Round Robin characterization

Marie Ernstsson, Ann-Sofi Kindstedt Danielsson and Karin Persson, RISE

Melina da Silva and Ola Lyckfeldt, RISE IVF

Szymon Sollami Delekta, Viktoriia Mishukova, Kristinn Gylfason, Frank Niklaus, Mikael Östling and Jiantong Li, KTH Royal Inst. of Technology

Johan Ek Weis, Chalmers Industriteknik

2019-03-06

Innehåll:

Introduction

There are many different kinds of graphene materials available on the market. However, the suppliers do not specify the material in an equivalent way. It can therefore be difficult to find graphene with desired and well-defined properties. In order to ensure the availability of quality-assured graphene, SIO Grafen have initiated characterization cheques where Swedish companies can get funding to characterise and quality-proof graphene materials. Data from these characterisations are used to build up an open database of quality assured graphene materials.

In order to accelerate the work of building the open database, this complementary Round Robin project was started. The purpose of the project was also to increase the knowledge within the Swedish network of how to characterise graphene.

Four measurement techniques X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), Thermal Gravimetric Analysis (TGA) and the Brunauer–Emmett–Teller (BET) method were used by three analysis providers to characterise six different graphene materials. Two of the techniques were used by two of the companies in parallel such that the results can be compared. The aim was to have all analysers use all the measurement techniques. However, we were not able to engage organisations offering all techniques.

Investigated material and characterisation techniques

A combination of different techniques was chosen in this project:

- Thermal Gravimetric Analysis (TGA) is a technique where the mass of a material is measured as a function of temperature. It can therefore give information of for example thermal decomposition.
- BET is a method for measuring the surface area. This is a relatively straightforward technique, with limited sample preparation needed. As the surface area of a monolayer is known (2 630 m^2/g), an approximate number of layers can be estimated by dividing this number by the measured surface area of the sample.
- X-ray Photoelectron Spectroscopy (XPS) was chosen as it is an excellent technique for chemical characterization of surfaces, and it is straightforward to quantify data into the

surface chemical composition expressed in atomic%, with very limited need for sample preparation.

- Scanning Electron Microscopy (SEM) is a common technique for imaging small objects. SEM images can provide a lot of information and the lateral size can be analysed. The drawback for SEM analysis of graphene, is that the sample preparation is important for the result and can be challenging.

Analysis providers within Sweden could apply to participate in the project through an open call. The participants and their characterisation techniques are listed in Table 1.

Table 1 Analysis providers and the characterisation techniques they used.

Analysis provider	Characterisation techniques
KTH Royal Institute of Technology	SEM
RISE Research Institutes of Sweden	BET and XPS (additionally TGA)
RISE IVF (previously SWEREA IVF)	BET and SEM (additionally helium pycnometry)

In order to ensure that graphene material relevant for the Swedish industry would be characterised, project managers of previous projects within SIO Grafen were invited to suggest materials to be analysed. The three suppliers with the highest number of votes were selected, and two different types of graphene material were purchased from each supplier. There was a larger interest in GNP materials (four products) compared to GO and rGO (one product each), as listed in Table 2. The program office of SIO Grafen redistributed the graphene samples in anonymous containers in order to eliminate any kind of unintentional bias by the analysis providers.

The analysis providers were informed of the type of graphene (GNP, rGO or GO) and any recommendations regarding solubility in any solvents as provided by the material suppliers. The term GNP is here used to describe any material with a lower oxygen content than rGO and GO, and not with the purpose of distinguishing between thinner and thicker material. This was needed in order to facilitate the handling of the material and for the sample preparation.

Table 2 Characterised graphene products, as selected by project managers of previous projects within SIO Grafen.

Supplier	Product	Type of graphene
2D Fab	Standard	GNP
2D Fab	Extra exfoliated	GNP
Abalonyx	1.8	GO
Abalonyx	2.1	rGO
XG Science	XGNP M25	GNP
XG Science	XGNP C750H	GNP

The good practice guide on characterisation of the structure of graphene[1] developed by the National Physical Laboratory (NPL) was used as a reference and starting point for the sample preparation and characterisation, especially for the SEM studies.

