IEC TS 62607-6-13

Edition 1.0 2020-07

TECHNICAL SPECIFICATION

colour
inside

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

IEC TS 62607-6-13:2020-07(en)

THIS PUBLICATION IS COPYRIGHT PROTECTED
Copyright © 2020 IEC, Geneva, Switzerland

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either IEC or IEC's member National Committee in the country of the requester. If you have any questions about IEC copyright or have an enquiry about obtaining additional rights to this publication, please contact the address below or your local IEC member National Committee for further information.

IEC Central Office
3, rue de Varembé
CH-1211 Geneva 20
Switzerland

Tel.: +41 22 919 02 11
info@iec.ch
www.iec.ch

About the IEC
The International Electrotechnical Commission (IEC) is the leading global organization that prepares and publishes International Standards for all electrical, electronic and related technologies.

About IEC publications
The technical content of IEC publications is kept under constant review by the IEC. Please make sure that you have the latest edition, a corrigendum or an amendment might have been published.

IEC publications search - webstore.iec.ch/advsearchform
The advanced search enables to find IEC publications by a variety of criteria (reference number, text, technical committee,…). It also gives information on projects, replaced and withdrawn publications.

IEC Just Published - webstore.iec.ch/justpublished
Stay up to date on all new IEC publications. Just Published details all new publications released. Available online and once a month by email.

IEC Customer Service Centre - webstore.iec.ch/csc
If you wish to give us your feedback on this publication or need further assistance, please contact the Customer Service Centre: sales@iec.ch.

Electropedia - www.electropedia.org
The world's leading online dictionary on electrotechnology, containing more than 22 000 terminological entries in English and French, with equivalent terms in 16 additional languages. Also known as the International Electrotechnical Vocabulary (IEV) online.

IEC Glossary - std.iec.ch/glossary
67 000 electrotechnical terminology entries in English and French extracted from the Terms and Definitions clause of IEC publications issued since 2002. Some entries have been collected from earlier publications of IEC TC 37, 77, 86 and CISPR.

IECNORM.COM : Click to view the full PDF of IEC TS 62607-6-13:2020

IEC TS 62607-6-13

Edition 1.0 2020-07

TECHNICAL SPECIFICATION

colour
inside

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

INTERNATIONAL
ELECTROTECHNICAL
COMMISSION

ICS 07.120 ISBN 978-2-8322-8726-2

CONTENTS

INTERNATIONAL ELECTROTECHNICAL COMMISSION

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

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

FOREWORD

1) The International Electrotechnical Commission (IEC) is a worldwide organization for standardization comprising all national electrotechnical committees (IEC National Committees). The object of IEC is to promote international co-operation on all questions concerning standardization in the electrical and electronic fields. To this end and in addition to other activities, IEC publishes International Standards, Technical Specifications, Technical Reports, Publicly Available Specifications (PAS) and Guides (hereafter referred to as "IEC Publication(s)"). Their preparation is entrusted to technical committees; any IEC National Committee interested in the subject dealt with may participate in this preparatory work. International, governmental and non-governmental organizations liaising with the IEC also participate in this preparation. IEC collaborates closely with the International Organization for Standardization (ISO) in accordance with conditions determined by agreement between the two organizations.

2) The formal decisions or agreements of IEC on technical matters express, as nearly as possible, an international consensus of opinion on the relevant subjects since each technical committee has representation from all interested IEC National Committees.

3) IEC Publications have the form of recommendations for international use and are accepted by IEC National Committees in that sense. While all reasonable efforts are made to ensure that the technical content of IEC Publications is accurate, IEC cannot be held responsible for the way in which they are used or for any misinterpretation by any end user.

4) In order to promote international uniformity, IEC National Committees undertake to apply IEC Publications transparently to the maximum extent possible in their national and regional publications. Any divergence between any IEC Publication and the corresponding national or regional publication shall be clearly indicated in the latter.

5) IEC itself does not provide any attestation of conformity. Independent certification bodies provide conformity assessment services and, in some areas, access to IEC marks of conformity. IEC is not responsible for any services carried out by independent certification bodies.

6) All users should ensure that they have the latest edition of this publication.

7) No liability shall attach to IEC or its directors, employees, servants or agents including individual experts and members of its technical committees and IEC National Committees for any personal injury, property damage or other damage of any nature whatsoever, whether direct or indirect, or for costs (including legal fees) and expenses arising out of the publication, use of, or reliance upon, this IEC Publication or any other IEC Publications.

8) Attention is drawn to the Normative references cited in this publication. Use of the referenced publications is indispensable for the correct application of this publication.

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

The main task of IEC technical committees is to prepare International Standards. In exceptional circumstances, a technical committee may propose the publication of a Technical Specification when

- the required support cannot be obtained for the publication of an International Standard, despite repeated efforts, or
- 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.

IECNORM.COM : Click to view the full PDF of IEC TS 62607-6-13:2020

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.

The contents of the corrigendum of October 2020 have been included in this copy.

IMPORTANT – The 'colour inside' logo on the cover page of this publication indicates that it contains colours which are considered to be useful for the correct understanding of its contents. Users should therefore print this document using a colour printer.

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.

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-based material – 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

  for powder consisting of graphene-based material like 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.

- 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

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).

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]

3.1.1.6

graphene-based material

GBM

graphene material

grouping of carbon-based 2D materials that include one or more of graphene, bilayer graphene, few-layer graphene, graphene nanoplate, and functionalized variations thereof as well as graphene oxide and reduced graphene oxide.

Note 1 to entry: "Graphene material" is a short name for graphene-based material.

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]

3.1.2.3

oxygen functional group

functional group containing oxygen atom

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.

