boehm titration, significant measurement errors can be introduced if not properly addressed.

[1] Numbers in square brackets refer to the Bibliography.

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 6-13: Graphene powder – Oxygen functional group content: Boehm titration method

1 Scope

This part of IEC TS 62607 establishes a standardized method to determine the chemical key control characteristic

- oxygen functional group content

  on graphite oxide, graphene oxide, reduced graphene oxide and other types of functionalized graphene by

- Boehm titration method.

In this document, the measured functional groups are carboxyl groups (also in the form of their cyclic anhydrides), lactone groups, hydroxyl groups and reactive carbonyl groups. Oxygen functional groups that exhibit no reactivity such as epoxides cannot be measured.

The oxygen functional group content is derived by the difference between $NaHCO_3$, Na_2CO_3, NaOH and C_2H_5ONa consumption of dispersed graphene powders.

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- The oxygen functional group content determined according to this document is listed as key control characteristic in the blank detail specification for graphene IEC 62565-3-1.
- The method is applicable for graphene powder and graphene related carbon 2D materials such as graphene oxide powder and reduced graphene oxide powder, which can be separated from the water and ethanol by centrifugation or filtration. This document is not applicable for sulfonate modified graphene.
- In this document, the lower limits of detection (Annex C) for carboxyl groups, lactone groups, hydroxyl and carbonyl are 0,015 mmol/g, 0,037 mmol/g, 0,014 mmol/g, and 0,072 mmol/g, respectively.
- This document targets graphene manufacturers and downstream users to guide their material design, production and quality control.

2 Normative references

There are no normative references in this document.

3 Terms, definitions, symbols and abbreviated terms

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

3.1 Terms and definitions

3.1.1 General terms

3.1.1.1
blank detail specification
BDS
structured generic specification of the set of key control characteristics which are needed to describe a specific nano-enabled product without assigning specific values and/or attributes

Note 1 to entry The templates defined in a blank detail specification list the key control characteristics for the nano-enabled material or product without assigning specific values to it.

Note 2 to entry Examples of nano-enabled products are: nanomaterials, nanocomposites and nano-subassemblies.

Note 3 to entry Blank detail specifications are intended to be used by industrial users to prepare their detail specifications used in bilateral procurement contracts. A blank detail specification facilitates the comparison and benchmarking of different materials. Furthermore, a standardized format makes procurement more efficient and more error robust.

3.1.1.2
graphene
graphene layer
single-layer graphene
monolayer graphene
1LG
single layer of carbon atoms with each atom bound to three neighbours in a honeycomb structure

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Note 1 to entry It is an important building block of many carbon nano-objects.

Note 2 to entry As graphene is a single layer, it is also sometimes called monolayer graphene or single-layer graphene and abbreviated as 1LG to distinguish it from bilayer graphene (2LG) and few-layered graphene (FLG).

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Note 3 to entry Graphene has edges and can have defects and grain boundaries where the bonding is disrupted.

[SOURCE: ISO/TS 80004-13:2017 [23], 3.1.2.1]

3.1.1.3
graphene oxide
GO
chemically modified graphene prepared by oxidation and exfoliation of graphite

[SOURCE: ISO/TS 80004-13:2017, 3.1.2.13, modified – ", causing extensive oxidative modification of the basal plane" has been deleted from the end of the definition.]

3.1.1.4
reduced graphene oxide
rGO
reduced oxygen content form of graphene oxide

[SOURCE: ISO/TS 80004-13:2017, 3.1.2.14]

3.1.1.5
graphene nanoplate
nanoplate consisting of graphene layers

[SOURCE: ISO/TS 80004-13:2017, 3.1.2.11]

3.1.2 Key control characteristics measured according to this document

3.1.2.1
key control characteristic
KCC
key performance indicator
material property or intermediate product characteristic which can affect safety or compliance with regulations, fit, function, performance, quality, reliability or subsequent processing of the final product

Note 1 to entry The measurement of a key control characteristic is described in a standardized measurement procedure with known accuracy and precision.

Note 2 to entry It is possible to define more than one measurement method for a key control characteristic if the correlation of the results is well-defined and known.

Note 3 to entry In ISO TC 16949 (now IATF 16949) , the term "special characteristic" is used for a KCC. The term key control characteristic is preferred since it signals directly the relevance of the parameter for the quality of the final product.

