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BSI Standards Publication

Nanotechnologies — Structural characterization of graphene

Part 1: Graphene from powders and dispersions

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The UK participation in its preparation was entrusted to Technical Committee NTI/1, Nanotechnologies.

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Nanotechnologies - Structural characterization of graphene - Part 1: Graphene from powders and dispersions (ISO/TS 21356-1:2021)

Nanotechnologies - Caractérisation structurelle du graphène - Partie 1: Graphène issu de poudres et de dispersions (ISO/TS 21356-1:2021)

Nanotechnologien - Strukturelle Charakterisierung von Graphen - Teil 1: Graphen aus Pulvern und Dispersionen (ISO/TS 21356-1:2021)

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Foreword

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This document was prepared jointly by Technical Committee ISO/TC 229, *Nanotechnologies*, and Technical Committee IEC/TC 113, *Nanotechnology for electrotechnical products and systems*.

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Introduction

Due to the many superlative properties of graphene and related 2D materials, there are many application areas where these nanomaterials could be disruptive, areas such as flexible electronics, nanocomposites, sensing, filtration membranes and energy storage.

There are barriers to commercialisation that are impeding the progress of products containing graphene, which need to be overcome. One of these crucial barriers is answering the question "What is my material?". End-users of the raw materials containing graphene should be able to rely on the advertised properties of the commercial graphene on the global market, instilling trust and allowing worldwide trade. Reliable and repeatable measurement protocols are required to address this challenge.

This document provides a set of flow-charts for analysts to follow in order to determine the structural properties of graphene from powders and liquid dispersions (suspensions). Initially, a quick check should be undertaken to determine if graphene and/or graphitic material is present. If it is, then further detailed analysis is required to determine if the samples contain a mixture of single-layer graphene, bilayer graphene, few-layer graphene, graphene nanoplatelets and graphite particles. Depending on the methods used, the samples are typically analysed after deposition on a substrate. The document describes how to assess what measurements are required depending on the type of sample and includes decision trees and flow diagrams to aid the user. This document describes a selected set of measurands that are needed, namely:

a) the number of layers/thickness of the flakes;

b) the lateral dimensions of flakes;

c) layer alignment;

d) the level of disorder;

e) the estimated number fraction of graphene or few-layer graphene;

f) the specific surface area of the powder containing graphene.

The above physical properties of the material can change during its processing and lifetime, for example, the samples can become more agglomerated, obtain different surface functionalities. The above measurand list for the initial material defines their inherent characteristics that, along with the chosen manufacturing processes, will determine the performance of real-world products. Generally, different material properties can be important in different application areas, depending on the functional role of the material.

The document provides methods for structural characterization of individual flakes of graphene, bilayer graphene, graphene nanoplatelets and graphite particles isolated from powders and/or liquid dispersions. It does not provide methods for determination of whether the powders and/or dispersions are composed solely of these materials. No recommendation is provided as to when or how often to measure samples, although it is not expected this would be for every batch of the same material. It is up to the user to determine when, how often and which characterization routes described in this document to take. As with all microscopical investigations, care is needed in drawing statistical conclusions dependant on representative sampling.

A set of annexes provide example protocols on how to prepare and analyse the samples, sources of uncertainty and how to analyse the data. The methods used are Raman spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM) and the BET (Brunauer–Emmett–Teller) method.

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Nanotechnologies — Structural characterization of graphene —

Part 1: Graphene from powders and dispersions

1 Scope

This document specifies the sequence of methods for characterizing the structural properties of graphene, bilayer graphene and graphene nanoplatelets from powders and liquid dispersions using a range of measurement techniques typically after the isolation of individual flakes on a substrate. The properties covered are the number of layers/thickness, the lateral flake size, the level of disorder, layer alignment and the specific surface area. Suggested measurement protocols, sample preparation routines and data analysis for the characterization of graphene from powders and dispersions are given.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 80004-1:2015, *Nanotechnologies — Vocabulary — Part 1: Core terms*

ISO/TS 80004-2:2015, *Nanotechnologies — Vocabulary — Part 2: Nano-objects*

ISO/TS 80004-6:2021, *Nanotechnologies — Vocabulary — Part 6: Nano-object characterization*

ISO/TS 80004-13:2017, *Nanotechnologies — Vocabulary — Part 13: Graphene and related two-dimensional (2D) materials*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/TS 80004-1:2015, ISO/TS 80004-2:2015, ISO/TS 80004-6:2021, ISO/TS 80004-13:2017 and the following apply.