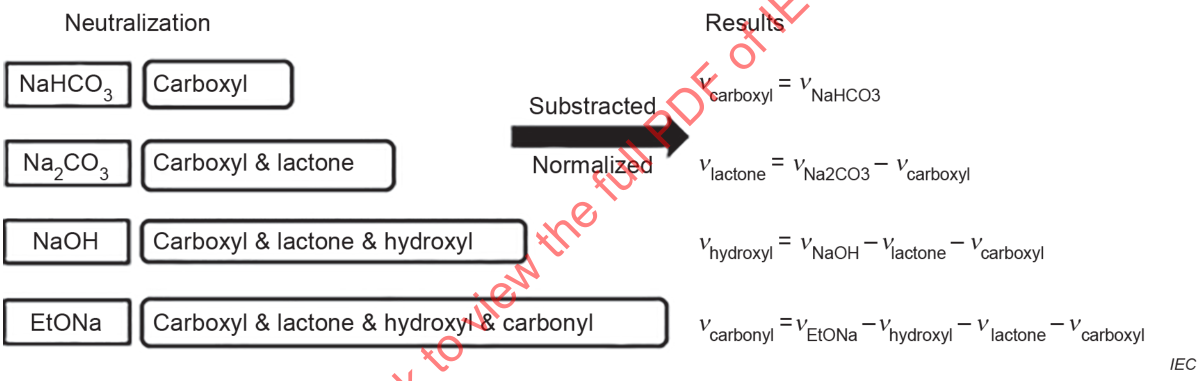
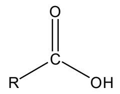
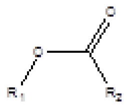
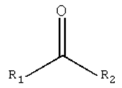


Figure 1 – Test principle of Boehm titration

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

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.

4.3 Description of measurement equipment / apparatus

4.3.1 Analytical balance, readability is 0,1 mg.

4.3.2 Electric thermostatic drying oven

4.3.3 Numerical control magnetic agitator/oscillator

4.3.4 Automatic potentiometer, with pH electrode and accurate to 0,1 mV.

4.3.5 HDPE bottles, the volume are 1 000 mL and 100 mL, with stopper.

4.4 Supporting materials

All reagents are listed in Table 2.[24][25][26]

Table 2 – Reagents used in this document

Item no.	Reagent name	Chemical formula	Purity, mass fraction %	Relative molecular mass g/mol	Source
1	Water	H_2O	Grade 2	18,02	ISO 3696:1987
2	Ethanol	C_2H_5OH	99,80	46,07	ISO 6353-2:1983
3	Sodium hydroxide	NaOH	98,00	40,00	ISO 6353-2:1983
4	Sodium carbonate	Na_2CO_3	99,80	105,99	ISO 6353-2:1983
5	Sodium bicarbonate	$NaHCO_3$	99,50	84,01	ISO 6353-3:1987
6	Sodium ethoxide	C_2H_5ONa	99,50	68,05	ISO 6353-2:1983
7	Hydrochloric acid	HCl	35,00	36,46	ISO 6353-2:1983

CAUTION: Take the necessary safety precautions when handling these materials.

4.5 Ambient conditions during measurement

The measurements can be performed under regular laboratory conditions without precise temperature and humidity control.

5 Measurement procedure

5.1 Detailed protocol of the measurement procedure

5.1.1 Preparation of solutions

5.1.1.1 General

In the following, the amounts of reactants needed in order to obtain 1 L of test solution are listed. All reactants should be dissolved using safe procedures. For complete dissolution of the chemical compounds during solution preparations, the solutions should first be prepared with 500 mL of water contained in a 1 L volumetric flask unless specified otherwise. Then, gentle shaking should be applied until complete dissolution is achieved. Finally, water should be added to obtain a total volume of 1 L. Solutions are stored in a 1 L high-density polyethylene bottle. Solutions shall always be used within 4 h after preparation to ensure they are fresh.

5.1.1.2 $NaHCO_3$ solution: 0,05 mol/L (solution A)

4,20 g of $NaHCO_3$ will yield 1 L of 0,05 mol/L solution.

5.1.1.3 Na_2CO_3 solution: 0,05 mol/L (solution B)

5,35 g of Na_2CO_3 will yield 1 L of 0,05 mol/L solution.

5.1.1.4 NaOH solution: 0,05 mol/L (solution C)

Dissolve 150 g of NaOH with 100 mL water in a beaker, shake well and store it in a PTFE bottle until its supernatant becomes clear. Then 2,70 mL of the supernatant will yield 1 L of 0,05 mol/L solution.

5.1.1.5 C_2H_5ONa solution: 0,1 mol/L (solution D)

Dissolve 6,805 g of C_2H_5ONa in high-purity, anhydrous, absolute ethanol, and dilute to mark in a 1 000 mL volumetric flask and mix. Alternatively, purchase a certified solution and dilute it to 0,1 mol/L.

5.1.1.6 Titrant acid: 0,05 mol/L

Preparation: Fill a 1 L volumetric flask with about 500 mL of water. Then slowly dissolve 4,17 mL of 12 mol/L HCl stock solution in the water. Finally, add more water until a total volume of 1 000 mL of HCl solution is obtained. The resulting solution is then poured into the titration bottle of the automatic potentiometer.

Calibration: The calibration of the HCl solution is carried out using the dried working reagent Na_2CO_3 which has previously been air dried in electric thermostatic drying oven at (270–300) °C as the primary standard. Dissolve 0,05 g (maximum permissible error of 0,000 1 g) of Na_2CO_3 in 30 mL of water in a titration cell of the automatic potentiometer. The obtained Na_2CO_3 solution with exact amount is then titrated with the above-mentioned HCl solution using an automatic potentiometer. The titration's equivalence point occurs when ΔE is a maximum or where the second differential $\Delta' E$ is zero. At least one blank titration is required. The volume of titrant needed to reach the titration's second equivalence point is recorded as V_1 and V_0. Therefore, the concentration of the prepared HCl solution is

$$C = \frac{2 \times m \times 1000}{(V_1 - V_0)M}$$

where

C is the concentration of the HCl solution, in mol/L;

m is the mass of Na_2CO_3, in grams;

V_1 is the volume of HCl titration consumed for Na_2CO_3 solution, in millilitres;

V_0 is the volume of HCl titration consumed for blank titration, in millilitres;

M is the molar mass of Na_2CO_3, in g/mol, [M (Na_2CO_3) = 105,99]

Perform at least three individual titrations for the calibration of the HCl solution, and then calculate the arithmetical average value, precise to 0,000 01 mol/L. The above calibrated HCl solution is titrant acid.

Cconcentrations of titrant acid can be decreased to 0,025 mol/L if the content of oxygen functional groups of graphene is lower than 0,072 mmol/g, which is the lower limit for carbonyl. 2,30 mL of HCl will yield 1 L of 0,025 mol/L titrant acid.

