FINAL PUBLISHABLE REPORT

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Project short name	ISO-G-SCoPe
Project full title	Standardisation of structural and chemical properties of graphene

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1 Overview

The overall aim of this project was to validate and standardise measurement and characterisation methods for the chemical and structural properties of graphene in powders and liquid dispersions for industrial applications. This was to overcome a "what is my material?" barrier for both users and producers leading to well-characterised highly tailored graphene, graphene oxide and chemically functionalised graphene. The project aimed to maximise innovation and competitiveness of European industries across the supply chains in multiple sectors including the energy sector, photovoltaics, lithium-ion batteries, flexible electronics, composites, consumer products, novel coatings, clothing, automotive and aerospace industries. The project has undertaken 4 VAMAS international interlaboratory studies of graphene related 2D materials (GR2M) using XPS, Raman spectroscopy SEM and AFM. The project led to the publication of the first ISO graphene measurement standard (ISO TS 21356-1) and has led or contributed to the development of a further 3 draft ISO standards (ISO TS 23359. ISO TS 23879 and ISO TS80004-13). These enable end users and producers to measure structural and chemical properties of GR2M in a standardised way.

2 Need

Graphene and related 2D materials are predicted to make a major impact in many technology areas, either through incremental advances via current material replacement or via disruptive changes. However, the uptake of these materials into commercial products is hindered as industrially produced "graphene" is often incompletely or not correctly characterised by the 100+ suppliers. This has been acknowledged as the single biggest issue by graphene companies, suppliers and standards bodies [e.g., ISO TC229 (nanotechnologies), BSI NTI/1 (nanotechnologies) and BSI UK-China JWG on graphene standardisation]. Issues include structural determination of the material as graphene or graphite, how many layers are present and what is the flake size distribution in different batches. Chemical determination issues include the amount of oxygen present (for graphene oxide and reduced graphene oxide), impurities and functionalisation. Before the project, there were no standard ways to measure these properties for the industry to take the material from the laboratory to large-scale production.

The industry is rushing to develop its own internal measurement procedures to obtain reproducible results for its process optimisation and for external sales. These remain poorly accepted by their peers and competitors. Before the project started, there were standardisation documents progressing through International Organization for Standardization (ISO) TC229/IEC TC113 and American Society for Testing and Materials (ASTM) E56, but these were either overview technical reports, focused on electrical measurements or other issues. They did not contain validated measurement protocols for structural and chemical properties. There were also no European Standards. European industries require international documentary standardisation of structural and chemical methods to characterise graphene validated via pre-normative Versailles Project on Advanced Materials and Standards(VAMAS) international interlaboratory testing. This allows end-users to compare technical datasheets of different commercially available ‘graphene’ products worldwide. This helps instil confidence and allows faster innovation and increased R&D productivity, as end-users will only need to test a few materials rather than hundreds. These end users will be able to match highly tailored 2D materials to performance requirements. Standardised characterisation procedures are also required for companies needing to comply with new nanomaterials regulations and in particular registering graphene nanoforms in the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) register [ECHA, 2017 Appendix R.6-1] allowing reliable toxicity testing of different products on the market.

The aim of this project was to build on the established work items at International Organization for Standardization (ISO) and International Electrotechnical Commission (IEC) in terminology and overview standards and add robust metrology, methodology and supply validated measurement methods and supporting data. This will lead to the publication of three industry-critical ISO standards via ISO TC229 (ISO Technical Committee 229 “Nanotechnologies”) which will become adopted as European standards via CEN TC352 (CEN Technical Committee 352 "Nanotechnologies").

3 Objectives

The overall objective of this project was to validate and standardise measurement and characterisation methods for the chemical and structural properties of graphene in powders and liquid dispersions for industrial applications.

The specific objectives of the project were:

1. To lead and provide a contribution to the publication “ISO TS 21356-1 Nanotechnologies – Structural characterisation of graphene: Part 1: Graphene from powders and dispersions”. The contribution will focus on measurement methods for the characteristics of graphene flakes in order to verify measurements made on commercial graphene flake products.
2. To lead and provide a contribution to the development of ISO/PWI 23359 "Nanotechnologies - Chemical characterisation for graphene in powders and suspensions" and to lead and provide a contribution to ISO/PWI 23879 "Nanotechnologies – Structural characterisation of graphene oxide flakes: thickness and lateral size measurement using Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM)”. The contribution will focus on developing validated quantitative measurement methods.
3. To provide a contribution to pre-normative international interlaboratory studies in VAMAS TWA 41 (graphene and related 2D materials), leading and participating in characterisation studies focused on structural and chemical properties using, X-ray Photoelectron Spectroscopy (XPS), AFM, Raman, and SEM techniques.
4. To work closely with the European and International Standards Developing Organisations, and pre-normative organisations, and the users of the Standards they develop, including the Graphene Flagship, to ensure that the outputs of the project are aligned with their needs and incorporated into Standards at the very earliest opportunity.

4 Results

The results of the project are detailed below against the project’s objectives:

4.1 ISO TS 21356-1 structural characterization standard

1. *To lead and provide a contribution to the publication “ISO TS 21356-1 Nanotechnologies – Structural characterisation of graphene: Part 1: Graphene from powders and dispersions”. The contribution will focus on measurement methods for the characteristics of graphene flakes in order to verify measurements made on commercial graphene flake products (WP1, WP2, WP3).*

Before the ISO Gscope project, there were no ISO standards on measurement and characterisation of graphene. This project aimed to lead and contribute to the development of key ISO standards in structural and chemical characterisation of graphene.

ISO TS 21356-1 Nanotechnologies – Structural characterisation of graphene: Part 1: Graphene from powders and dispersions was developed in ISO TC229 (nanotechnologies) and led by NPL, UK. NPL are also consortium leaders of the ISO GScope project. The development of 21356-1 began before the project and was initiated in 2015, with the initial text based on the NPL good practice guide to the characterisation of graphene.The document was developed over the next 5 years.

The ISO GScope project started in Autumn 2020. The consortium contributed to the final writing and editing of the text of the draft international standard. The standard was published in March 2021. The scope of the document is “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”.

Figure 1 shows the sequence of measurement for graphene flakes as published in ISO TS 21356-1 and also a consortium peer-reviewed publication in Nature Review Physics. Table 1 shows the table of contents for ISO TS 21356-1.

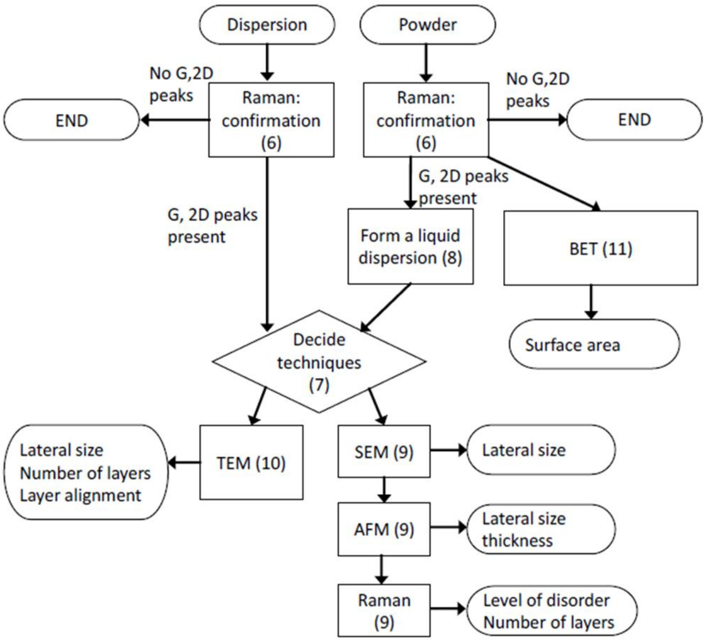

Figure 1. Order of methods for characterizing graphene flakes [after ISO TS 21356/1 and Clifford et al, Nat Rev Phys, 3 233-235 (2021)