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

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
graphene
graphene layer
single-layer graphene
monolayer graphene
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) (3.3) and *few-layer graphene* (FLG) (3.4).

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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, 3.1.2.1]

3.2
graphite
allotropic form of the element carbon, consisting of *graphene layers* (3.1) stacked parallel to each other in a three-dimensional, crystalline, long-range order

Note 1 to entry: Adapted from the definition in the IUPAC Compendium of Chemical Terminology.

Note 2 to entry: There are two primary allotropic forms with different stacking arrangements: hexagonal and rhombohedral.

[SOURCE: ISO/TS 80004-13:2017, 3.1.2.2]

3.3
bilayer graphene
2LG
two-dimensional material consisting of two well-defined stacked *graphene layers* (3.1)

Note 1 to entry: If the stacking registry is known, it can be specified separately, for example, as "Bernal stacked bilayer graphene".

[SOURCE: ISO/TS 80004-13:2017, 3.1.2.6]

3.4
few-layer graphene
FLG
two-dimensional material consisting of three to ten well-defined stacked *graphene layers* (3.1)

[SOURCE: ISO/TS 80004-13:2017, 3.1.2.10]

3.5
graphene nanoplate
graphene nanoplatelet
GNP
nanoplate consisting of *graphene layers* (3.1)

Note 1 to entry: GNPs typically have thickness of between 1 nm to 3 nm and lateral dimensions ranging from approximately 100 nm to 100 µm.

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

3.6
lateral size
flake size
<2D material> lateral dimensions of a 2D material flake

Note 1 to entry: If the flake is approximately circular then this is typically measured using an equivalent circular diameter or if not via x, y measurements along and perpendicular to the longest side.

[SOURCE: ISO/TS 80004-13:2017, 3.4.1.15]

3.7
graphene oxide
GO
chemically modified *graphene* (3.1) prepared by oxidation and exfoliation of *graphite* (3.2), causing extensive oxidative modification of the basal plane

Note 1 to entry: Graphene oxide is a single-layer material with a high oxygen content, typically characterized by C/O atomic ratios of approximately 2,0 depending on the method of synthesis.

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[SOURCE: ISO/TS 80004-13:2017, 3.1.2.13]

3.8
reduced graphene oxide
rGO
reduced oxygen content form of *graphene oxide* (3.7)

Note 1 to entry: This can be produced by chemical, thermal, microwave, photo-chemical, photo-thermal or microbial/bacterial methods or by exfoliating reduced *graphite* oxide.

Note 2 to entry: If graphene oxide was fully reduced, then *graphene* (3.1) would be the product. However, in practice, some oxygen containing functional groups will remain and not all sp^3 bonds will return back to sp^2 configuration. Different reducing agents will lead to different carbon to oxygen ratios and different chemical compositions in reduced graphene oxide.

Note 3 to entry: It can take the form of several morphological variations such as platelets and worm-like structures.

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

4 Abbreviated terms

For the purposes of this document, the following abbreviated terms apply.

NOTE The final "M", given as "microscopy", can be taken equally as "microscope" depending on the context.

1LG	single-layer graphene
2D	two dimensional
2LG	bilayer graphene
AFM	atomic force microscopy
BET method	Brunauer–Emmett–Teller method
CVD	chemical vapour deposition
FLG	few-layer graphene
FWHM	full width at half maximum
GNP	graphene nanoplate or graphene nanoplatelet
GO	graphene oxide
NMP	1-methyl-2-pyrrolidinone also known as N-methylpyrrolidone
rGO	reduced graphene oxide
SAED	selected area electron diffraction
SEM	scanning electron microscopy
TEM	transmission electron microscopy

5 Sequence of measurement methods

This clause presents the sequence of measurement methods necessary to most efficiently characterize graphene, bilayer graphene, few-layer graphene and graphene nanoplatelets from powders and liquid dispersions (suspensions). In this document, graphene, bilayer graphene, few-layer graphene and