5.1.2 Reactions between graphene and bases

a) Weigh four aliquot masses of 0,15 g to 0,5 g of dried sample into A1, B1, C1 and D1 HDPE bottles, respectively; record the mass of graphene sample to the nearest 0,000 1 g as m_1, m_2, m_3 and m_4. Then add 50,0 g of solution A into A1 HDPE bottle, add 50,0 g of solution B into B1 HDPE bottle, add 50,0 g of solution C into C1 HDPE bottle, and add 40,0 g of solution D into D1 HDPE bottle; record the exact mass of solutions A, B, C, and D to the nearest 0,000 1 g as m_A, m_B, m_C and m_D, respectively. For each bottle, seal with cap immediately after adding the solution and shake to mix the sample with the solution well. Then A1, B1, C1 and D1 mixtures are obtained.

NOTE 1: After mixing NaOH with sample, N_2 bubbling can be used for at least 20 minutes to remove CO_2. However, both scientific reports [20][27] and experiment results have proved that the effect of CO_2 on results is very limited and can be negligible (see Annex B for details). So, it can be easily determined without going through a pre-degassing process to remove the effect of atmospheric carbon dioxide (CO_2).

b) Solution blanks (no sample) of each base are also conducted, i.e. add 50,0 g of solution A into A0 HDPE bottle, add 50,0 g of solution into B0 HDPE bottle, add 50,0 g of solution C into C0 HDPE bottle, and add 40,0 g of solution D into D0 HDPE bottle. The A0–B0 blanks are obtained after sealing with a cap.

c) Sample blanks (no base solution) are meanwhile conducted in E HDPE bottles, i.e. mix 0,15 g to 0,5 g of graphene sample with 50,0 g of water and seal well with cap, record the precise mass of sample and water to the nearest 0,000 1 g as m_5 and m_E, respectively. E sample blank is obtained after mixing well.

d) All nine sealed HDPE bottles are shaken for at least 3 h at (25 ± 2) °C using an oscillator.

e) Quickly filtrate all water solution bottles (A0, A1, B0, B1, C0, C1, E). For each bottle, perform suction-filtration by means of a funnel with flat perforated plate using a filter paper to separate the sample and the solution. For each bottle, abandon the first 15 mL of filtrate, then without changing the filter paper or funnel, collect the remaining filtrate in another dry filter bottle. The collected filtrate shall be titrated immediately after collection.

f) Centrifuge all ethanol solution bottles (D0, D1) to remove the graphene sample. For each bottle, quickly transfer the solution into a 50 mL centrifuge tube and separate the sample by means of a centrifugal separator at 10 000 r/min for 10 min. The supernatant shall be titrated immediately after centrifugation.

NOTE 2 Before weighing sample into the HDPE bottle, both HDPE bottle and sample could be pretreated by an electrostatic eliminator to avoid the loss during sample transfer.

NOTE 3 The concentration of the first 15 mL filtrate is lower than that of bulk filtrate owing to absorption of the filter paper.

CAUTION: Take the necessary safety precautions when handling these materials.

5.1.3 Instrument preparation

Flush pipes of the automatic potentiometer at least three times before the titration experiment. Ensure that gas bubbles in the automatic potentiometer pipes are expelled completely.

5.1.4 Titration of the filtrate

a) Weigh 10,0 g of the above collected A0 filtrate, A1 filtrate, B0 filtrate, B1 filtrate, C1 filtrate, C0 filtrate, D0 supernatant solution, D1 supernatant solution into eight corresponding titration cells of the automatic potentiometer and add 15,0 mL of water. The accurate mass of supernatant solution or filtrate to the nearest 0,000 1 g are recorded as $m_{A0,t}$, $m_{A1,t}$, $m_{B0,t}$, $m_{B1,t}$, $m_{C0,t}$, $m_{C1,t}$, $m_{D0,t}$, and $m_{D1,t}$, respectively.

b) Weigh 20,0 g of the above collected E filtrate with 10,0 g of the above collected C0 filtrate into a titration cell of the automatic potentiometer. The accurate mass of E filtrate and C0 filtrate in titration to the nearest 0,000 1 g are recorded as $m_{E,t}$ and $m_{EC,t}$, respectively.

c) These solutions are titrated with titrant acid conducted using an automatic potentiometer, until the second titration's equivalence point occurs when ΔE is maximum. Record the volume V (HCl) of titrant acid corresponding to the second end-point as V_{A0}, V_{A1}, V_{B0}, V_{B1}, V_{C0}, V_{C1}, V_{D0}, V_{D1} and V_E, respectively.

5.2 Measurement uncertainty

The uncertainties associated with measuring the surface oxygen functional groups of graphene should be estimated from various origins as listed below:

a) uncertainties associated with weighing the mass of the powder, the working Na_2CO_3, the solution A, B, C and D in reaction and filtrates in titration, which include the balance calibration, weighing operation, and loss during sample transfer;

b) uncertainties associated with titration of the HCl solution and filtrates, which include the uncertainty of automatic potentiometer, determination of the endpoint of titration curve.

5.3 Operation procedure, key control steps and case study

See Annex A for the operation procedure and key control steps, and Annex E for case study.

6 Data analysis / interpretation of results

6.1 Normalized base consumption

The number of bases (in mol) consumed for the neutralization reaction on the surface oxygen functional groups of graphene sample, and normalized molar alkalinity of sample suspension η_E, in mmol/g, are determined as follows:

$$\eta_A = (V_{A0} \times C / m_{A0,t} - V_{A1} \times C / m_{A1,t}) \times m_{A1} / m_1$$

$$\eta_B = (V_{B0} \times C / m_{B0,t} - V_{B1} \times C / m_{B1,t}) \times m_{B1} / m_2$$

$$\eta_C = (V_{C0} \times C / m_{C0,t} - V_{C1} \times C / m_{C1,t}) \times m_{C1} / m_3$$

$$\eta_D = (V_{D0} \times C / m_{D0,t} - V_{D1} \times C / m_{D1,t}) \times m_{D1} / m_4$$

$$\eta_E = ((V_E \times C - V_{C0} \times C / m_{C0,t} \times m_{EC,t}) / m_{E,t}) \times m_E / m_5$$