3.1.2.2
functional group
atom, or a group of atoms that has similar chemical properties whenever it occurs in different compounds, which defines the characteristic physical and chemical properties of families of organic compounds

[SOURCE: IUPAC]

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3.1.2.3
oxygen functional group
functional group containing oxygen atom

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3.1.3 Terms related to the measurement method

3.1.3.1
Boehm titration method
method to identify and quantify the functional groups through neutralization between oxygen functional groups of different acidity and bases of different strength

Note 1 to entry Oxygen functional groups usually influence or determine the chemical and physical properties of organic compound.

Note 2 to entry: See [14] and [15].

3.2 Symbols and abbreviated terms

HDPE high-density polyethylene

ΔE differential of potential to titrant volume

RSD relative standard deviation

4 General

4.1 Measurement principle

Oxygen functional groups on graphene of different acidities can be neutralized by bases of different strengths (Figure 1). Sodium ethoxide (C_2H_5ONa) is the strongest base used here that can neutralize acids including carboxyl groups (also in the form of their cyclic anhydrides), lactone groups, hydroxyl groups and reactive carbonyl groups. Sodium hydroxide (NaOH) is the second strongest base that can neutralize carboxyl groups (also in the form of their cyclic anhydrides), lactone groups and hydroxyl groups. Sodium carbonate (Na_2CO_3) neutralizes lactone groups and carboxyl groups (also in the form of their cyclic anhydrides). And sodium bicarbonate ($NaHCO_3$) is the weakest base used here that neutralizes carboxyl groups (also in the form of their cyclic anhydrides) only. Therefore, the content of each type of oxygen functional group (mmol/g) can be determined from the difference between the normalized base consumptions η (mmol/g), which are derived by dividing total base consumption (mmol) by mass of reacting sample (g). For example, the difference between NaOH normalized consumption (η_{NaOH}) and Na_2CO_3 normalized consumption (η_{Na2CO3}) corresponds to the weakly acidic hydroxyl group content. These four kinds of functional group (Table 1) can be differentiated by neutralization with 0,05 mol/L solutions of $NaHCO_3$, Na_2CO_3, NaOH and 0,1 mol/L sodium ethoxide, respectively.

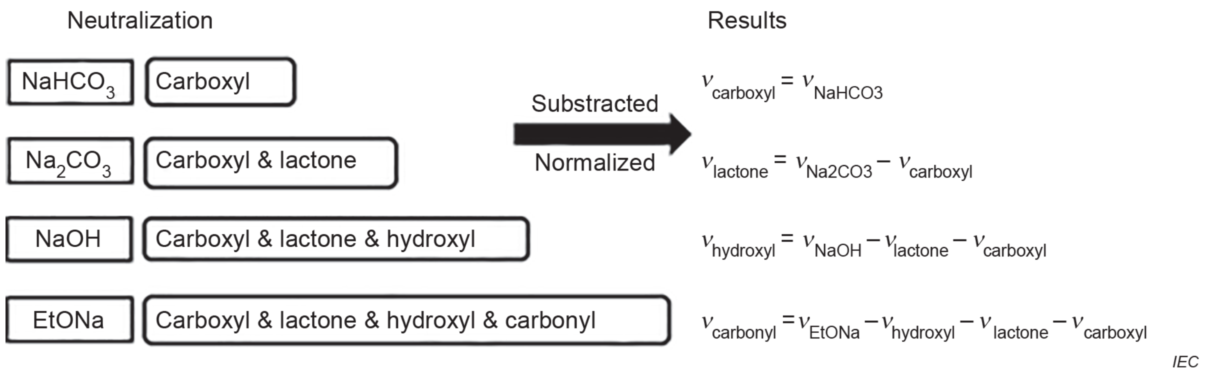

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Figure 1 – Test principle of Boehm titration

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Table 1 – Four types of oxygen functional group and their structures

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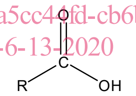
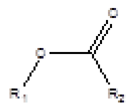
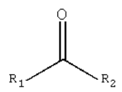
Terms	Structure
Carboxyl	
Lactone	
Hydroxyl	Ph—OH
Carbonyl	

4.2 Sample preparation method

All the test specimens need to be dried prior to testing to remove residual moisture. Keep graphene sample in a vacuum oven at (80 ± 5) °C until it is completely dry. Then cool it to room temperature and store in a desiccator for use.