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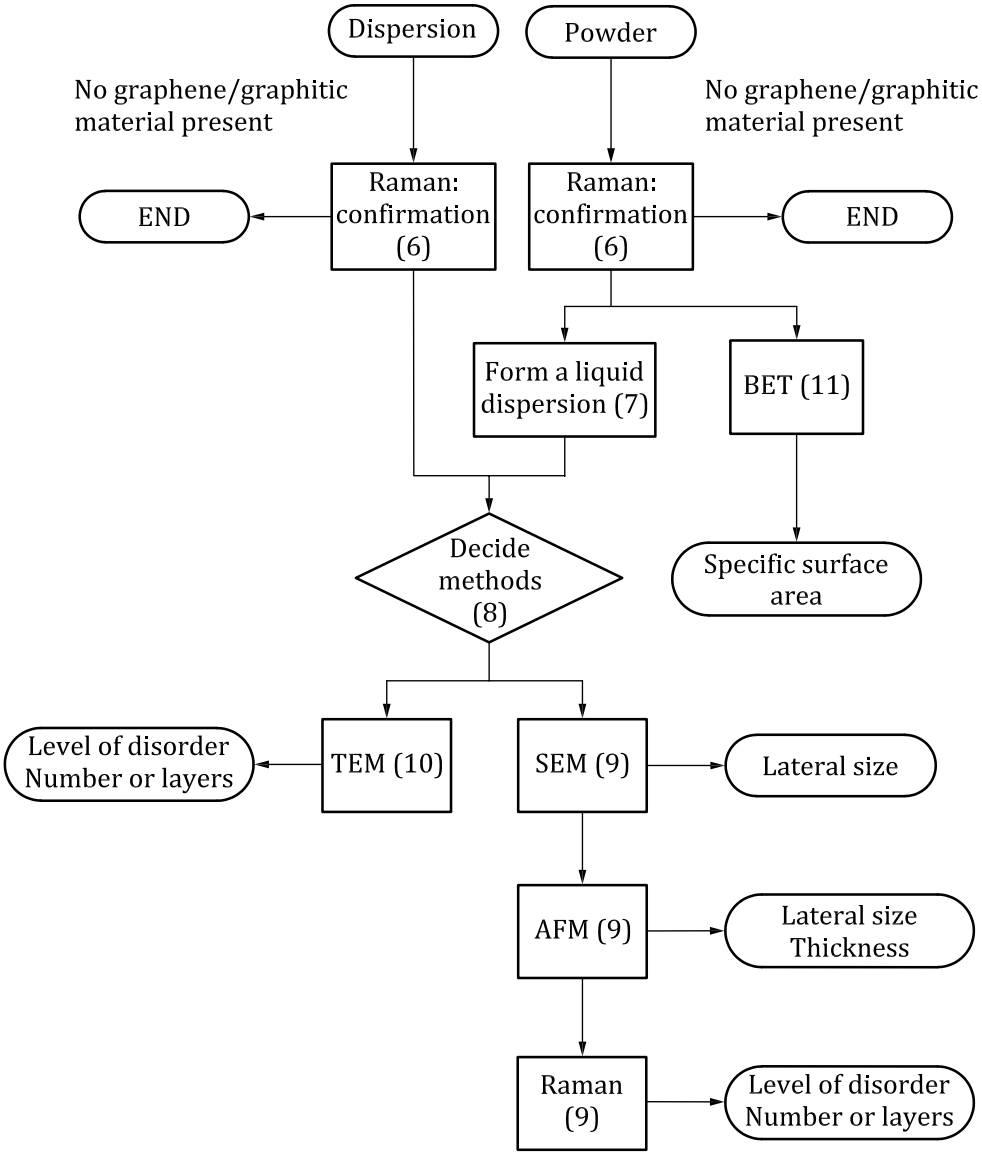
graphene nanoplatelets are in the form of flakes of limited lateral dimensions. However, samples also typically contain significant amounts of flakes having thicknesses that exceed ten layers, which are flakes of graphite by definition.

After an initial examination by Raman spectroscopy, and assuming the sample is graphene or graphitic in nature, a more detailed characterization should follow. Various characterization routes are then possible, as shown in Figure 1. The characterization method or methods to be used will depend on the time and equipment available and the measurands that the user requires.

NOTE 1 As the flakes are from a powder or liquid dispersion, they will typically require deposition onto a substrate before analysis.



NOTE The numbers in brackets refer to the clauses where the item is detailed.