Table 1. Table of contents for the first version of ISO/TS 21356-1:2021(en) Nanotechnologies — Structural characterization of graphene — Part 1: Graphene from powders and dispersions

Foreword	Annex B Structural characterization protocol using SEM, AFM and Raman spectroscopy
Introduction	B.1 General
1 Scope	B.2 Sample preparation
2 Normative references	B.3 SEM analysis
3 Terms and definitions	B.4 AFM analysis
4 Abbreviated terms	B.5 Raman spectroscopy
5 Sequence of measurement methods	Annex C Structural characterization using TEM
6 Rapid test for graphitic material using Raman spectroscopy	C.1 General
7 Preparing a liquid dispersion	C.2 Sample preparation for TEM
7.1 General	C.3 Measurement protocol
7.2 Preparing a dispersion of the correct concentration	C.4 Data analysis
8 Determination of methods	Annex D Lateral size and number fraction calculation
9 Structural characterization using optical microscopy, SEM, AFM and Raman spectroscopy	D.1 General
10 Structural characterization using TEM	D.2 Average lateral flake size
11 Surface area determination using the BET method	D.3 Number fraction
12 Graphene lateral size and number fraction calculation	Annex E Brunauer–Emmett–Teller method
Annex A Rapid test for graphitic material using Raman spectroscopy	E.1 General
A.1 General	E.2 Sample degassing
A.2 Sample preparation	E.3 Method

A.3 Method	E.4 Analysis Annex F Additional sample preparation protocols Bibliography

As can be seen in Table 1, for the first version of TS21356-1, the measurement protocols were only included in informative Annexes of the technical specification rather than as normative text in the main body. This was due to the fact that at the time interlaboratory tests had not been undertaken to validate the methods. These interlaboratory tests were run as part of this project. With NPL leading the AFM/SEM study of graphene flakes and INRIM leading the Raman spectroscopy study on graphene flakes. For these interlaboratory tests, protocols were developed by the consortium members based on the ISO technical specification measurement annex plus knowledge generated during the project. Details of the interlaboratory studies are provided in section 4.3. These interlaboratory studies tested and improved the protocols and enabled NPL, BAM and INRIM to understand sources of measurement uncertainties.

Following near completion of the interlaboratory studies, NPL presented the results and status at the May ISO TC229 meeting. This included presentation details on the measurement methods. The JWG2 committee decided to revise the document and to also convert it to a full international standard (IS) as opposed to its current state as a technical specification. An ISO TC229 ballot was held 3 June 2023 to 31 July 2023 to ratify this decision. This was approved with 23 countries voting yes and 8 countries nominating experts. Following this ballot is became an active work item in ISO TC229 with the first meeting of the revision taking place at the November 2023 meeting of ISO TC229.

In summary, the first version of ISO TS 21356-1 was published in March 2021. Interlaboratory testing was then held to develop, test and validate the measurement methods. In 2023 ISO TC229 open a new work item to revise 21356-1 and convert it into a full ISO standard. In conclusion this objective was achieved in full.

4.2 ISO TS 23359 chemical standard and ISO TS 23879 GO standard

2. *To lead and provide a contribution to the development of "ISO/PWI 23359 Nanotechnologies - Chemical characterisation for graphene in powders and suspensions" and to lead and provide a contribution to ISO/PWI 23879 "Nanotechnologies – Structural characterisation of graphene oxide flakes: thickness and lateral size measurement using AFM and SEM". The contribution will focus on developing validated quantitative measurement methods (WP2, WP4).*

As well as the structural characterisation of graphene flakes, other important international standards in two-dimensional materials that needed developing are a) in the chemical characterisation of graphene related two-dimensional materials (GR2M). This includes graphene, graphene oxide and functional variations of graphene. b) A standard on the structural characterisation of graphene oxide flakes using AFM and SEM.

For the chemical characterisation, before the project started NPL launched a provisional work item, namely "ISO/PWI 23359 Nanotechnologies - Chemical characterisation for graphene in powders and suspensions. When the project started, BAM and NPL wrote the first draft of the XPS method section of ISO PWI 23359, this included initial text, sub-headings and draft figures. In addition, NPL with BAM and in-liaison with NIM, China wrote the first draft of the whole of ISO PWI 23359. A metrology check-list and a draft new work item proposal form were written and sent to ISO TC229 JWG2 and circulated to the JWG2 committee in April 2021 and presented to the consortium and discussed at the May 2021 ISO TC229 JWG meeting. The go ahead to launch a new work item ballot was given. This ballot was held June to October 2021. The ballot was approved by a large margin with 9 pages of comments from experts. The document become an ISO work item. The ballot comments were discussed at the November 2021 ISO TC229 meeting.

BAM and NPL updated the XPS section of the draft standard based on the comments from the new work item ballot and those discussed at the November 2021 ISO TC229 meeting. The whole of the document was also updated led by NPL in conjunction with international experts (Univerity of Adlaide, Austrlia fo rhte TGA section and NIM, China for the other sections). This included the results of a TGA interlaboratory study undertaken outside of this project. The updates to the document were discussed at the May 2022 and November 2022 ISO TC229 meetings

The later meeting discussion particularly focused on the XPS interlaboratory study (ILC) (WP4). In addition, effort was made to collaborate well with the Chinese delegates such that their ILCs for other techniques finished well and could be incorporated in the standard. For one technique (FTIR) this proved not possible and the technical section was moved to an Annex. Following the May meeting, the document was updated by NPL and BAM including an annex detailing the XPS interlaboratory study (WP4) led by BAM. The document was then sent to the committee manager who initiated the committee draft consultation ballot where comments from all international participating countries will be discussed. The results from this consultation ballot will be discussed at the November 2023 ISO TC229 meeting.

The key figure from the draft ISO standard on chemical characterisation is shown in Figure 2 providing an overview of the standard.