Thermal Gravimetric Analysis, TGA

TGA was not included as one of the initially intended measurement techniques. It was added as the information from a TGA analysis could provide important information for the sample preparation for the BET and XPS measurements. The TGA measurements were performed using a Mettler Toledo TGA 2 system under a nitrogen flow of 50 ml/min. The ash content was analysed after 10 min at 800 °C under an oxygen flow of 50 ml/min.

The TGA measurements showed good reproducibility between runs. The moisture content (weight loss under 100 °C) was significantly higher for GO than the other samples, as expected. The GO additionally had a very sharp weight loss at approximately 210 °C. These weight losses are assumed to correspond to the removal of oxygen containing groups on the surface of the flakes.

The rGO is manufactured by reduction of GO. This process removes the more volatile oxygen groups and leaves more stable oxygen groups on the edges of the flakes. The TGA analysis of rGO therefore shows a significantly larger relative weight loss at higher temperatures than the GO. The proportion of this weight loss is similar for rGO and GO if the signals are normalized after the most volatile components of GO have been removed. That is, the amount

of more stable oxygen groups in rGO and GO are similar. This is not unexpected as the GO and rGO are from the same producer, but significantly different result could be observed when comparing rGO and GO from different producers.

Both GNP samples from 2D Fab had a very small weight loss (0.5 wt%) all the way up to 800 °C. The GNP samples from XG Science behaved similarly to each other with 2-3 wt% loss up to 100 °C and 8-9 wt% in the high temperature range, see   Table 3. Only a very limited amount of ash content was detected in the investigated samples.

Table 3 Weight loss in different temperature ranges as measured by TGA.

Sample	Weight loss 25-100 °C (wt%)	Weight loss 100-250 °C (wt%)	Weight loss 250-800 °C (wt%)	Ash (wt%)
XGNP M25	1.8	0.8	8.1	0.4
Abalonyx 2.1	3.4	0.8	23.4	1.3
XGNP C750H	3.1	1.0	8.9	-0.3
2D Fab extra	0.0	0.4	0.2	0.9
Abalonyx 1.8	11.9	78.9	3.7	0.2
2D Fab standard	0.1	0.1	0.2	0.3

BET **–** method

The density of the samples was initially measured by helium pycnometry. This was done due to that some BET-software requires information of the density, in order to calibrate the results with a known sample. Some suppliers specify the density, but this is not standard. The measurements resulted in similar results for the different samples, see Table 4.

The only sample preparation for the BET measurements was degassing. The GNP samples were degassed for 2 h at 100 °C. No significant difference was found between vacuum (13.33 Pa, used by RISE) and nitrogen (used by RISE IVF) atmospheres. The GO and rGO samples were also degassed at 40 °C for 12 h, which resulted in better curve fits in the BET procedure.

There is a standard for BET analysis of carbon-based powders (ASTM D6556-10), which recommends degassing at 300 °C for 3 h. The degassing temperature used here was kept lower as the TGA measurements had shown significant weight loss for especially the GO at lower temperatures. Which also could explain why the degassing at lower temperatures gave better curve fits in the BET procedure for the GO and rGO samples.

The BET measurements were made with a Gemini VII 2390, Micromeritics system at RISE IVF and a Micromeritics 3Flex system at RISE.