Figure 1 — Overview of the sequence and process of the measurement methods used to determine the structural properties of graphene from a powder or liquid dispersion sample

Firstly, determine if the sample contains graphene and/or graphitic material, that is bilayer graphene, FLG, GNPs or graphite by undertaking a rapid analysis using Raman spectroscopy, as detailed in Clause 6 and Annex A. The sample needs to be in powder form deposited as a thin layer on a substrate, therefore if a liquid dispersion has been supplied, the material will first need to be removed from the solvent, as detailed in A.2.

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Decide which methods to use as outlined in Clause 8. Either use TEM or a combination of SEM, AFM and Raman spectroscopy to determine the distribution of lateral flake sizes and the relationship with flake thickness. For this stage, clearly separated flakes on a substrate are required. To prepare these samples by deposition, a liquid dispersion is initially required, therefore, if the material was provided as a powder, it requires dispersing in a suitable solvent, as described in Clause 7, before subsequent deposition onto a suitable substrate with example procedures outlined in Annexes B and C.

If TEM is used (see Clause 10), prepare the sample on a TEM support grid as outlined in C.2, otherwise prepare the sample on a silicon dioxide on silicon substrate, B.2. Then use optical microscopy as a quick quality check to determine if the sample is too agglomerated and therefore cannot be accurately measured. Optimize the sample preparation until an even deposition of the material across the substrate occurs. Then undertake a combination of SEM, AFM and Raman spectroscopy measurements (see Clause 9 and Annex B) or TEM (see Clause 10, Annex C). SEM, AFM and Raman spectroscopy should be used in combination and not in individual isolation in order to determine the measurands listed in Figure 1.

If required, use BET to determine the specific surface area of the powder (see Clause 11 and Annex E).

Once all the necessary measurements have been undertaken, calculate the median lateral flake size, the range of flake sizes, the graphene 1LG number fraction and FLG number fraction, as discussed in Clause 12 and Annex D. Here, number fraction is the fraction by number of graphene or FLG over the total number of flakes, this can also be expressed as a percentage.

NOTE 2 It is assumed that the sample contains graphene/2LG/FLG/graphite. If the sample has different chemistries, for example contains graphene oxide or functionalised graphene, this will not produce the same Raman spectroscopy results as those described in this document. However, optical microscopy, SEM and AFM characterization of lateral dimensions and thicknesses (but not number of layers) can still be applied to these materials.

NOTE 3 There is currently no quantitative or standardised method for determining the specific surface area of the graphitic material when the sample is in or from a liquid dispersion form.

6 Rapid test for graphitic material using Raman spectroscopy

Firstly, test the sample, in powder form deposited on a substrate using Raman spectroscopy to determine whether the sample supplied contains graphene and/or graphitic material. This test can also provide qualitative information on the structural properties of the material, including the level of disorder and the dimensions of the flakes. If the sample is supplied in a liquid dispersion, then remove the liquid from the dispersion and analyse the sample in powder form.

A thin layer of powder is required for this rapid Raman spectroscopy analysis step. If a powder has been provided, this should be analysed with a significant amount of the sample secured on adhesive tape (see A.2) such that only the flakes rather than the substrate are analysed.

A measurement protocol and sample preparation method are detailed in Annex A.

To confirm the presence of graphitic material, a sharp (< 30 cm^{-1} full width at half maximum (FWHM)) G-peak at approximately 1 580 cm^{-1} and a 2D-peak (sometimes referred to as the G' peak) at approximately 2 700 cm^{-1} should be consistently observed in the Raman spectra as shown in the graphene spectrum in Figure 2. If an intense symmetric Lorentzian peak shape is found for the 2D-peak with close to or greater intensity than the G-peak, this suggests the sample could contain single-layer graphene. However, restacked few-layer graphene flakes can also show a single Raman 2D-peak. If the 2D-peak is not symmetric, this suggests flakes of multiple layers are present. A prominent shoulder in the 2D-peak is indicative of layered material, with a thickness of over ten graphene layers (i.e. graphite). If the G- and 2D-peaks are not present, further characterization is not required, as the sample does not contain graphene or graphite, however, a sufficient ratio of the Raman peak signal to background noise (S/N) ratio should be established before this conclusion can be made, see Annex A for example details. To improve the S/N ratio, longer acquisition times can be used, or averaging multiple scans with short acquisition times can be used.