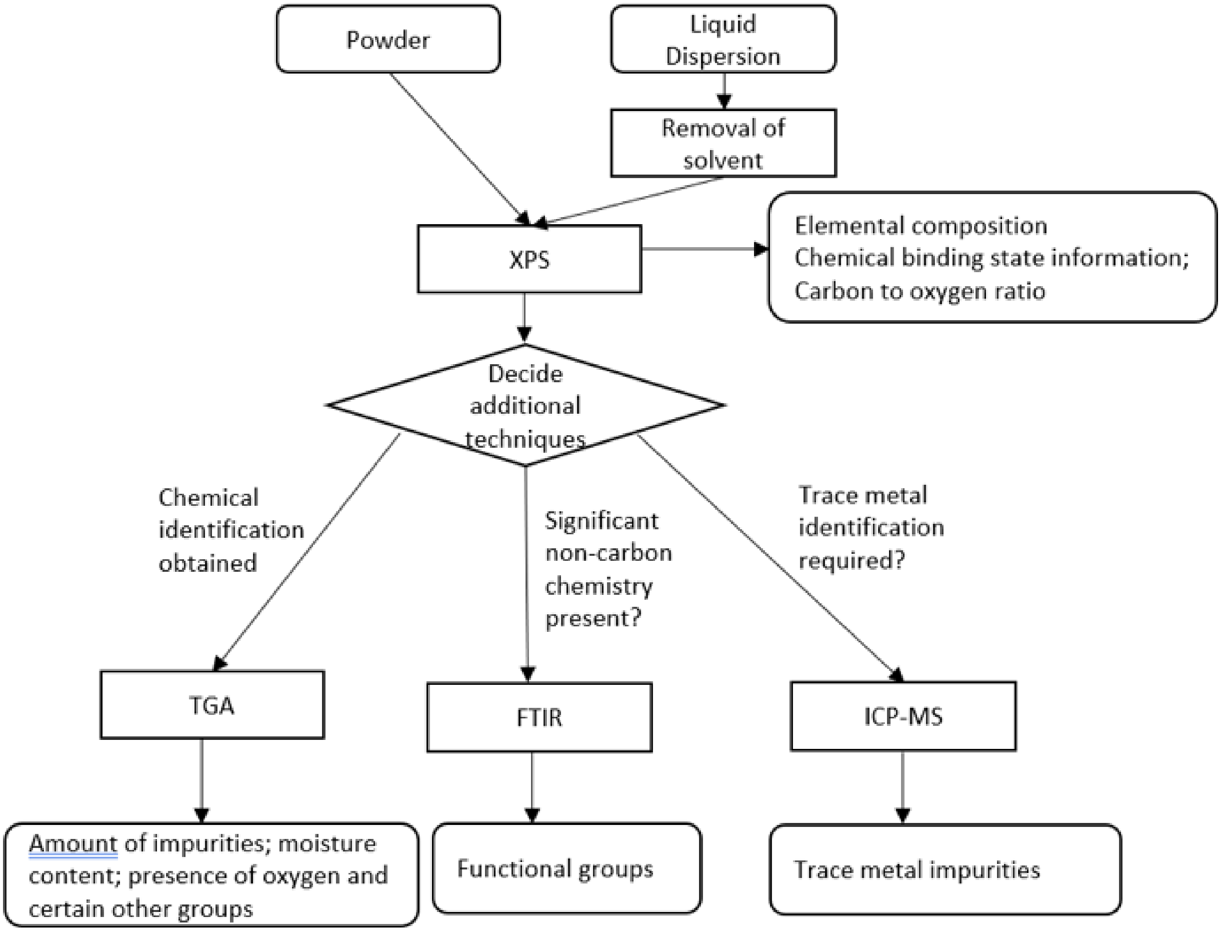

Figure 2. Overview of the sequence and process of the measurement methods used to determine the chemical properties of graphene-related two-dimensional materials from a powder or liquid dispersion included in ISO TS 23359.

Table 2 shows the table contents for the CD version of ISO TS 23359.

Table 2. Table of contents for ISO/TS 23359 Nanotechnologies — Chemical characterisation for graphene in powders and suspensions

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3 Terms and definitions 1	8 Thermogravimetric analysis (TGA) 15
4 Abbreviated terms 4	8.1 Introduction 15
5 Approaches to chemical characterisation 5	8.2 Sample preparation 17
6 X-ray photoelectron spectroscopy (XPS) 7	8.2.1 Instrument conditions 17
6.1 Introduction 7	8.2.2 Preparation of crucible 17
6.2 Instrument preparation 7	8.2.3 Measurement procedures 18
6.2.1 Instrument 7	8.3 Data processing 18
6.2.2 Relevant standards 7	8.3.1 Data plotting 18
6.3 Sample preparation 8	8.3.2 number of mass change steps 19
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For the other ISO standard developed as part of this deliverable: ISO/PWI 23879 Nanotechnologies- Structural characterization of graphene oxide flakes: thickness and lateral size measurement using AFM and SEM. This document is led by NIM in China, with NPL, UK as a co-lead. At the start of the project NPL, in liaison with NIM, drafted the first version of ISO/PWI 23879. This included a SEM method section and an AFM method section. These were circulated to ISO TC229 JWG2 experts and the document was presented at the November 2021 meeting. The JWG2 committee gave the go ahead for a new work item ballot led by China. As the document is led by China (Lingling Ren at NIM, China), the Chinese standardisation body (SAC) had to formally give its approval to launch the ballot. This approval took a while to come thought but it was finally given thanks to NPL and BREC for following this up with the Chinese. The new work item ballot was held 24 March 2022 until 17 June 2022. The document was approved as a work item with 26 countries approving the document and 13 countries nominating experts. Changes were made to the document by NIM and NPL in light of the comments received. This standards project was discussed at the May 2023 meeting of ISO TC229 held in Japan and also online. Changes were made to the document by NIM and NPL in light of the comments received.

While the committee procedures and comments were being received, BAM supported by NPL was working on improving the method and preparing for the interlaboratory study. Difficulties were encountered in preparing isolated flakes on substrates and removing “coffee ring” effects. Good samples were produced and BAM and NPL undertook a mini-international interlaboratory study. These efforts detailed in section 4.3 below. The knowledge gained from this mini-ILC in terms of SEM measurement method and data analysis document led to NPL updating the text of the draft standard. The document was then sent to the convenor of ISO TC229/JWG2 and project leader at NIM. The standard will continue to be developed beyond the lifetime of this project.

Figure 3 shows an overview of the measurement methods detailed in ISO TS23359 and table 3 details the table of contents in the standard.

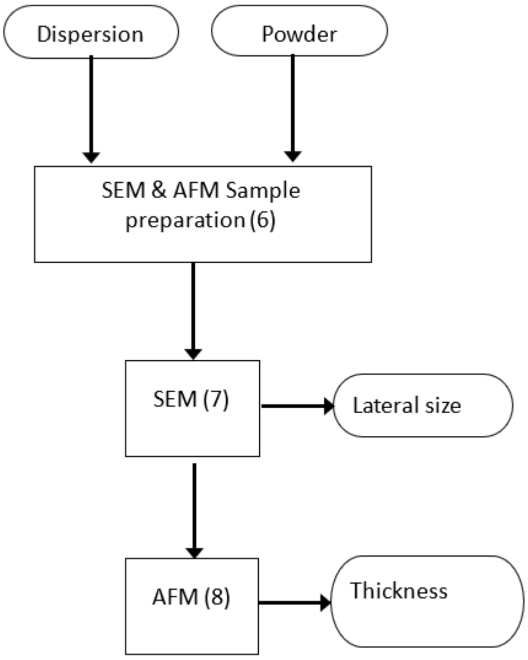

Figure 3. Overview of the sequence and process of the measurement methods used to determine the lateral size and thickness of graphene oxide flakes

Table 3. Table of contents for ISO/TS 23359 Nanotechnologies — Chemical characterisation for graphene in powders and suspensions

Foreword iv	9 Image and data analysis to obtain flake height 9
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2 Normative references 1	10 Reporting 10
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8 Atomic Force Microscopy 7	C.1 Introduction 17
8.1 Introduction 7	C.2 Summary of results 17
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In conclusion the consortium led the development of "ISO/PWI 23359 Nanotechnologies - Chemical characterisation for graphene in powders and suspensions" and led and provided a contribution to ISO/PWI 23879 "Nanotechnologies – Structural characterisation of graphene oxide flakes: thickness and lateral size measurement using AFM and SEM". This objective was achieved in full.

4.3 Interlaboratory studies

3. *To provide a contribution to pre-normative international interlaboratory studies in VAMAS TWA 41 (graphene and related 2D materials), leading and participating in characterisation studies focused on structural and chemical properties using XPS, AFM, Raman spectroscopy and SEM techniques (WP2, WP3, WP4).*

Versailles Project on Advanced Materials and Standards (VAMAS) supports world trade in products dependent on advanced materials technologies, through International collaborative projects aimed at providing the technical basis for harmonized measurements, testing, specifications, and standards. It is split into a number of technical working areas (TWAs) on various measurement aspects and types of materials. TWA41 is focused on Graphene and Related 2D Materials. The objective of this TWA is to validate different methodologies of measurement for graphene and related 2D materials. Studies aimed to determine the uncertainties associated in measurement, sample preparation, and data analysis where interlaboratory studies are conducted and the results will form the basis for future standardisation. Other relevant TWAs are TWA2 on surface chemical analysis and TWA20 on Raman spectroscopy and microscopy.

The consortium led four VAMAS studies on the analysis of GR2M. These were on i) XPS of functionalised graphene led by BAM, ii) Raman spectroscopy of graphene flakes led by INRIM, iii) SEM of graphene oxide led by BAM and AFM and iv) SEM of graphene flakes led by NPL. Running four interlaboratory studies enabled the consortium to develop a good framework and process when organising these studies.