where

η_A, η_B, η_C, η_D	is the mole of $NaHCO_3$ (A), Na_2CO_3 (B), NaOH (C) and C_2H_5ONa (D) consumed for reaction between graphene sample and bases A, B, C and D, respectively, in mmol/g;
η_E	is the alkalinity of graphene sample suspension, in mmol/g;
m_A, m_B, m_C, m_D, m_E	is the mass of the solution A, B, C and D and water in A1, B1, C1 and D1 mixtures and in E sample blank, respectively, in grams;
C	is the concentration of titrant acid, in mol/L;
m_1, m_2, m_3, m_4, m_5	is the mass of the dried graphene specimens in A, B, C and D reaction mixtures and F sample blank, respectively, in grams;
$m_{A0,t}$, $m_{A1,t}$	is the mass of A0 filtrate and A1 filtrate in titration, respectively, in grams;
V_{A0}, V_{A1}	is the volume of the titrant acid consumed by titration of A1 filtrate and A0 filtrate, respectively, in millilitres;
$m_{B0,t}$, $m_{B1,t}$	is the mass of B0 filtrate and B1 filtrate in titration, respectively;
V_{B0}, V_{B1}	is the volume of the titrant acid consumed by titration of B1 filtrate and B0 filtrate, respectively, in millilitres;

$m_{\mathrm{C0,t}}$, $m_{\mathrm{C1,t}}$	is the mass of C0 filtrate and C1 filtrate in titration, respectively;
V_{C0}, V_{C1}	is the volume of the titrant acid consumed by titration of C1 filtrate and C0 filtrate, respectively, in millilitres;
$m_{\mathrm{D0,t}}$, $m_{\mathrm{D1,t}}$	is the mass of D0 filtrate and D1 filtrate in titration, respectively;
V_{D0}, V_{D1}	is the volume of the titrant acid consumed by titration of D1 filtrate and D0 filtrate, respectively, in millilitres;
V_{E}	is the volume of the titrant acid consumed by titration of E filtrate, in millilitres;
$m_{\mathrm{EC,t}}$, $m_{\mathrm{E,t}}$	is the mass of C0 filtrate and E filtrate in titration of E filtrate, respectively

Perform two individual measurements for the same sample. If the relative error of base consumption in two parallel determinations does not exceed 10 % of the mean value, take the arithmetical average value as the results, precise to 0,001 mmol/g, and report the relative error. If the relative error in two parallel determinations exceeds 10 %, a repetition test is needed. It is recommended to increase the sample amount to be reacted with the base solution in the repetition test.

6.2 Oxygen functional group content

Content of oxygen functional groups on graphene, in mmol/g, are calculated as follows:

$$\eta_{\mathrm{carboxyl}} = \eta_{\mathrm{A}} + \eta_{\mathrm{E}}$$

$$\eta_{\mathrm{lactone}} = \eta_{\mathrm{B}} + \eta_{\mathrm{E}} - \eta_{\mathrm{carboxyl}}$$

$$\eta_{\mathrm{hydroxyl}} = \eta_{\mathrm{C}} + \eta_{\mathrm{E}} - \eta_{\mathrm{carboxyl}} - \eta_{\mathrm{lactone}}$$

$$\eta_{\mathrm{carbonyl}} = \eta_{\mathrm{D}} + \eta_{\mathrm{E}} - \eta_{\mathrm{carboxyl}} - \eta_{\mathrm{lactone}} - \eta_{\mathrm{hydroxyl}}$$

where

η_{carboxyl}	is the content of surface carboxyl groups on graphene sample, in mmol/g;
η_{lactone}	is the content of surface lactone groups on graphene sample, in mmol/g;
η_{hydroxyl}	is the content of surface phenolic hydroxyl groups on graphene sample, in mmol/g;
η_{carbonyl}	is the content of surface reactive carbonyl groups on graphene sample, in mmol/g.

7 Results to be reported

7.1 General

The results of the measurement shall be documented in a measurement report, including the date and time of the measurement as well as the name and signature of the person responsible for the accuracy of the report. Guidelines are given in Annex D.

7.2 Product/sample identification

The report shall contain all information to identify the test sample and trace back the history of the sample:

- general procurement information, according to blank detail specification IEC 62565-3-1;
- general material description according to blank detail specification IEC 62565-3-1, including a technical drawing.

7.3 Test results

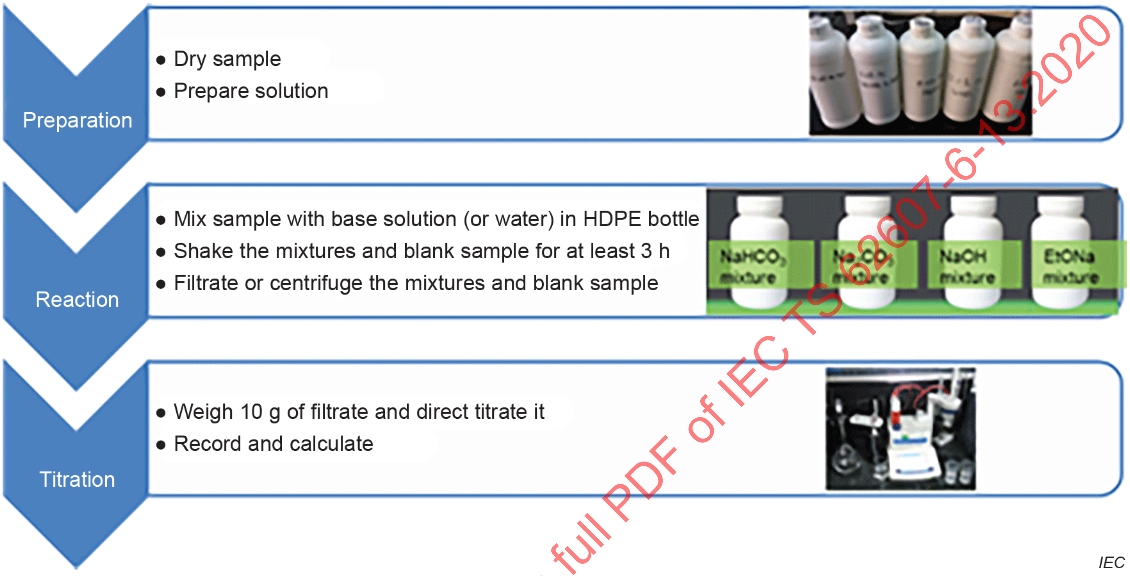
- Raw data and titration curve.
- Results of oxygen functional group content measured according to this document.