BET measurements were conducted at 11 partial pressures in the range of 0.05-0.30 P/P_0 and suitable pressures were chosen for best linear fit in the BET transform plot, see Figure 1.
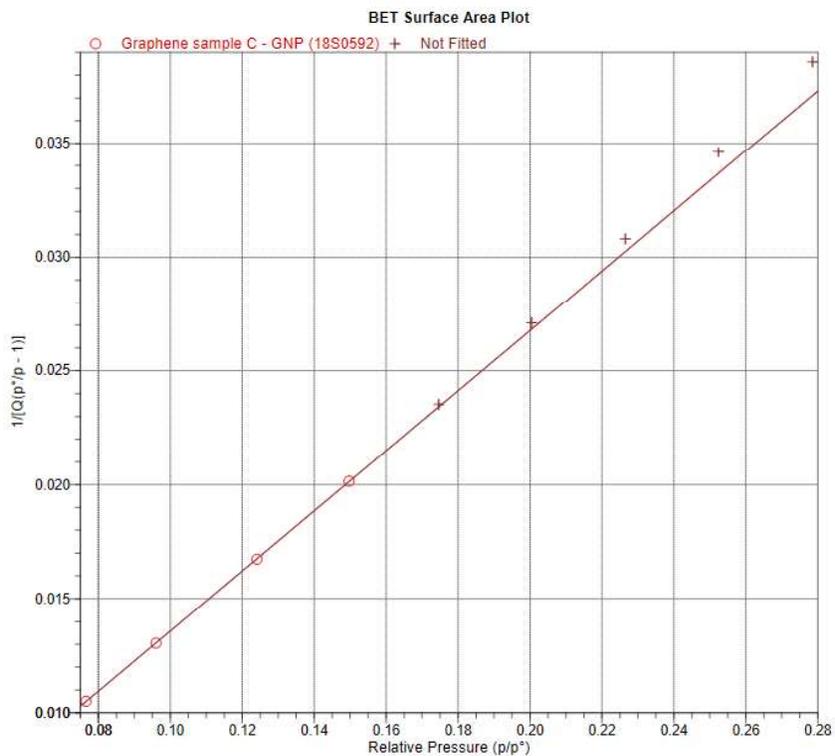
Figure 1 BET transform plot of XGnP C750 and linear fitting, yielding a surface area of 738 m^2/g, which can be compared with 750 m^2/g as stated by the supplier. The slope is related to the surface area and the intercept to the C value.

The measurements performed at the two different locations resulted in very similar results, see Table 4.

The C value in the BET fitting procedure should be in the range 50-300. However, both test sites found negative values of the C value for sample XGNP M25. This is due to low affinity

to the nitrogen gas, and therefore the BET theory is not valid for this measurement. This could explain the different value given by the supplier (120-150 m^2/g) compared to the measured values here (60.6 and 60.2 m^2/g).

The other main difference can be seen in the GO sample Abalonyx 1.8. The C parameter for this GO sample measured at RISE was higher than 300, which indicates a strong affinity to nitrogen. The C parameter measured at RISE IVF was 166, which could explain the difference in results.

One sample measured here (XGnP C750) was also measured in a study by Kovtun *et al.*[2], who used higher degassing temperatures (300 °C). The reported surface area for this sample was similar as measured by Kovtun *et al.*[2] (745±50 m^2/g), the supplier (750 m^2/g) and here (738 m^2/g and 702 m^2/g). However, exfoliation of graphene has been reported at 195°C and high vacuum (<1Pa)[3]. The limiting vacuum for this is not known.

Table 4 Comparison of the surface area of the samples as measured by RISE, RISE IVF and as stated by the supplier. Not all suppliers specify the surface area.

Sample	Density [g/cm^3]	Surface area according to supplier [m^2/g]	Surface area measured by RISE IVF [m^2/g]	Surface area measured by RISE [m^2/g]
XGNP M25	1.89	120 -150	60.6	60.2
Abalonyx 2.1	2.40	-	417.4	428.8
XGNP C750H	2.03	750	702.3	738
2D Fab extra	2.11	-	26.8	26.9
Abalonyx 1.8	1.88	-	3.00	12.5
2D Fab standard	2.21	-	23.5	23.8

X-ray Photoelectron Spectroscopy, XPS

XPS spectra were recorded using a Kratos AXIS Ultra[DLD] x-ray photoelectron spectrometer (Kratos Analytical, Manchester, UK). The samples were analysed using a monochromatic Al x-ray source, and the ultra-high vacuum during XPS analysis was about 2 x 10^{-8} torr.

The graphene powders were analysed as received, with each powder poured directly into a circular cavity (with a diameter of about 5 mm), on a sample holder made of copper. The analysis area was below 1 mm^2, with most of the signal from an area of about 700 x 300 μm^2. The obtained XPS data were consequently average values collected from many particles.