The flyer for the XPS VAMAS study is shown in Figure 4. The aim of this ILC was to verify if reliable quantitative chemical analysis using XPS on functionalised graphene samples was possible with a relative uncertainty of less than 20%. And to use the method developed to fed into deliverable 3 on developing ISO TS23359, as detailed in section 4.2. Initial a mini-ILC was performed between NPL, KIT and BAM to evaluate the protocol before launching the main study.

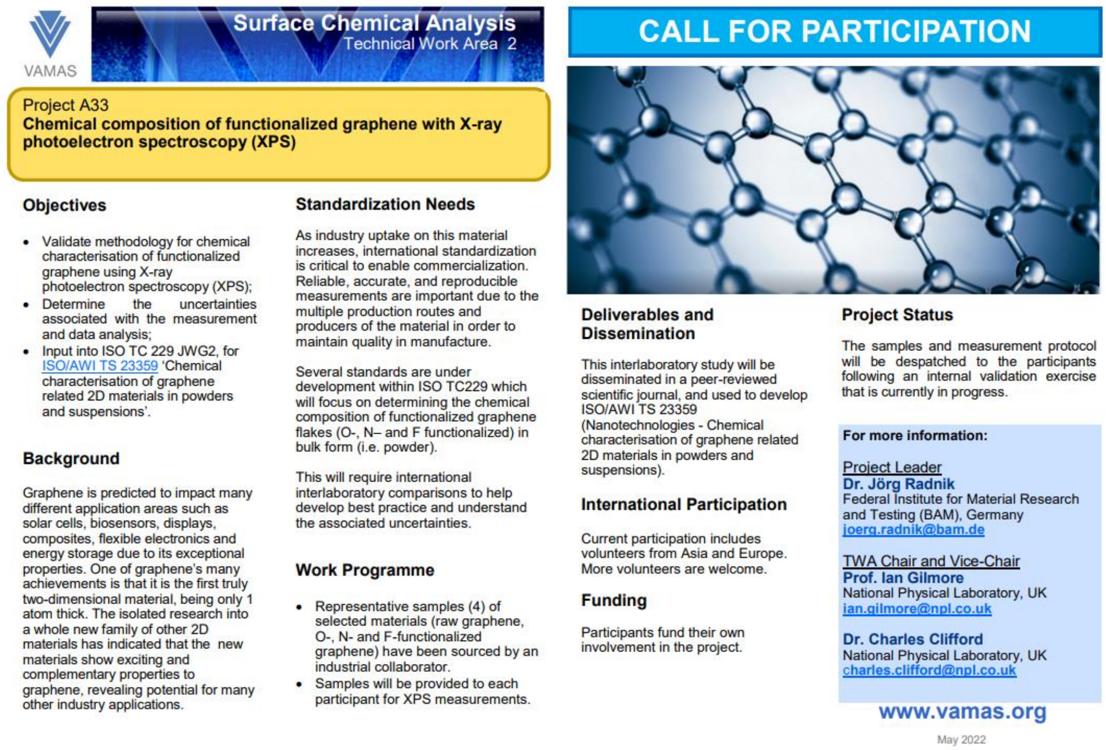

Figure 4. Flyer for the XPS VAMAS study led by BAM.

One of the things this studied was sample preparation and the differences between analysing powders versus pelletised powders. Figure 5 shows that pelletizing led to a lower amount of measured Oxygen using XPS compared to powder analysis. In addition, repeatability and standard deviation is lower for the pellet measurements. This showed that sample preparation must be considered.

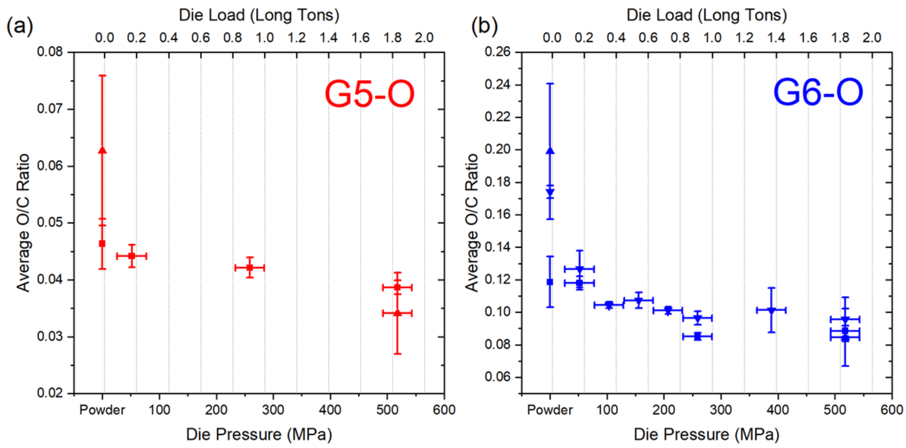

Figure 5 Effect of powders vs pellets (and pelletisation die pressure) on two different oxygen functionalised graphene samples (adapted from B.P. Reed et al. *Carbon* (2023) DOI: 10.1016/j.carbon.2023.1180540)

The full ILC had 27 participants from 14 different countries from Europe, Asia, North and South America. 21 participants sent results by the end of the study. The split of participants was 54% from research organisations, 14% from NMIs and 32% from industry. They were sent 4 graphene samples of unfunctionalised (raw), N, O and F functionalised graphene. These samples were prepared by Haydale. Participants are asked to analyse using both powders and pellet samples. Participants were also sent two reference samples to help calibrate their instruments, namely an ionic liquid, that was being tested as a potential reference material and a reference polymer sample. One example result from the ILC is shown in Figure 6 for the oxygen functionalised graphene.

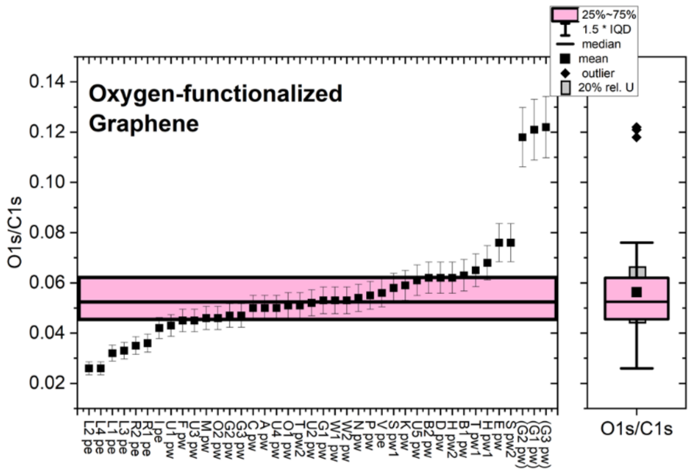

Figure 6 Result for the oxygen functionalised graphene sample from the XPS ILC.

Figure 6 shows that powder preparation is much more popular than using the pellet method. There were three outliers from one laboratory. This was found to be due to humidity in the lab. For the results, 20 % relative uncertainty covered more than 50% of the results. In conclusion for the XPS study it was found that reliable quantification with XPS is possible for industrial graphene nanoplatelets. The relative uncertainty of the measurements of approximately 20 % is realistic. It is important that information about the sample preparation (pellet, powder in recess or on tape) is provided when undertaking measurements of this type as sample prep affects the results. In addition humidity can play a role and additional nformation about the morphology (SEM, XRD, BET) if helpful when for evaluating the quantification results. The learning from this study aided the development of ISO TS23359.