Annex A
(informative)

Operation procedure and key control steps

A.1 Operation procedure

See Figure A.1.



Preparation

- Dry sample
- Prepare solution

Reaction

- Mix sample with base solution (or water) in HDPE bottle
- Shake the mixtures and blank sample for at least 3 h
- Filtrate or centrifuge the mixtures and blank sample

Titration

- Weigh 10 g of filtrate and direct titrate it
- Record and calculate

Figure A.1 – Operation procedure

A.2 Key control steps

See Figure A.2.

Figure A.2 – Key control steps

Annex B
(informative)

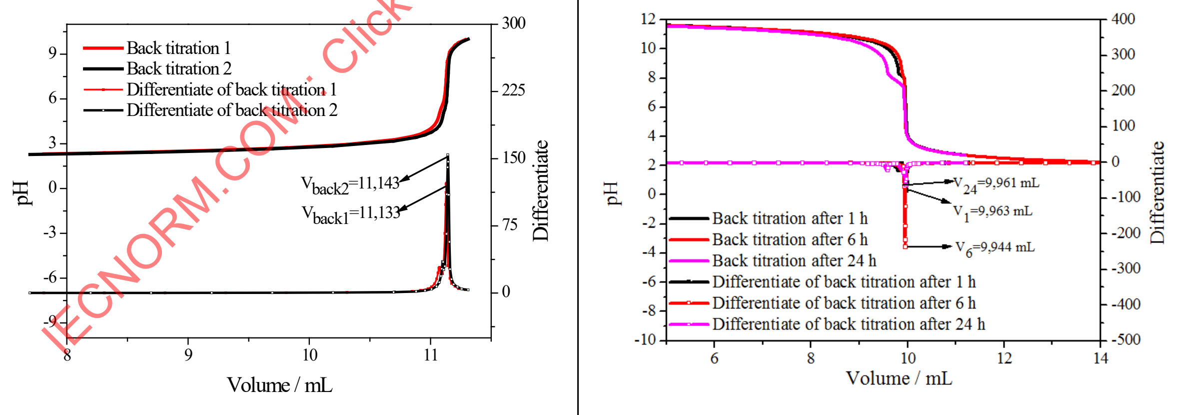
Influence of CO_2

B.1 Effect of CO_2 on titration of base concentration

The principle of Boehm titration is to determine the difference of total base between before and after graphene has reacted with base solution. Therefore, it is important to accurately determine the total base concentration of base solution. NaOH solution will absorb CO_2 easily, setting titration of NaOH solution as an example to verify if CO_2 would affect the titration result of total base concentration of NaOH solution. Two groups of experiments were conducted.

- One group is back titration: two aliquot masses of 10 g of NaOH solution were mixed with 20 g of titrate acid, the mixed solutions were pre-degassed with N_2 gas to remove the carbon dioxide (CO_2) for 20 mins, and then back titrated with titrate base (titration curves are shown in Figure B.1a).
- The other group is direct titration:10 g of NaOH solution after preparation for 1 h, 6 h and 24 h were directly titrated with titrate acid (titration curves are shown in Figure B.1b).

The results (in Table B.1) proved that CO_2 cannot affect the titration of total base concentration of NaOH solution if the second equivalence point at the titration curve was determined in direct titration. The effects of CO_2 on titration of $NaHCO_3$ solution, Na_2CO_3 solution and C_2H_5ONa solution are same as for NaOH solution [20][27]. Therefore, both back titration and direct titration can be used to determine the total base concentration. However, for back titration, bubbling N_2 is needed to remove CO_2 and it takes more than 25 min per base solution sample to titrate. For direct titration, there is no need to operate a complicated bubbling N_2 gas process and it only takes several minutes per base solution sample to titrate. Obviously, direct titration is more convenient and efficient. Therefore, in this document, direct titration is recommended to determine the concentration of all base solutions without the need to remove CO_2.



a) back titration

b) direct titration

Figure B.1 – Titration curves of NaOH solution

Table B.1 – Titration results of back titration and direct titration of NaOH solution

Experiment		Mass of NaOH solution g	Concentation of titrate acid mol/L	Mass of titrate acid g	Concentration of titrate base mol/L	Volume of titrate base mL	Concentration mol/g
Back titration	1	10,000 4	0,054 83	20,052 3	0,049 80	11,143	0,054 45
	2	10,018 1	0,054 83	20,052 1	0,049 80	11,133	0,054 40
Direct titration	1 h	10,033 0	0,054 83	9,963	0		0,054 45
	6 h	10,021 0	0,054 83	9,944			0,054 41
	24 h	10,033 0	0,054 83	9,963			0,054 45

B.2 Effect of CO_2 on base consumption

Determination of normalized NaOH consumption is used as an example to verify if the CO_2 would affect the base consumption. Two groups of experiments were conducted.

- One group uses the N_2 bubbling for 20 min to remove CO_2 after mixing NaOH solution with sample to determine the NaOH consumption.
- The other group directly mixes the sample with NaOH solution to determine the NaOH consumption.

NaOH consumption of these two groups are shown in Table B.2, it proves that the effect of CO_2 on base consumption is very limited. Meanwhile with the degassing process, more or less of the solvent water will be taken away, resulting in an increase in concentration of NaOH, showing a decrease in the normalized base consumption and an increase in RSD. Therefore, in this document, reaction between sample and base solution can be recommended to be easily conducted by directly mixing these two without going through a pre-degassing process using N_2 bubbling.

Table B.2 – Results of base consumption of NaOH with and without bubbling N_2

Test condition	NaOH normalized consumption mmol/g	Average mmol/g	RSD %
Without bubbling N_2	5,623	5,688	1,10
	5,748		
	5,692		
With bubbling N_2	5,435	5,602	2,59
	5,672		
	5,698		

Annex C
(informative)

Lower limit of determination

C.1 Experiment of lower mass of reacted sample A

A series of experiments were conducted to find out what amount of sample A should be reacted with base solution, i.e. different amounts of sample (from 10 mg to 300 mg) were reacted with solutions A through D. From the results shown in Figure C.1, it can be seen that in order to ensure test result accuracy for sample A, the minimum necessary amount of sample A is approximately 0,15 g.