Wide range spectra were first run to detect elements in the surface layer, see Figure 2. Detailed spectra were thereafter run for each element, with extra high resolution spectra for the carbon peak. Detailed spectra for the Auger C KLL peak were finally run to obtain information about the carbon hybridization (sp2/sp3 ratio). Details of the measurement setup can be found in Appendix.
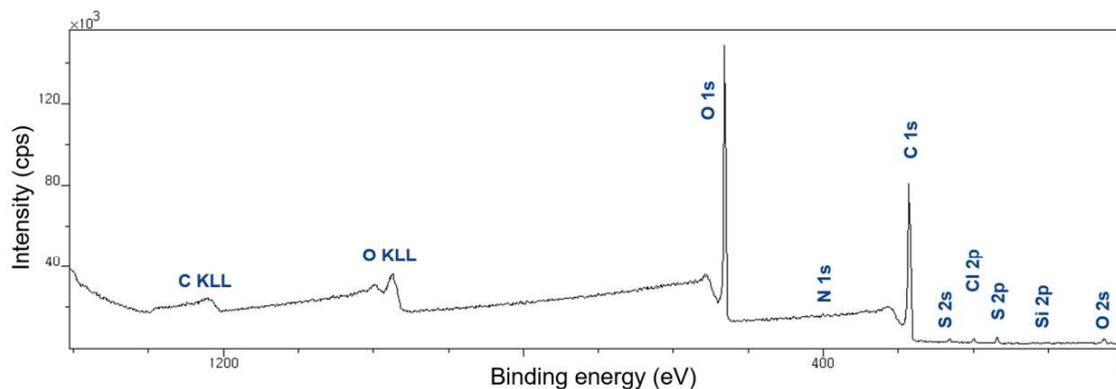
Figure 2 Wide range XPS spectra of graphene oxide.

The surface chemical compositions of the four GNP samples were similar, with mainly carbon present (93-95 atomic% C), about 5 atomic% O and low amounts (≤ 0.7 atomic%) of other elements N, S, Cl and Si, see Table 5.

The relative amount of oxygen was higher for rGO (sample Abalonyx 2.1) than for GNP, and was even higher for GO (sample Abalonyx 1.8), as expected. Most data was similar to what was stated by the suppliers, except for sample XGNP M25, which contained significantly more oxygen.

Table 5 Relative surface composition in atomic % as measured by XPS.
- = signal in detailed spectra at noise level (below about 0.05-0.1 atomic %)
( ) = weak peak, signal close to noise level in detailed spectra

Sample	Data According to supplier	Atomic%						Atomic Ratio
Sample		C	O	N	Si	Cl	S	O/C
XGNP M25	C > 99,5% O < 1%	92.9	5.8	0.7	-	-	0.5	0.06
Abalonyx 2.1	C ~85%	85.8	13.8	-	-	0.2	0.3	0.16
XGNP C750H	N ~1% O ~8%	95.1	4.7	(0.1)	(<0.05)	-	-	0.05
2D Fab extra		94.6	5.1	-	(<0.05)	(<0.1)	0.2	0.05
Abalonyx 1.8	C/O ratio 2,5-2,6	65.9	32.4	0.2	0.4	0.3	0.7	0.49
2D Fab standard		94.9	4.9	-	-	(<0.1)	(<0.1)	0.05

All samples except XGNP C750H contained a low amount of sulphur (≤ 0.7 atomic% S). A peak at about 169 eV was obtained for all of these samples, which corresponds to the oxidized form of sulphur (sulphate/sulphonate functional groups). The spectrum from the XGNP M25 sample additionally had a peak at 164 eV, which indicates the presence of unoxidized sulphur (e.g. thiol or disulphide groups).

One main peak was observed in the carbon 1s spectra (at 284.5-284.7 eV) of the GNP samples. The main peak has a very long slope on the high-binding energy side, corresponding to the energy loss structure of the C 1s peak (noted for carbon compounds with some conductivity, e.g. graphene and graphite). The slope contains both chemically shifted low intensity peaks, and true loss structures such as aromatic ring shake-up peaks, but the shape of the slope is complex rendering specific assignments difficult. This shape of the C 1s peak is typical for graphite and graphene samples.

Additional chemically shifted peaks corresponding to different C-O functional groups were detected in the slope on the high-binding energy side (overlapping with the energy loss

structure) in the spectra of the rGO and GO samples. These peaks correspond to different functional groups. However, it is not straightforward to curve-fit and quantify these shifted peaks, due to overlap with the energy loss structure.