Figure 7 shows the VAMAS flyer for the Raman spectroscopy VAMAS study led by INRIM. The objectives of the study were to study the localization of the flakes and the quantification of the number of layers of graphene nanoplatelets. In a broad sense to validate a standard methodology for the determination of the number of layers of few-layer graphene flakes using Raman spectroscopy and to determine the uncertainties associated with the measurement and data analysis. Hence to input into the revision of ISO/TS 21356-1 "Structural Characterization of Graphene" within ISO TC229 JWG2

VAMAS

Graphene and Related 2D Materials
Technical Work Area 41

CALL FOR PARTICIPATION

Project 11

Determination of disorder and number of layers of graphene flakes by Raman Spectroscopy

Objectives

- Validate a methodology for the determination of disorder and number of layers of graphene flakes deposited on Si/SiO_2 substrates, using Raman spectroscopy;
- Determine the uncertainties associated with the measurement and data analysis;
- Input into ISO TC229 JWG2, for ISO/TS 21356-1 'Structural Characterisation of Graphene'.

Background

Graphene is predicted ito impact many different application areas such as solar cells, biosensors, displays, composites, flexible electronics and energy storage due to its exceptional properties. One of graphene's many achievements is that it is the first truly two-dimensional material to be synthesised, being only one atom thick. The isolated research into a whole new family of other 2D materials has indicated that these new materials show exciting properties complementary to graphene, revealing potential for many other industry applications.

Standardization Needs

There are currently over 100 commercial 'graphene' producers worldwide, including leading graphene producers in Europe, with an 'on paper' offering of materials with vastly different properties and types. However, many suppliers (and buyers) are hindered due to uncharacterised material that can be more often than not ascribable to graphite rather than graphene, or have high batch to batch variations.

On the other hand, standards cannot be developed without proven and verified methodologies. Normative documentary standards are based on methods or procedures developed through interlaboratory studies and verified internationally.

With this project and the resultant standard, the entire supply chain of graphene from manufacturers to application builders and consumers will profit from clear material specifications and globally accepted characterisation standards. The suppliers will see a stable demand for their high value high quality products. Application builders will profit from reliable and traceable materials supply as well as comparability and traceability of various parameters to metrological standards. This will further enhance the development of advanced graphene applications, and consumers will ultimately profit with greater choices of technology, as well as reliable functionality due to well-specified materials used in the products. The impact is therefore on the entire supply chain and it does not depend on the graphene price or application hype in the market.

Work Programme

Graphene flakes deposited onto Si/SiO_2 substrates will be used for Raman spectroscopy measurements. Samples will be sourced in the framework of the EMPIR project ISO-G-SCoPe and provided to each participant following a preliminary study for defining the optimal conditions for the Raman spectroscopy measurements.

Deliverables and Dissemination

This interlaboratory study will be disseminated in a peer-reviewed scientific journal, and used to contribute to "ISO TS 21356-1 Nanotechnologies. Structural characterisation of graphene: Part 1: Graphene from powders and dispersions", focusing on the standardisation of the measurement methods.

International Participation

Current participation includes volunteers from Italy, UK, and Spain. More volunteers are welcome.

Funding

Participants fund their own involvement in the project.

Status

The project is in progress with a duration of 18 months for completion.

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www.vamas.org
April 2022

Figure 7. Flyer for the Raman spectroscopy VAMAS interlaboratory study led by INRIM.

For this study, two samples were used and prepared by LNE, NPL, Haydale and UoM. Electrochemically exfoliated (ECE) were from a commercially available powder containing few layer graphene and deposited onto substrates made by C2N. The aim here was to test the method for commercial samples. The second sample of mechanically exfoliated flakes was used to demonstrate the ability of Raman spectroscopy to locate flakes and to identify the number of layers of the graphene nanoplatelets.

The samples were characterised by AFM and Raman spectroscopy by INRIM. Participants then performed their own measurements with the data sent back to INRIM who also analysed the data. Ten participants took part from Europe, USA, Brazil, China and Japan. The measurements based on Raman spectroscopy for identification of number of layers in graphene were found to be consistent in the ILC. Here, the identification of single layer graphene has the highest consistency. When the results were not consistent, it was found that it was clearly a problem of location of the same exact area between participants. The results are shown in Figure 8.

The results taken on graphene samples with more than one layer show some variations in the ILC results It was found that the nature of layer stacking should be also considered while analysing the samples with Raman spectroscopy as twisted graphene show signatures (2D peak width) similar to single layer graphene. Hence optical microscopy and or other techniques should be used in conjunction as a complementary tool to determine the number of layers. The position of the 2D peak can also be used as an alternative criterion for determining the number of layers. There could be variation in results because of the different fitting methods used to fit the 2D peak. The ILC was completed successfully.