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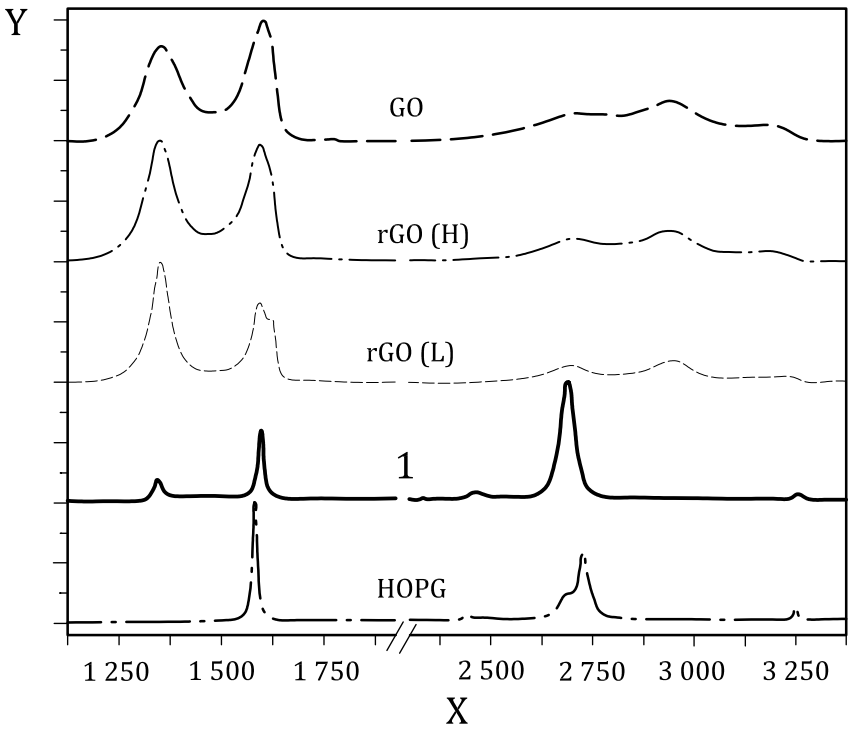
If functionalised graphene or graphene oxide is present, Raman spectroscopy will show the D- and G-peaks, but not necessarily a 2D-peak, and the D- and G-peaks will have much larger FWHM values (> 30 cm^{-1}) than expected for graphene. Here, additional chemical characterization should be undertaken to determine the oxygen content and any other components, which if found to be high means that the material is out of the scope of this document.



Key

X Raman shift, cm^{-1}

Y normalized intensity, arbitrary units

1 graphene

Figure 2 — Example Raman spectra of highly oriented pyrolytic graphite (HOPG), graphene, reduced graphene oxide with lower oxygen content [rGO(L)], reduced graphene oxide with higher oxygen content [rGO(H)] and graphene oxide (GO)

This step should not be confused with the processes used later for measurement of individual flakes with AFM and Raman spectroscopy (detailed in Clause 9 and Annex B) after further sample preparation.

NOTE 1 Adhesive tape is specified to stop the powder moving for both health and safety reasons and to stop possible electrostatic attraction and contamination of the lens.

NOTE 2 Chemical characterization of graphene including thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS) will be detailed in a further ISO document in development at the time of publication of this document.

NOTE 3 Other methods such as X-ray diffraction (XRD) can be used to determine the presence of graphitic material. Raman spectroscopy is used here as a rapid confirmation step, as Raman spectroscopy is also required for the detailed analysis of individual flakes (see Clause 9).

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7 Preparing a liquid dispersion

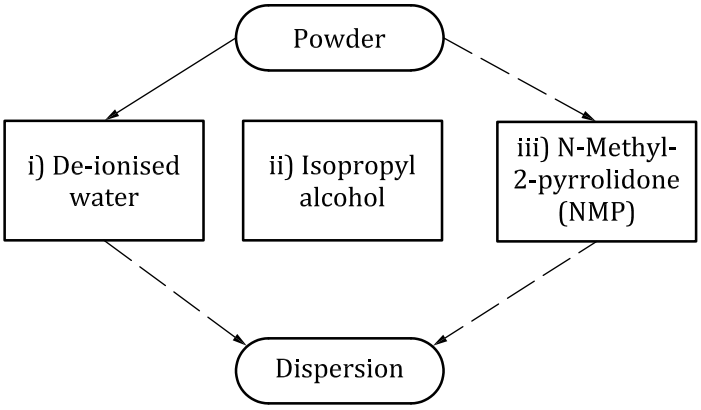
7.1 General

For further, more detailed characterization of the sample, the flakes should be prepared such that they are isolated on a substrate. This allows the next characterization steps, as shown in Figure 1, to be performed either using a combination of SEM, AFM and Raman spectroscopy with the sample on a silicon dioxide on silicon substrate, or TEM with the sample on a TEM grid. For the preparation of the flakes on a substrate, initially a liquid dispersion is required, therefore, if the material is provided as a powder, it requires dispersing in a suitable solvent.