A curve-fit could in principle be done by adjusting the baseline in order to exclude the energy loss structure. However, this is difficult to do with high certainty. An easy test to check the validity of any fitting procedure is to compare the oxygen to carbon atomic ratio calculated from the functional groups from the fitting of the carbon 1s peak, with the ratio calculated from the total amount of oxygen and carbon (in atomic%).

Information about the carbon hybridization (sp2/sp3) can be obtained from the differentiated x-ray induced Auger spectra (XAES) of the C KLL signal. The line widths of the Auger peak C KLL can be associated to the D-parameter, the distance between the maximum and minimum in the derivate of C KLL spectra. A value of 22-23 was found for the GNP and rGO samples, mainly corresponding to sp2 carbon. Two values of the D-parameter were obtained for the GO sample, 22 (sp2 carbon) and 17 (ca 40% sp2 and 60% sp3 carbon). This is expected for graphene oxide, where both sp2 and sp3 type of carbons are present.

Scanning electron microscopy, SEM

NPL's good practice guide[1] was used as a starting point for sample preparation. The samples for SEM were prepared by similar, but slightly different, methods by KTH and RISE IVF. In brief, the graphene was dispersed in water at a concentration of approximately 0.1 mg/ml. If this did not result in a stable dispersion, isopropanol (IPA) was used as solvent instead. The dispersion was thereafter sonicated for 10 min.

KTH centrifuged the dispersion (500 rpm for 3 min) and drop-casted the supernatant on a 300 nm SiO_2/Si wafer. The sample was then left to dry in a fumehood for two days. RISE IVF left the dispersion to stand, instead of the centrifugation step.

Acceleration voltages of 3-5 kV and working distances of 3-4 mm were used in the SEM. Representative regions with many non-overlapping flakes were imaged. Two different methods were used to analyse the flake size distribution by the two organisations. KTH used an **image processing software to quickly get a statistical distribution of all particles** in the image. The 25th and 75th percentiles can be found using the software, which gives a significantly more reliable picture of the sample than a mean or median value. RISE IVF, on

the other hand, **manually measured individual flakes,** resulting in an upper and lower estimate of the flake size, see Table 6.

The procedure using the software analysis and centrifugation during the sample preparation consistently gives lower values of the flake size than the procedure using the manual analysis and natural sedimentation during the sample preparation. This difference is approximately a factor 6 over all the investigated samples, see Figure 4 in appendix. One part of the explanation to this could be that whereas the manual analysis specifically investigates single flakes, the automatic software analysis includes everything contained in the sample. The great number of small particles (< 100 nm) therefore reduces the size estimates when using the software as compared to the manual analysis. Another reason could be that the centrifugation step is significantly more efficient at separating different sizes, and thereby leaving smaller particles in the deposited supernatant.

Table 6 Data from the SEM characterisation where the image processing was done manually and using an image processing software compared with data from the suppliers.

Sample	Solvent for sample preparation	According to supplier [μm]	Software analysis		Manual analysis	
			25th percentile [μm]	75th percentile [μm]	Lower estimate [μm]	Upper estimate [μm]
XGNP M25	DI water	25	0.094	0.75	0.5	4
Abalonyx 2.1	IPA	-	0.087	0.41	0.5	2
XGNP C750H	DI water	< 2	0.089	0.24		0.5
2D Fab extra	IPA	-	0.051	0.26	0.5	2
Abalonyx 1.8	DI water	-	0.34	3.5	2	20
2D Fab standard	IPA	-	0.069	0.18		0.5

Only one of the suppliers (XG Science) specified the flake size. The sizes measured here are significantly smaller than stated by the supplier. This could partly be due to different measurement methods. Both this measured difference and the fact that most producers did not

specify the size/size distribution, highlights the importance of characterization and validation of purchased materials.

The sample preparation was more challenging than expected. It is imperative for the analysis to prepare samples with a high density of flakes on the surface, but these flakes should not be overlapping. This is complicated as it is not straightforward to prepare a proper suspension of graphene.

One advantage of SEM compared to other techniques is that it gives information about the shape of the particles. Although the technique was used to quantify the lateral dimensions here, SEM can also give an impression of whether the flakes are thin or thick and the general shape, such as if they for example are large and flat, or more equiaxed spheres.