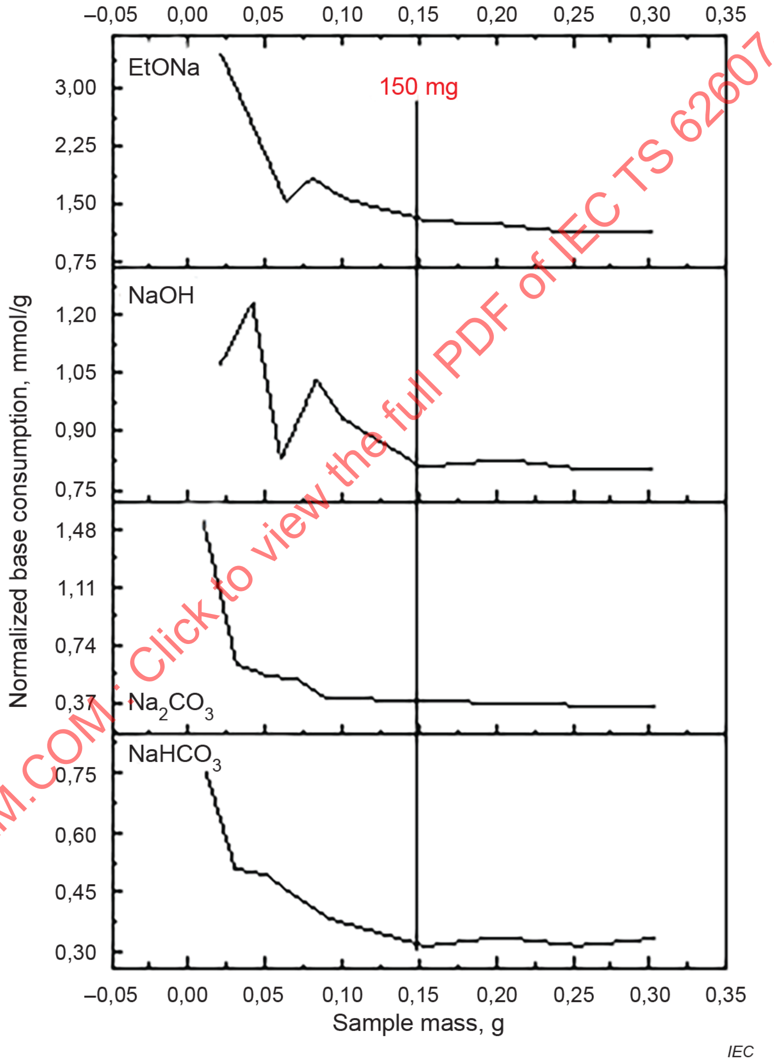


Figure C.1 – The normalized base consumption of different amounts of sample A

C.2 Determination of detection limits

12 aliquots of 0,15 g of sample A were reacted with solution A, B, C and D. The standard deviations for these 12 parallel experiments are shown in Table C.1.

For this method, the titration of the filtrate is the main factor limiting the accuracy of the method. As shown in Table C.1, the relative standard deviations (RSDs) of η_{NaHCO3}, η_{Na2CO3}, η_{NaOH}, and $\eta_{C2H5ONa}$ are 8 %, 6 %, 2 % and 8 %, respectively. Therefore, if the difference of normalized base consumption between two parallel determinations is less than 10 %, take the arithmetical average value as the results of normalized consumption.

Table C.1 – Base consumption result of sample A

Exp.	$NaHCO_3$		Na_2CO_3		NaOH		C_2H_5ONa	
	Total Cons. n_A mmol	Norm. Cons. η_A mmol/g	Total Cons. n_B mmol	Norm. Cons. η_B mmol/g	Total Cons. n_C mmol	Norm. Cons. η_C mmol/g	Total Cons. n_D mmol	Norm. Cons. η_D mmol/g
1	0,032	0,21	0,106	0,70	0,125	0,83	0,153	1,02
2	0,030	0,20	0,096	0,64	0,126	0,84	0,153	1,02
3	0,033	0,22	0,094	0,62	0,123	0,82	0,141	0,94
4	0,027	0,18	0,108	0,72	0,128	0,85	0,155	1,04
5	0,030	0,20	0,108	0,72	0,123	0,82	0,142	0,94
6	0,032	0,21	0,106	0,70	0,123	0,82	0,14	0,93
7	0,036	0,24	0,106	0,70	0,123	0,82	0,146	0,97
8	0,030	0,20	0,096	0,64	0,119	0,79	0,149	0,99
9	0,027	0,18	0,112	0,74	0,125	0,83	0,173	1,15
10	0,029	0,19	0,100	0,66	0,122	0,81	0,168	1,12
11	0,029	0,19	0,106	0,70	0,123	0,82	0,174	1,16
12	0,030	0,20	0,094	0,62	0,122	0,81	0,161	1,07
SD	0,003	0,017	0,006	0,042	0,002	0,015	0,012	0,081
Average	0,030	0,20	0,103	0,68	0,124	0,82	0,155	1,03
RSD	8 %	8 %	6 %	6 %	2 %	2 %	8 %	8 %

Exp. = Experiment
Cons. = Consumption
Norm. = Normalized

From Table C.2, the detection limits of total content for carboxyl, lactone, hydroxyl and carbonyl can be derived as three times the respective measured standard deviation. This yields 0,008 mmol, 0,018 mmol, 0,006 mmol and 0,036 mmol, respectively. The detection limit of normalized content can be decreased by increasing the mass of sample reacted with base solution (Table C.3). In this document, the largest sample amount reacted with base solution is specified to be 0,5 g. Therefore, the lower limits of detection for carboxyl groups, lactone groups, hydroxyl groups and carbonyl groups are 0,015 mmol/g, 0,037 mmol/g, 0,014 mmol/g, and 0,072 mmol/g, respectively (Table C.3).