7.2 Preparing a dispersion of the correct concentration

7.2.1 Powder samples

Disperse the powder in a solvent such that a concentration of approximately 0,1 mg/ml is achieved. The suitability of the solvent should be determined through the observation of how quick and how much, if any, sedimentation of the material occurs. There are a number of different solvents that can be used. Use the solvent that will disperse the powder and allow flakes to be characterized with the minimum of unwanted residue on the surface. The order of preference of three solvents is given in Figure 3.



NOTE An order of preference of the solvent to be used is outlined.

Figure 3 — Flowchart for the creation of a dispersion

Firstly, try to disperse the powder with deionised water. Place the liquid and powder in a glass vial or bottle and agitate. Sonicate the dispersion for up to a maximum of 10 min in a table-top ultrasonic bath at 30 kHz to 40 kHz. Longer sonication times can cause changes to the structural properties, including basal-plane scission (reducing the lateral size) and further exfoliation (reducing thickness/layer number). Observe the dispersion over a period of several minutes. If a significant amount of sedimentation occurs and occurs quickly then repeat the procedure using a different solvent.

If deionised water does not disperse the material, isopropanol should be used as the solvent using the same method. If this does not work, then N-methylpyrrolidone (NMP) should be used as the solvent as graphene disperses well in this. However, due to the high boiling point of NMP (203 °C), this can affect the characterization results in the form of solvent residue.

The deposition of the material onto a substrate is detailed in Clauses 9 and 10 and in particular in Annexes B and C.

Typically, graphene flakes will stay dispersed in deionised water only if a stabilizing agent, such as a surfactant, is present as part of the manufacturing process. However, it should be noted that significant use of surfactants can influence both the sample condition and the later measurement of the materials, see examples in B.2.

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Using a significant amount of ultrasonication to disperse the material can induce flake scission and therefore affect the structural characterization results obtained for a sample. The amplitude (commonly expressed as power) and duration of ultrasonication should therefore be kept to the minimum required to disperse the flakes. A comparison of flake size measurement as a function of the amplitude and duration of ultrasonication can be undertaken to check if flake scission occurs and to optimize sonication conditions, if required.

NOTE ISO/TS 22107[1)] provides general guidance on the definition of dispersibility and deals with processing and the achieved final dispersed state.

7.2.2 Samples already in a dispersion

If the sample is already provided as a dispersion, this should be diluted to approximately 0,1 mg/ml using the same solvent. However, if the solvent is a water/surfactant mix, the dilution should be carried out using deionised water, to reduce the level of surfactant.

NOTE In cases where the concentration of the dispersion provided is not known, the dilution needs to be approximated. This concentration is chosen such to produce dispersed flakes in solution and individual flakes on the substrate when cast.

8 Determination of methods

For detailed characterization, two characterization routes are possible, as shown in Figure 1. Determine whether to use a combination of SEM, AFM and Raman spectroscopy measurements (see Clause 9 and Annex B) or use TEM (see Clause 10 and Annex C). For powder samples, BET can be used to determine the specific surface area, as described in Clause 11 and Annex E. Which method or methods are used depends on the time and equipment available and the measurands that the user requires.

For either set of the microscopy methods, the samples shall be prepared firstly as a dispersion, as detailed in Clause 7, and then deposited on the correct substrate as discussed in B.2 or C.2.

9 Structural characterization using optical microscopy, SEM, AFM and Raman spectroscopy

This clause details the sequence of measurements to determine lateral flake dimensions, associated flake thickness, level of disorder and number of graphene layers using a combination of SEM, AFM and Raman spectroscopy. Use the methods as ordered in Figure 4.

1) Under preparation. Stage at the time of publication: ISO/DTS 22107:2021.