One drawback of the SEM procedure is that there is a risk that the graphene flakes agglomerate during the sample preparation. In some images it is possible to see smaller flakes laying on top of larger particles, see for example Figure 3.
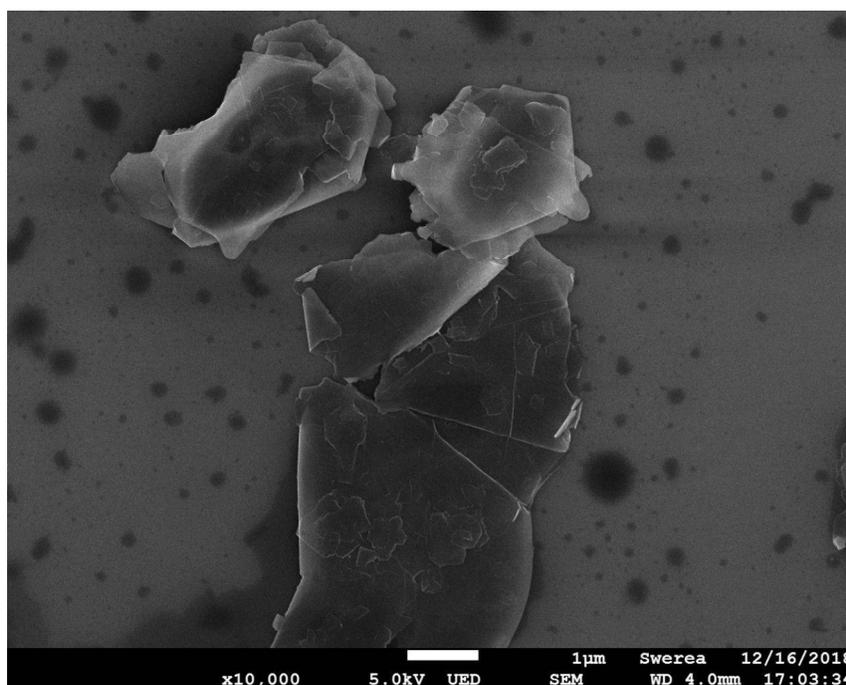
Figure 3 Smaller and thinner flakes can be found on top of larger particles.

Comparison of BET, SEM and XPS

It is interesting to compare the results from the different characterization methods. The sample which contained the largest and thinnest flakes among these in the SEM study was the

GO product 1.8 from Abalonyx. This is in contrast to the low surface area according to the BET characterisation, where no dispersion had been used. This supports that the dispersion method (or lack of it) strongly influences the SEM and BET results. The good results after dispersion in water or IPA using SEM, may also be due to that GO is easier to disperse, than GNP and rGO.

Only limited sample preparation is required for the BET, TGA and XPS analysis. The corresponding surface area (BET) and chemical composition data (XPS) measured here was also in general in agreement with the data provided by the suppliers. The surface area measured at the two different locations in this study were also in agreement.

On one hand, the limited sample preparation is a huge advantage for these techniques as the sample is largely unaffected by the characterisation procedure. On the other hand, the most interesting surface area is not that of the pristine powder, but rather how the material performs in combination with other materials, for example in a formulated product or in a composite. The extent to which graphene materials deagglomerate or exfoliate during processing varies significantly between different materials, and the dispersion techniques used. The final surface area between the graphene and a potential matrix will therefore be different from the surface area of the untreated powder as measured here by BET. That is, a graphene sample with lower surface area as measured by BET, could potentially still have a higher effective surface area exposed to the matrix. It could, in the future, be interesting to compare how well different graphene materials can be dispersed in standard solvents, as is being done with carbon black in application labs today.

SEM characterisation requires more sample preparation. The lateral sizes measured by similar, but different, methods at the two locations in this study differed approximately by a factor 6 for all samples. The values provided by the suppliers were significantly larger than any measured here. This could both be due to the sample preparation and unintentional bias when selecting the investigated areas. Nevertheless, SEM is a powerful technique for characterising the morphology and size.