Table C.2 – Oxygen functional group content result

Exp.	Carboxyl		Lactone		Hydroxyl		Carbonyl	
	Total content n mmol	**Norm. content** η mmol/g	**Total content** n mmol	**Norm. content** η mmol/g	**Total content** n mmol	**Norm. content** η mmol/g	**Total content** n mmol	**Norm. content** η mmol/g
1	0,032	0,21	0,076	0,50	0,022	0,15	0,034	0,20
2	0,030	0,20	0,066	0,44	0,023	0,16	0,034	0,20
3	0,033	0,22	0,064	0,42	0,020	0,14	0,022	0,12
4	0,027	0,18	0,078	0,52	0,025	0,17	0,036	0,22
5	0,030	0,20	0,078	0,52	0,020	0,14	0,023	0,12
6	0,032	0,21	0,076	0,50	0,020	0,14	0,021	0,11
7	0,036	0,24	0,076	0,50	0,020	0,14	0,027	0,15
8	0,030	0,20	0,066	0,44	0,016	0,11	0,030	0,17
9	0,027	0,18	0,082	0,54	0,022	0,15	0,054	0,33
10	0,029	0,19	0,07	0,46	0,019	0,13	0,049	0,30
11	0,029	0,19	0,076	0,50	0,020	0,14	0,055	0,34
12	0,030	0,20	0,064	0,42	0,019	0,13	0,042	0,25
Standard deviation	0,003	0,017	0,006	0,042	0,002	0,015	0,012	0,081
Lower limit K × SD (K = 2,98)	0,008	0,051	0,018	0,125	0,006	0,046	0,036	0,24

Exp. = Experiment

Norm. = Normalized

Table C.3 – Detection limits for different sample amounts

	Sample mass	**Carboxyl**	**Lactone**	**Hydroxyl**	**Carbonyl**
Lower limit of total content (mmol)		0,008	0,019	0,007	0,036
Lower limit of normalized content (mmol/g)	0,15 g	0,050	0,125	0,045	0,240
	0,50 g	0,015	0,037	0,014	0,072

Annex D
(informative)

Test report

D.1 Example of a test record

See Table D.1 and Table D.2.

Table D.1 – Data for calibration of titrant acid

Calibration	m_{Na2CO3} g	V (HCl) mL	C mol/L	Average C mol/L
Calibration 1				
Calibration 2				
Calibration 3				

Table D.2 – Data for Boehm titration

Sample	Mass of tested sample g		Mass of reacted solution g			Mass of titrated filtrate g		Volume of consumed titrant mL	
A0	A blank	0	A solution	m_{A0}		$m_{A0,t}$		V_{A0}	
A1	$m_{1,1}$			m_{A1}		$m_{A1,t}$		V_{A1}	
A2	$m_{1,2}$			m_{A2}		$m_{A2,t}$		V_{A2}	
B0	B blank	0	B solution	m_{B0}		$m_{B0,t}$		V_{B0}	
B1	$m_{2,1}$			m_{B1}		$m_{B1,t}$		V_{B1}	
B2	$m_{2,2}$			m_{B2}		$m_{B2,t}$		V_{B2}	
C0	C blank	0	C solution	m_{C0}		$m_{C0,t}$		V_{C0}	
C1	$m_{3,1}$			m_{C1}		$m_{C1,t}$		V_{C1}	
C2	$m_{3,2}$			m_{C2}		$m_{C2,t}$		V_{C2}	
D0	D blank	0	D solution	m_{D0}		$m_{D0,t}$		V_{D0}	
D1	$m_{4,1}$			m_{D1}		$m_{D1,t}$		V_{D1}	
D2	$m_{4,2}$			m_{D2}		$m_{D2,t}$		V_{D2}	
E	m_5		Water	m_E		$m_{E,t}$		V_E	
						$m_{EC,t}$			

D.2 Format of the test report

The form of the report shall be oriented on the relevant material specification (e.g. IEC 62565-3-1, a related sectional blank detail specification or detail specification. Table D.3 to Table D.5 are guidelines to write the report and can be modified to fulfil the requirements of the involved parties.

Table D.3 – Product identification (according to IEC 62565-3-1)

Item no.	Item			Information
1.1	Supplier			
1.2	Trade name			
1.3	ID number			
1.4	Traceability requirements	☐ Batch number ☐ Serial number ☐ Others, specify …………………………		
		Manufacturing date		
1.5	Specification	☐ Number		
		☐ Revision level		
		☐ Date of issue		
1.6	Material safety data sheet (MSDS) available	☐ No		
		☐ Yes	Reference	

Table D.4 – General material description (according to IEC 62565-3-1)

Item no.	Item	Information
2.1	Material type	
2.2	Manufacturing method	
2.3	Shelf life	
2.4	Typical batch size	

Table D.5 – Measurement results

	η_{NaHCO3}	η_{Na2CO3}	η_{NaOH}	η_{C2H5ONa}	$\eta_{\mathrm{alkalinity}}$
Normalized base consumption (mmol/g)					
Average					
Relative deviation					
Content of oxygen functional group (mmol/g)	η_{carboxyl}	η_{lactone}	η_{hydroxyl}	η_{carbonyl}	–

Annex E
(informative)

Case study

E.1 Preparation of solution

a) Titrant acid

Preparation: Add 500 mL of water to a 1 000 mL volumetric flask. Then dissolve 2,3 mL of concentrated HCl in the water. Finally, add more water until a total volume of 1 000 mL of HCl solution is obtained and mix. The resulting solution is then poured into the titration bottle of the automatic potentiometer.