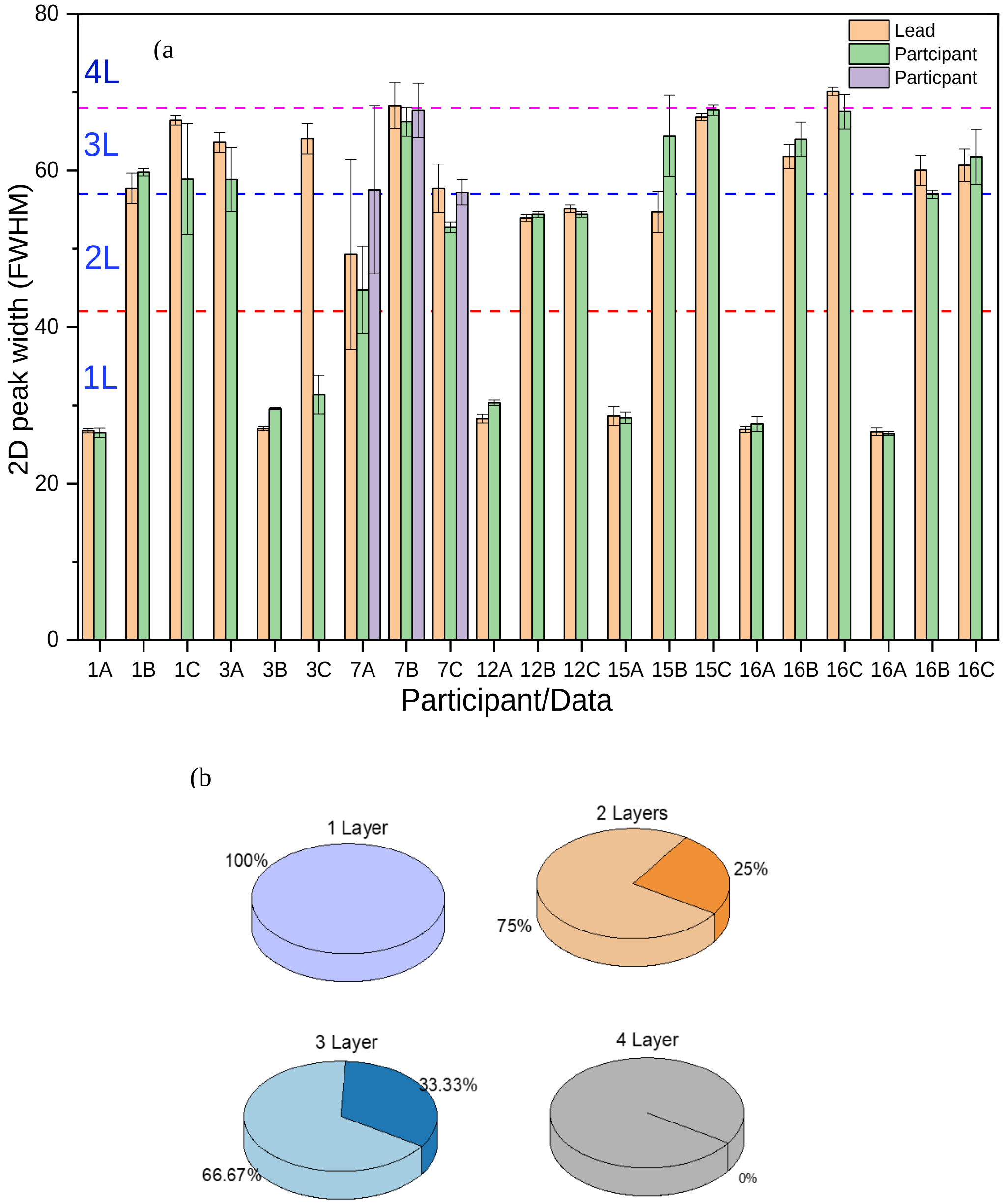
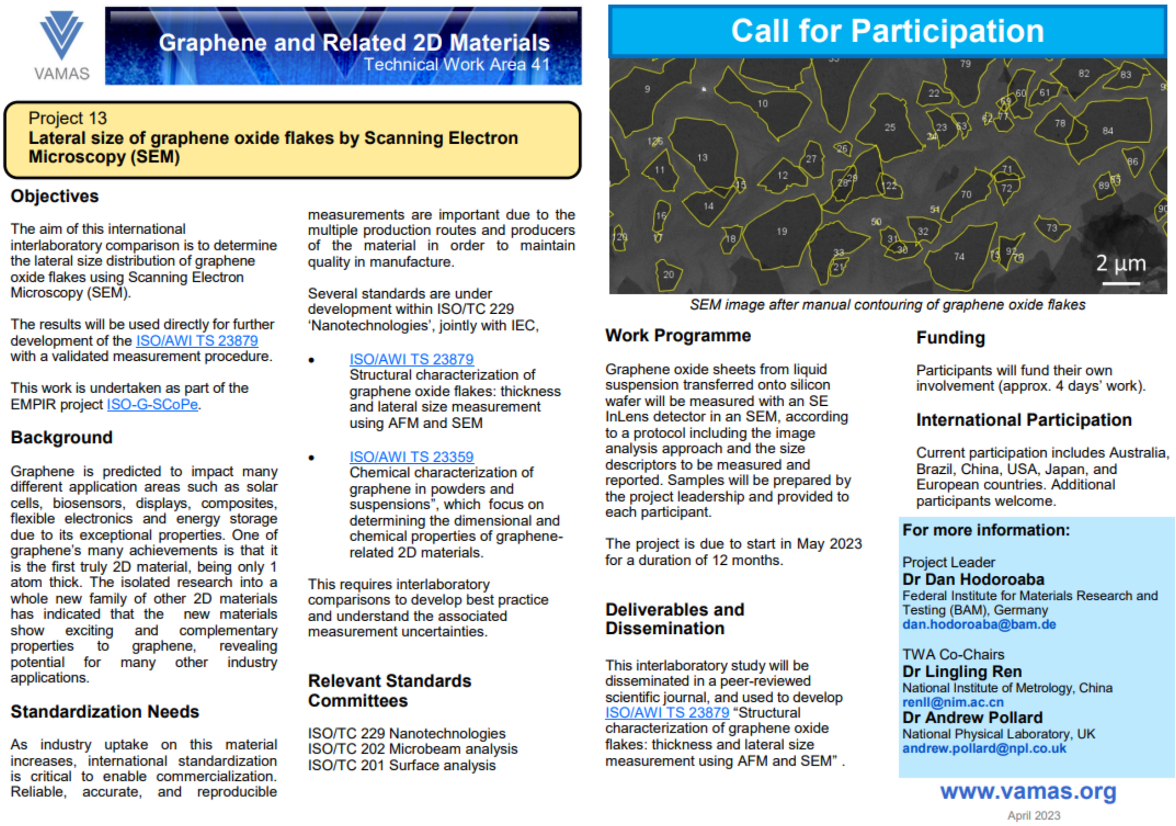


Figure 8. Results of the ILC study for the validation of Raman spectroscopy as at tool for the identification of number of layers on Mechanically exfoliated graphene samples a) Peak width values and standard uncertainty. b) Number of samples in accordance between participant and Lead Partner: 100 % for single-layer, 75 % for two-layer, 67 % for three-layer, and 0 % for four-layer.

Figure 9 shows the VAMAS flyer for the SEM of graphene oxide flakes VAMAS study led by BAM. Due to a number of issues, this study is continuing beyond the end of the lifetime of the project. Hence the consortium and particularly BAM and NPL focused on preparing samples and the protocol for the main VAMAS interlaboratory study under VAMAS TWA41 and a mini-interlaboratory study run between BAM and NPL.

BAM produced a draft protocol which was edited by NPL. Samples were prepared by BAM and consisted of a commercial graphene oxide sample deposited onto a Si/SiO2 substrate by BAM. Lately these have been sent out to at least 8 international participants for the VAMAS interlaboratory study, a flyer for which is shown in Figure 9.


VAMAS

Graphene and Related 2D Materials
Technical Work Area 41

Project 13
Lateral size of graphene oxide flakes by Scanning Electron Microscopy (SEM)

Objectives

The aim of this international interlaboratory comparison is to determine the lateral size distribution of graphene oxide flakes using Scanning Electron Microscopy (SEM).

The results will be used directly for further development of the ISO/AWI TS 23879 with a validated measurement procedure.

This work is undertaken as part of the EMPIR project ISO-G-SCoPe.

Background

Graphene is predicted to impact many different application areas such as solar cells, biosensors, displays, composites, flexible electronics and energy storage due to its exceptional properties. One of graphene's many achievements is that it is the first truly 2D material, being only 1 atom thick. The isolated research into a whole new family of other 2D materials has indicated that the new materials show exciting and complementary properties to graphene, revealing potential for many other industry applications.

Standardization Needs

As industry uptake on this material increases, international standardization is critical to enable commercialization. Reliable, accurate, and reproducible measurements are important due to the multiple production routes and producers of the material in order to maintain quality in manufacture.

Several standards are under development within ISO/TC 229 'Nanotechnologies', jointly with IEC,

- ISO/AWI TS 23879
  Structural characterization of graphene oxide flakes: thickness and lateral size measurement using AFM and SEM
- ISO/AWI TS 23359
  Chemical characterization of graphene in powders and suspensions", which focus on determining the dimensional and chemical properties of graphene-related 2D materials.

This requires interlaboratory comparisons to develop best practice and understand the associated measurement uncertainties.

Relevant Standards Committees

ISO/TC 229 Nanotechnologies
ISO/TC 202 Microbeam analysis
ISO/TC 201 Surface analysis

Call for Participation

2 µm

SEM image after manual contouring of graphene oxide flakes

Work Programme

Graphene oxide sheets from liquid suspension transferred onto silicon wafer will be measured with an SE InLens detector in an SEM, according to a protocol including the image analysis approach and the size descriptors to be measured and reported. Samples will be prepared by the project leadership and provided to each participant.

The project is due to start in May 2023 for a duration of 12 months.

Deliverables and Dissemination

This interlaboratory study will be disseminated in a peer-reviewed scientific journal, and used to develop ISO/AWI TS 23879 "Structural characterization of graphene oxide flakes: thickness and lateral size measurement using AFM and SEM" .

Funding

Participants will fund their own involvement (approx. 4 days' work).

International Participation

Current participation includes Australia, Brazil, China, USA, Japan, and European countries. Additional participants welcome.

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April 2023

Figure 9. Flyer for the SEM of Graphene Oxide VAMAS study led by BAM.

For the mini-ILC. 2 samples were analysed using Scanning Electron Microscopy (SEM) by both BAM and NPL. At least 200 flakes on each sample were measured and analysed. Detailed image and data analysis of the flakes' lateral dimension was undertaken through an image processing software. This invoved the comparison of two methods: a) perpendicular bisector method and contouring method. In addition, the same images obtained from the measured are then analysed according to two different approaches. Example results are shown in Figure 10.