The lateral size, thickness and chemical composition are some of the most important properties of graphene flakes. However, many suppliers don't provide this data, potentially as there are no standards for this yet. This again highlights the importance of standardisation and validation.

Outlook

Characterisation and standardisation of graphene are seen as some of the main challenges for the continued development of graphene technology. There is several ongoing activities done in this area. The [International Electrotechnical Commission (IEC) TC 113](#) currently has approximately 30 projects/documents related to development of standardisation of graphene.

The British Standards Institution published a Publicly Available Specification (PAS) regarding properties of graphene flakes[4] during this project. The scope of this PAS was to guide graphene suppliers and manufacturers on what properties to specify. The particle thickness, lateral size, specific surface area, moisture content, bulk density and a chemical analysis are deemed as the most important properties that should be supplied. The PAS does not discuss how these properties should be measured, but the methods chosen here (BET, SEM and XPS) analyse these recommended properties.

Some notable recent academic publications include the work by Kauling *et al.*[5] where they have looked at the worldwide graphene flake production and found that a vast majority of the commercial products are dominated by thicker graphite microplatelets rather than graphene flakes. The study investigated material from 60 producers, but did unfortunately not reveal them, which raises some concerns as discussed by Böggild.[6] However, the study once again highlights the need for standardisation and characterization.

Kovtun *et al.* investigated 12 different commercial graphene materials using light scattering, BET and XPS.[7] They discuss that although the light scattering technique is developed for spherical particles, it is a complete, fast and reliable method to describe the size distribution.

In one of the few characterisation cheques which have been utilised within SIO Grafen, SEM was used to estimate the particle size distribution. This estimated the particle size as approximately 20 times smaller than the laser diffraction method used by the supplier.

The National Physical Laboratory (NPL) are involved and leading many of the projects on graphene standardisation in Europe. NPL also published the Good practice guide on characterisation of the structure of graphene.[1] They have recently been investigating Differential centrifugal sedimentation (DCS) as a good method for characterising the size distribution quickly. This method can then be used together with more advanced techniques for calibration.

An advantage of light scattering techniques and DCS is that they don't require the sample preparation that for example electron microscopy does where particles for example might agglomerate. The whole sample is also measured, which eliminates any risk of unintentional bias, when choosing representative regions as in the SEM study.

On the other hand, images from SEM give more information about the shape that can be difficult to quantify, whereas light scattering and DCS "just" gives a number (or distribution).

Summary and conclusion

Six graphene materials were characterised using four techniques (BET, SEM, TGA and XPS) by three different analysis providers. The procedure was set up as a blind test where the analysis providers were unaware of exactly what materials were investigated.

The BET and XPS analysis in general resulted in similar data as provided by the suppliers. There was a larger difference between the lateral size measured by SEM here and that provided by the suppliers. There was also a difference between the values found at the two locations in this study, which could be due to the difference in sample preparation (centrifugation vs natural sedimentation) and data analysis (manual of individual flakes vs image processing software). Only a limited amount of data was provided by the suppliers, which highlights the importance of standardised characterization.

The analysis also shows that there is a broad range of flake and particle sizes in the samples. Consequently, there is a need to specify not only the flake size of the largest flakes, but also the distribution of flake sizes and distribution of graphene vs other forms of carbon particles.

It is therefore also imperative that the sample preparation results in a representative picture of the whole sample, which can be challenging. A combination of manual and software analysis is recommended in order to ensure that a statistically relevant number of representative flakes is investigated.

The data found here has been added to the open database.

The knowledge of how to characterise graphene was increased in the participating teams and this document can be used to facilitate future measurements.

Graphene can be characterised using many different techniques. Many of these which are used today are advanced and expensive techniques, which require expert operators often

situated at research institutes or universities. There is therefore a need to also establish easier and faster techniques which can be used as routine measurements in-house at companies.

This study consolidates the need to improve best practises of sample preparation, for training on 2D material analysis even for skilled characterising operators, as well as a need for graphene providers to specify the content of their product.

Bibliography

1. Pollard, A. J., Paton, K. R., Clifford, C. A. & Legge, E. Good Practice Guide No. 145 - Characterization of the Structure of Graphene. (2017).