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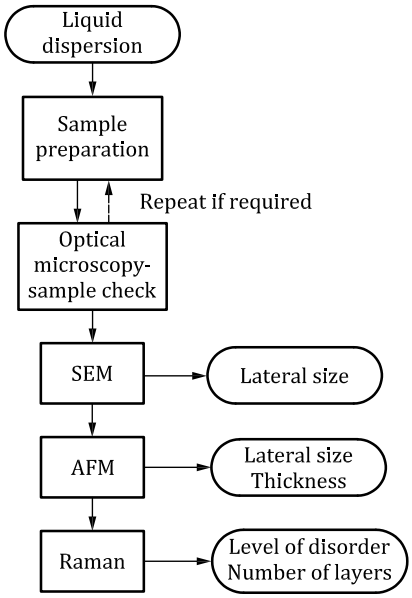

Figure 4 — Flow diagram and decision-making process for determining the range of lateral dimensions, thickness of flakes, number of layers and level of disorder

Firstly, the sample should be prepared from a liquid dispersion and placed on an appropriate substrate. Use optical microscopy to check the sample preparation. Once an appropriate sample has been produced, use SEM, AFM and Raman spectroscopy to characterize the sample and analyse the results to extract the measurands as detailed in Figure 4.

Sample preparation methods, measurement protocols and data analysis protocols are outlined in Annex B.

NOTE 1 The SEM measurements are performed on a different substrate and use different flakes to the AFM and Raman spectroscopy measurements.

NOTE 2 ISO 19749[2)] provides guidance for measuring size and shape distribution of nanoparticles including general principles, sample preparation, qualification of the SEM, image acquisition, particle and data analysis.

10 Structural characterization using TEM

In a transmission electron microscope (TEM) a high energy beam of electrons is passed through a thin electron transparent sample in a high vacuum environment.

TEM can be used to determine the lateral size and number of layers in flakes, as well as layer alignment, through diffraction contrast TEM imaging, lattice resolution imaging and selected area electron diffraction (SAED), which are achievable with most modern TEM instruments. It should be noted that, for liquid-phase exfoliated flakes, the presence of surfactants and common contaminants from the environment (H, C, O, Si, Na and Cl) can cause difficulties in imaging.

Users should consult ISO 21363:2020 for useful information on instrument set up and particle analysis.

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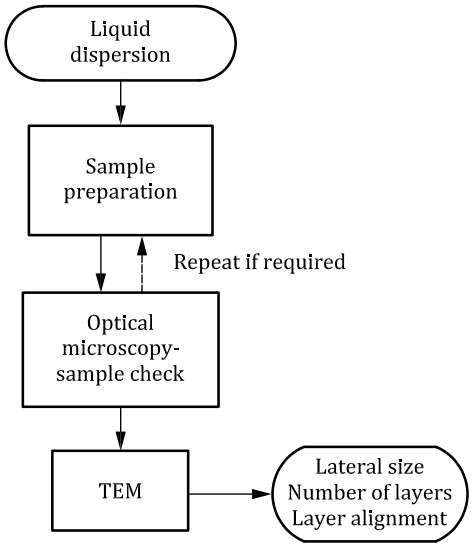

Figure 5 — Flowchart for TEM to determine lateral size, number of layers and layer alignment

Follow the order of operations as detailed on Figure 5 to determine the lateral size, number of layers and layer alignment of different flakes. The flakes should be deposited onto an appropriate TEM grid from a dispersion. Optical microscopy should be used to check the sample preparation and positions of flakes prior to analysis in the TEM. After TEM, the data should be analysed to determine the required measurands.

A sample preparation method, measurement protocol and data analysis method are detailed in Annex C.

11 Surface area determination using the BET method

The Brunauer–Emmett–Teller (BET) method determines the total specific surface area of disperse powders by measuring the amount of physically adsorbed gas. It utilizes the model developed by Brunauer, Emmett and Teller for interpreting gas adsorption isotherms. Use the BET method to determine the specific surface area of a powder sample.

A sample preparation method, measurement protocol and data analysis procedure are detailed in Annex E.

12 Graphene lateral size and number fraction calculation

Analyse the data produced from the dimensional characterization. Calculate the median lateral flake size, the range of flake sizes, the graphene 1LG and FLG number fraction and report which techniques are used to do this. A method to calculate this data is given in Annex D.

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