The main conclusions of the mini-ILC were:

i) The influence of the SEM operator as well as the possible local inhomogeneities of the GO flakes with different sizes were observed and different flakes chosen to analyse were found to be the main source of uncertainties in the final result of size.

ii) Somewhat surprisingly, no systematic deviations between the shapes of the GO flakes were found, even if the flake sizes differ.

iii) Regarding the two proposed image analysis approaches A1 and A2, the size difference is below 5%, but the difference in shape is 7-8%. The explanation is that the size descriptors measured in the two approaches are slightly different.

iv) More statistics as that provided by a full international interlaboratory study will consolidate the results found in the mini-ILC.

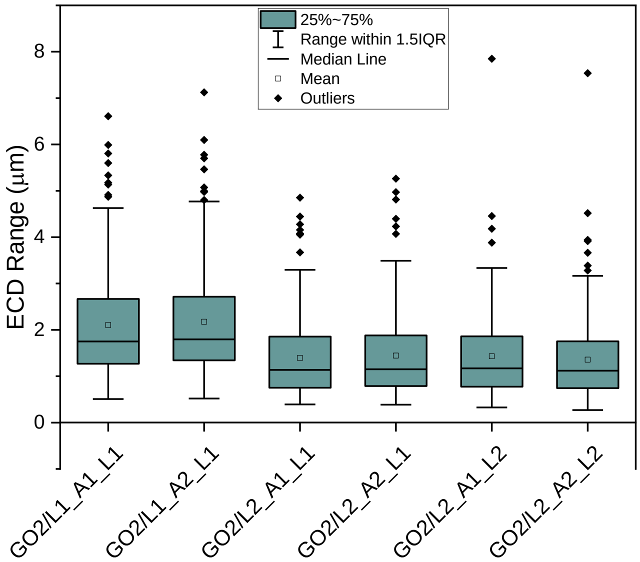

Figure 10. Bar chart representation of the ECD distributions for GO2 for both contouring (A1) and perpendicular bisector (A2) approach, on the same images, same flakes, and by two different image analysts L1 and L2.

Guidance developed in this objective includes i) how to prepare properly GO flakes on a substrate for SEM measurements, ii) under which exact conditions should the SEM measurements run, iii) which approaches and size and shape descriptors can and shall be used in the analysis of the images acquired, iv) how to compile the data, and how v) to report the results.

The fourth ILC involved combining AFM and SEM to measure commercial graphene flakes and was led by NPL. The flyer for this is shown in Figure 11.


VAMAS

Graphene and related 2D materials
Technical Work Area 41

CALL FOR PARTICIPATION

Project 12

Distribution of lateral size and thickness of few-layer graphene flakes using SEM and AFM

Objectives

The aim of this international interlaboratory comparison is to determine the lateral flake size distribution of graphene nanoplatelets (GNPs) using scanning electron microscopy (SEM), and correlate these to measurements of lateral flake size and thickness, using atomic force microscopy (AFM).

The results of the study will be used directly for future revision of ISO/TS 21356-1 with a validated measurement procedure. This work is undertaken as part of the EMPIR project ISO-G-SCoPe.

Background

Graphene is an exciting advanced material, present in the form of flakes in powders or liquid dispersions and in larger sheets grown through bottom-up processes. GNPs in flake form are already starting to find commercial application via small-to-medium enterprises (SMEs) to multi-national corporations, for a large range of application areas. There are currently over 100 commercial 'graphene' producers worldwide, including leading graphene producers in Europe, with an 'on paper' offering of materials with vastly different properties and types. However, many suppliers (and buyers) are hindered due to uncharacterised or poorly characterised material that can be more often graphite rather than GNPs or have large batch-to-batch variations. Products and applications suffer as a result. The aim is to produce validated measurement methods of GNPs.

Standardisation Needs

The recently published ISO/TS 21356-1 'Structural characterisation of graphene from powders and liquid dispersions' details protocols to characterise the lateral size and thickness of graphene and few-layer graphene flakes. However, these sections remain informative, until the typical variation in values obtained by different users/equipment can be validated through a VAMAS study.

Issues addressed by this standard include structural determination on the number of layers present, their thickness, homogeneity and flake size distribution between the batches. These are all issues at the nanoscale, especially thickness where a combination of measurement method, metrology and correlative imaging is needed.

Example SEM image focused on an individual flake. The yellow lines drawn on the flake indicate the lateral size measurements.

Work Programme

GNPs deposited onto different Si/ SiO_2 substrates will be provided for each participant for SEM and AFM measurements.

Participants will be asked to measure these samples along with calibration check samples and report the lateral flake size and thickness observed.

Duration

One year beginning June 2022.

Deliverables and Dissemination

Report will evaluate the variance observed of the associated measurement protocol, to guide further development. Results will be published in a peer-reviewed journal and will be directly used in ISO/IEC standards.

High resolution topographic AFM image of an individual flake.

Funding

Participants in the interlaboratory comparison will fund their own involvement (approx. 4 days' work).

International Participation

Current participants represent the UK, EU, China and the USA. Wider regional participation would be greatly welcomed.

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April 2022

Figure 11. Flyer for the AFM/SEM VAMAS study led by NPL.

The aim of the study was to determine the lateral flake size distribution of graphene nanoplatelets (GNPs) using scanning electron microscopy (SEM), and to then correlate this distribution to measurements of lateral flake size and thickness using atomic force microscopy (AFM). The outcomes of the ILC directly inputted in the future revision of the international standard ISO/TS 21356-1, providing an insight on method variability and objective data to build robust and widely applicable measurement procedures across different instrument models and laboratories.

The samples consisting of samples for SEM and AFM along with calibration grids (built into the sample for AFM) were sent out to 26 participants from Africa, Australia, America, Asia and Europe. From those 17 participants submitted results. These sample sets were analysed both the participants and also by the lead participant (NPL). Example results for 13 participants using SEM to measure the graphene flakes is shown in Figure 12.

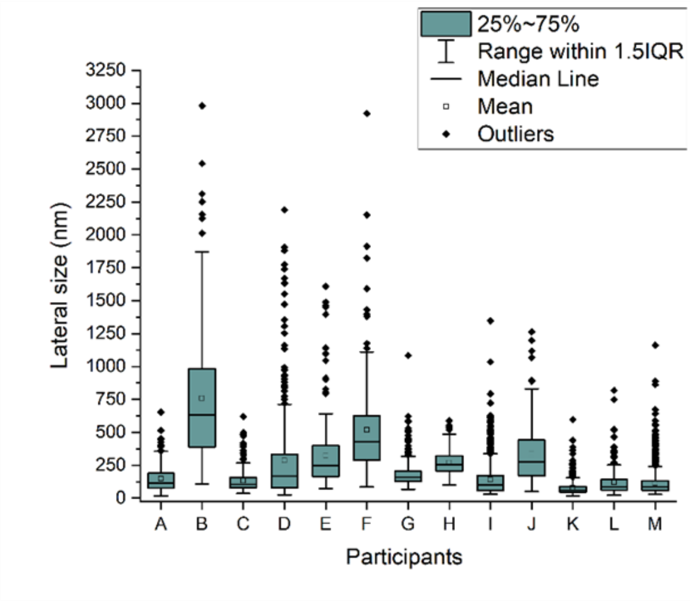

Figure 12: Example results for the SEM/AFM interlaboratory study. Here Boxplots with the median, the mean and the interquartile range (IQR) of the SEM data are shown. The inner 50 % of the results (25%~75%) are highlighted.

Differences in average lateral size and thickness results were seen, these were due mainly to incorrect flake selection by the participants with three outliers particular identified. Poor flake selection proved to be the main source of uncertainty for this study. Several participants were asked to repeat results after which improved results were found.

The results provided us with the factors that most contribute to the uncertainty in this type of measurements. In particular, this study has shown that user bias in flake selection is a major source of uncertainty, and variation between the different laboratories. This is particularly important when working with a ‘real world’ graphene sample that are used by industry, as in this case. Greater guidance on flake selection is required in the ISO standards. The results also highlight that the measurements require a high degree of expertise in SEM, AFM measurements of graphene. The study has also shown that in this type of industrial samples there is not an obvious correlation between the thickness and lateral size of flakes. For these reasons, verified standard protocols are required. The results from this study will enable improved methods within the revision of ISO/TS 21356-1 (Structural characterization of graphene from powders and liquid dispersion).