2. Kovtun, A. *et al.* Benchmarking of graphene-based materials: real commercial products versus ideal graphene - Supporting info. *2D Mater.* **6,** 025006 (2019).

3. Lv, W. *et al.* Low-Temperature Exfoliated Graphenes: Vacuum-Promoted Exfoliation and Electrochemical Energy Storage. *ACS Nano* **3,** 3730–3736 (2009).

4. Properties of graphene flakes – Guide. (2018).

5. Kauling, A. P. *et al.* The Worldwide Graphene Flake Production. *Adv. Mater.* 1803784 (2018). doi:10.1002/adma.201803784

6. Bøggild, P. The war on fake graphene. *Nature* **562,** 502–503 (2018).

7. Kovtun, A. *et al.* Benchmarking of graphene-based materials: real commercial products versus ideal graphene. *2D Mater.* **6,** 025006 (2019).

Appendix XPS procedure

The different XPS spectra were run in the following order:

1.Wide (survey) spectra were run to detect elements present in the surface layer.

Wide spectra: pass energy 160, step size 1 eV

2.High-resolution carbon spectra were thereafter run, to see if any chemical shifts due to different functional groups could be observed.

High-resolved carbon spectra: pass energy 20, step size 0.1 eV

3.Detail spectra were then run for each element, and the relative surface compositions expressed in atomic % were quantified from the detail spectra.

Detail spectra: pass energy 80, step size 0.1 eV

4.Auger C KLL spectra were finally run, to see if any information could be obtained about the carbon hybridization (sp2/sp3 ratio) from the D-parameter.

Auger C KLL spectra: pass energy 40, step size 0.1 eV

Appendix Flake size by SEM
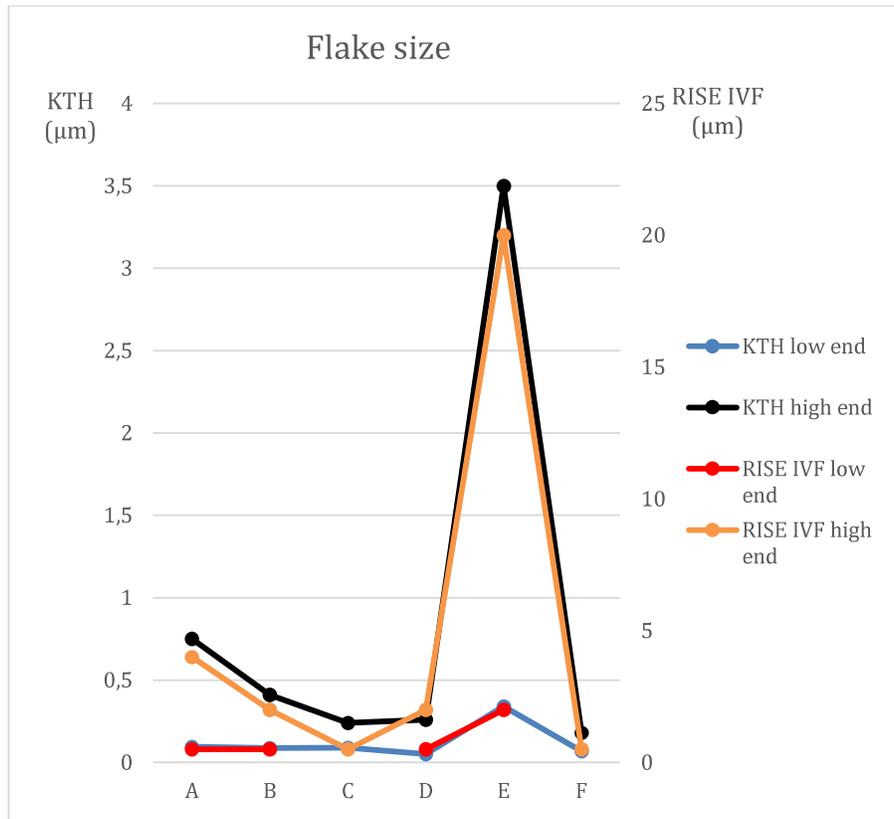
Figure 4 Comparison of the estimated flake size as measured by KTH and RISE IVF. The trends are very similar although the values differ approximately by a factor 6.