Calibration: Weigh 0,051 2 g, 0,050 9 g and 0,051 0 g of working reagent Na_2CO_3, which has previously been air dried in an electric thermostatic drying oven at 300 °C and transfer into three titration cells of the automatic potentiometer; add 30 mL of water. The blank is to add 30 mL of water into a titration cell. The obtained Na_2CO_3 solutions and blank are titrated with the above-mentioned HCl solution using an automatic potentiometer. The volume of titrant needed to reach the titration's second equivalence point is recorded as V_1 = 38,188 mL, V_2 = 37,979 mL, V_3= 38,039 mL and V_0 = 0,001 mL. Therefore, the concentration of the prepared HCl solution is as follows.

$$C_{01}=\frac{2\times m\times 1000}{(V_1-V_0)\times \mathrm{M}}=\frac{2\times 0{,}0512\times 1000}{(38{,}188-0{,}001)\times 105{,}99}=0{,}025\,31\ \mathrm{mol/L}$$

$$C_{02}=\frac{2\times m\times 1000}{(V_2-V_0)\times \mathrm{M}}=\frac{2\times 0{,}0509\times 1000}{(37{,}979-0{,}001)\times 105{,}99}=0{,}025\,29\ \mathrm{mol/L}$$

$$C_{03}=\frac{2\times m\times 1000}{(V_3-V_0)\times \mathrm{M}}=\frac{2\times 0{,}0510\times 1000}{(38{,}039-0{,}001)\times 105{,}99}=0{,}025\,30\ \mathrm{mol/L}$$

$$C=\frac{C_{01}+C_{02}+C_{03}}{3}=\frac{0{,}025\,31+0{,}025\,29+0{,}025\,30}{3}=0{,}025\,30\ \mathrm{mol/L}$$

b) Base solutions

Solution A, solution B, solution C and solution D are prepared according to 5.1.1.

E.2 Sample preparation

Keep reduced graphene oxide sample 1 in a vacuum oven at (80 ± 5) °C for 12 h to completely dry. Then cool it to room temperature and store in a desiccator. The general material information is described in Table E.3 and Table E.4.

E.3 Reactions between graphene and bases

a) Label 13 HDPE bottles as A0, A1, A2, B0, B1, B2, C0, C1, C2, D0, D1, D2, and E.

b) Weigh nine aliquots of 0,15 g of the dried sample 1 into A1, A2, B1, B2, C1, C2, D1, D2, and E HDPE bottles; record the sample 1 mass to the nearest 0,000 1 g as $m_{1,1}$, $m_{1,2}$, $m_{2,1}$, $m_{2,2}$, $m_{3,1}$, $m_{3,2}$, $m_{4,1}$, $m_{4,2}$, m_5. The data are recorded in Table E.1.

c) Add 50,0 g of solution A into A0, A1 and A2, add 50,0 g of solution B into B0, B1 and B2, add 50,0 g of solution C into C0, C1 and C2, add 40,0 g of solution D into D0, D1 and D2, add 50,0 g of water into E. Record the corresponding mass of added solution or water to the nearest 0,000 1 g as m_{A1}, m_{A2}, m_{B1}, m_{B2}, m_{C1}, m_{C2}, m_{D1}, m_{D2} and m_E. The data are recorded in Table E.1.

d) For each bottle, seal with cap immediately after adding solution and shake to mix sample with solution well.

e) All sealed HDPE bottles are shaken for 3 h at (25 ± 2) °C and at 150 r/min using an oscillator.

f) After shaking, quickly filtrate all water solution bottles (A0, A1, A2, B0, B1, B2, C0, C1, C2, and E). Suction-filtration A1 by a funnel with flat perforated plate using a filter paper to separate the sample and solution. While filtering A1 solution, abandon the first 15 mL of filtrate, then without changing the filter paper or funnel, collect the remaining filtrate into another dry filter bottle to get A1 filtrate. To avoid the evaporation of solvent, A1 filtrate shall be titrated immediately after collection, i.e. use dropper to draw 10 g of A1 filtrate into a clean and known-mass titrate cell immediately after A1 filtrate is collected. Record the corresponding mass of A1 filtrate added in the titrate cell to the nearest 0,000 1 g as $m_{\mathrm{A1,t}}$, and then add about 20 mL of water to immerse the electrode and stir.

g) Filtrate the remaining bottles A0, A2, B0, B1, B2, C0, C1, C2, and E in the same way as for filtrating A1; thus, A0 filtrate, A2 filtrate, B0 filtrate, B1 filtrate, B2 filtrate, C0 filtrate, C1 filtrate, C2 filtrate, and E filtrate are obtained. The obtained filtrates are weighed immediately in nine clean titration cells by droppers respectively. Record the corresponding mass of filtrate added in the titrate cell to the nearest 0,000 1 g as $m_{\mathrm{A0,t}}$, $m_{\mathrm{A2,t}}$, $m_{\mathrm{B0,t}}$, $m_{\mathrm{B1,t}}$, $m_{\mathrm{B2,t}}$, $m_{\mathrm{C0,t}}$, $m_{\mathrm{C1,t}}$, $m_{\mathrm{C2,t}}$, and $m_{\mathrm{E,t}}$. Add about 20 mL of water into the titration cells of A0 filtrate, A2 filtrate, B0 filtrate, B1 filtrate, B2 filtrate, C0 filtrate, C1 filtrate, and C2 filtrate. Add 10,0 g of C0 filtrate into titrate cell with E filtrate. Record the corresponding mass of C0 filtrate added into the titration cell of E filtrate to the nearest 0,000 1 g as $m_{\mathrm{EC,t}}$.

h) Centrifuge D0, D1, and D2 bottles to remove the graphene sample. For each bottle, quickly transfer solution into a 50 mL centrifuge tube and separate the sample by means of a centrifugal separator at 10 000 r/min for 10 min. After centrifugation, immediately weigh 10,0 g of supernatant solution into the known-mass titration cell by droppers and then add about 20 ml of water into the titration cell. Record the corresponding mass of supernatant added into the titration cell to the nearest 0,000 1 g as $m_{\mathrm{D0,t}}$, $m_{\mathrm{D1,t}}$, $m_{\mathrm{D2,t}}$. All data is recorded in Table E.1.

E.4 Titration of the filtrate

a) Pour the prepared titrant acid into the titration bottle of the automatic potentiometer. Flush pipes of the automatic potentiometer at least three times before the titration experiment. Ensure that gas bubbles in the automatic potentiometer pipes are expelled completely.

b) All prepared titration cells are placed at an automatic potentiometer and titrated with titrant acid, until the second titration's equivalence point (EQP) occurs when the maximum ΔE is observed, as shown in Figure E.1. Record the volume V (HCl) of titrant acid corresponding to the second EQP as V_{A0}, V_{A1}, V_{A2}, V_{B0}, V_{B1}, V_{B2}, V_{C0}, V_{C1}, V_{C2}, V_{D0}, V_{D1}, V_{D2}, and V_{E}, respectively. All data is recorded in Table E.1.