In conclusion, the consortium has led four pre-normative international interlaboratory studies on characterisation studies focused on structural and chemical properties using XPS, AFM, Raman spectroscopy and SEM techniques of graphene, functionalized graphene and graphene oxide. This objective was completed in full.

5 Impact

The consortium put a strong emphasis on impact from the outset and throughout the duration of the project. There was strong engagement with key stakeholders both in Europe and internationally via the interlaboratory studies and the accompanying standards development. This included international metrology institutes (for example from USA, Canada, Japan, China, Brazil and India) as well as large and SME industry companies and academia. The consortium partnered with the Graphene Flagship project and industry associations such as the Graphene Council and the nanotechnologies industry association as well as industry, standards bodies and other key players. This included joint workshops, conferences and YouTube videos. Strong engagement and input into the project were received by these at the stakeholder's advisory group meeting.

Sustained awareness and impact have been achieved throughout the project via 51 presentations at international, European and national conferences and workshops including many invited talks. Consortium members were extremely active in key standardisation committees including ISO TC229. Members have participated in 46 meetings, including general participation, presentation of the project, and leading the development of new standards.

A website was created to provide general information and to promote news stories from the project. The consortium had Twitter and LinkedIn accounts, with consortium members also posting updates of the project on Linkedin using their own accounts. The first publication highlighting the publication of the first graphene measurement standard (ISO TS21356-1 led by the consortium) was published in Nature Review Physics. A second publication on Raman spectroscopy of graphene has also been published. A third publication on the preparation of graphene material has been published. Two other papers on XPS of functionalised graphene were published. Four of the publications were joint publications between different consortium members.

Impact on industrial and other user communities

At the start of the project, there were over 100 commercial ‘graphene’ producers worldwide, including leading graphene producers in Europe, with an 'on-paper' offering of materials with vastly different properties and types. However, many suppliers (and buyers) were hindered due to uncharacterised material that can be more often graphite rather than graphene or have batch-to-batch variations. With this project and the resultant standards, the entire supply chain of graphene from manufacturers to application builders and final consumers will profit from clear material specifications and globally accepted characterisation standards. This will lead to suppliers seeing a stable demand for their high-value high-quality products.

Application builders will profit from reliable and traceable materials supply as well as comparability and traceability of various parameters to metrological standards. This will further enhance the development of advanced graphene applications and will ultimately profit ordinary consumers with greater choices of technology as well as reliable functionality due to well-specified materials used in the products. The impact is therefore on the entire supply chain and it does not depend on the graphene price or application hype in the market.

Once the material itself is characterised reproducibly and in a way that allows cross-comparison, real-world products can be tailored and improved using specific types of graphene and related 2D materials. These products include those in solar cell and battery production, composites and coatings, aerospace and automotive products (that need strong lightweight components), along with advanced clothing and consumer products. Transparent and consensus-driven metrology of graphene will enable companies that are producing and using graphene in these and other future applications to have a clear and sustainable business, reliable products and a safer environment.

Impact on the metrology and scientific communities

Based on the project's results, validated methods for characterising the structural and chemical properties of graphene using SEM, AFM, XPS and Raman spectroscopy were and will be made available to the metrology and scientific communities via peer-reviewed publications and European and international standards. This will create a large impact on measurement and test laboratories which will be able to measure the increasing number of materials being produced by companies worldwide to an accredited standard. In addition, academics will be able to better reproduce scientific results, assess the applicability of results to different technology areas under investigation and understand how the material properties affect the performance of lab-scale products for different application areas.

The uncertainties for measuring the properties of graphene such as flake size, chemical composition, thickness, number of layers, etc were up to 50 % currently and will reduce typically by at least a factor of two.

The metrology and scientific communities had the opportunity to take part in international interlaboratory studies enabling them to benchmark themselves against peers, along with a chance to improve their abilities to measure graphene more accurately. On a broader scope, the project has strengthened the collaboration of European NMIs in the area of nanomaterials and will increase their competitiveness and consistency in graphene characterisation in a competitive international market.

Impact on relevant standards

Standards cannot be developed without proven and verified methodology. Normative documentary standards are based on methods or procedures developed through interlaboratory studies and verified internationally. Before the project commenced there were no graphene standards available beyond terminology and an overview technical report, neither of which contains such verified methodology. This project targeted the current gaps by leading four international interlaboratory studies and leading the development of three international standards in ISO TC229 and IEC TC113. This project will directly lead to the faster publication of these standards internationally and as European standards via CEN TC352. To this end, the first graphene measurement standard ISO TS 21356-1 on structural characterization of graphene was published in March 2021 led by the consortium with the other standards led by the consortium due to be published in the next year or two.

Longer-term economic, social and environmental impacts

Standards in general, but graphene standards in particular, aim to provide a level-playing field for the graphene industry where the main beneficiary is the customer – the innovative product developer and the final consumer. Without clear standards and accepted specifications, it is impossible to develop such a sustainable supply chain. Some previous nanomaterials have bypassed specification developments with companies arguing their unique properties and have subsequently found low acceptance and application of their “wonder material” by the global market. Without this project, these standards would have taken substantially longer to publish and would not have a larger amount of informative content, both of which would have hampered the industry and led to the possibility that companies would have developed different internal processes. This would have led to a substantial amount of time and investment wasted and require further effort to rectify. As most companies in this industry are SMEs, this could have led to otherwise very profitable companies struggling to survive financially. This would have been a substantial loss to the market overall and hamper advances in technology.

Many industries that use graphene including flexible electric/photonics, solar cells, and various medical, chemical and industrial processes will benefit from the well-characterised graphene that will be able to be obtained as a result of this project. The purchasers of graphene will also benefit from the confidence of being able to purchase graphene with known properties and less batch-to-batch variability. Without overcoming this metrological barrier, the potential of this disruptive material will not be truly realised and thus advancements in many important grand challenges, such as the aging population, the internet of things, light-weighting, and improvements in energy storage, will be slower.

6 List of publications

1. Clifford, C.A., Martins Ferreira, E.H., Fujimoto, T. et al. The importance of international standards for the graphene community. Nat Rev Phys 3, 233–235 (2021). https://doi.org/10.1038/s42254-021-00278-6

2. Sacco A.,Portesi C.,Giovannozzi A.M., Rossi A.M. Graphene edge method for three-dimensional probing of Raman microscopes focal volumes. Journal of Raman Spectroscopy 52(10) 1671-1684 (2021) https://doi.org/10.1002/jrs.6187

3. Chemello G., Radnik J., Hodoroaba V-D. Analysis of Industrial Graphene-Based Flakes – First Results on Morphological Characterization, Sample Preparation and Chemical Composition. Microscopy and Microanalysis, 28(S1), 1006–1008 (2022), https://doi.org/10.1017/S1431927622004342

4. Reed B. P., Marchesini S., Chemello G, Morgan D.J., Vyas N., Howe T., Radnik J., Clifford C.A., Pollard A.J., The influence of sample preparation on XPS quantification of oxygen-functionalised graphene nanoplatelets, Carbon 211, 118054 (2023) https://doi.org/10.1016/j.carbon.2023.118054

5. Chemello G., Knigge X., Ciornii D, Reed B.P., Pollard A.J., Clifford C.A., Howe T., Vyas N., Hodoroaba V.-D., RadnikJ. Influence of the Morphology on the Functionalization of Graphene Nanoplatelets Analyzed by Comparative Photoelectron Spectroscopy with Soft and Hard X-Rays, Advanced materials interfaces, 10(20) 2300116 (2023) https://doi.org/10.1002/admi.202300116

This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/

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