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► **To cite this version:**

Pei Lay Yap, Farzaneh Farivar, Åsa Jämting, Victoria Coleman, Sam Gnaniah, et al.. International Interlaboratory Comparison of Thermogravimetric Analysis of Graphene-Related Two-Dimensional Materials. *Analytical Chemistry*, 2023, 95 (12), pp.5176-5186. 10.1021/ACS.ANALCHEM.2C03575 . hal-04061730

**HAL Id: hal-04061730**

**<https://hal.science/hal-04061730>**

Submitted on 18 Oct 2023

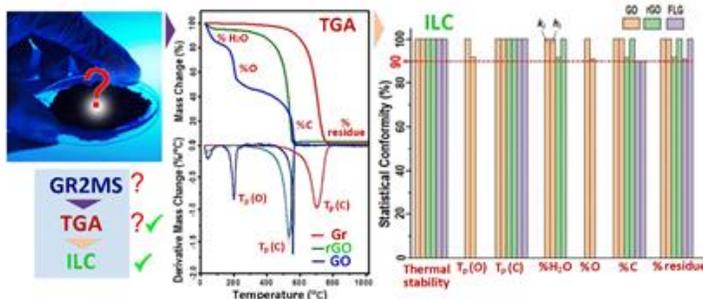
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# International Interlaboratory Comparison (ILC) of Thermogravimetric Analysis (TGA) of Graphene Related 2D Materials (GR2Ms)

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**ABSTRACT:** Research on graphene related 2D materials (GR2Ms) in recent years is strongly moving from academia to industrial sectors with many new developed products and devices on the market. Characterization and quality control of the GR2Ms and their properties are critical for growing industrial translation, which requires the development of appropriate and reliable analytical methods. These challenges are recognized by International Organization for Standardization (ISO 229) and International Electrotechnical Commission (IEC 113) committees to facilitate the development of these methods and standards which are currently in progress. Towards



these efforts, the aim of this study was to perform an international interlaboratory comparison (ILC), conducted under Versailles Project on Advanced Materials and Standards (VAMAS) Technical Working Area (TWA) 41 “Graphene and Related 2D Materials” to evaluate the performance (reproducibility and confidence) of thermogravimetric analysis (TGA) method as a potential new method for chemical characterization of GR2Ms. Three different types of representative and industrially manufactured GR2Ms samples, namely pristine few-layer graphene (FLG), graphene oxide (GO) and reduced graphene oxide (rGO), were used and supplied to ILC participants to complete the study. The TGA method performance was evaluated by series of measurements of selected parameters of the chemical and physical properties of these GR2Ms including number of mass loss steps, thermal stability, temperature of maximum mass change rate ( $T_p$ ) for each decomposition step, and the mass contents (%) of moisture, oxygen groups, carbon and impurities (organic and non-combustible residue). TGA measurements determining these parameters were performed using provided optimized TGA protocol on the same GR2Ms by 12 participants across academia, industry stakeholders and national metrology institutes. This paper presents these results with corresponding statistical analysis showing low standard deviation and statistical conformity across all participants that confirms that TGA method can be satisfactorily used for characterization of these parameters and the chemical characterization and quality control of GR2Ms. The common measurement uncertainty for each parameter, key contribution factors were identified with explanations and recommendations for their elimination and improvements toward their implementation for the development of ISO/IEC standard for chemical characterization of GR2Ms.

## INTRODUCTION

Graphene is a two-dimensional (2D) carbon material with a single layer of  $sp^2$  carbon atoms organized in a hexagonal planar structure. Since its isolation in 2004, due to its many outstanding properties, graphene has been considered as a new disruptive material.<sup>1,2</sup> GR2Ms such as FLG, GO, rGO, and functionalized graphene are predicted to make a significant impact across broad sectors and applications such as water purification, composites, protective coatings, energy storage, solar cells, sensors, catalyst, displays, electronic devices, flexible electronics and etc.<sup>3-6</sup> GR2Ms have also opened up an

exciting area of research and development by combination with other 2D materials and their properties to design new types of materials and devices not imaginable before.<sup>7-9</sup> GR2Ms are currently manufactured by many methods, in the form of films, powders, dispersions, inks, pastes, and foams with a large variation of properties, creating challenges for their industrial applications and also standardization and characterization.<sup>10-14</sup>

**Manufacturing of GR2Ms and their quality challenges.** GR2Ms currently available on market are produced by +20 different scalable processes by +500 manufacturing

companies worldwide. Most of these methods are based on physical or physico-chemical exfoliation of graphene from natural graphite, but synthetic methods using carbon sources from gases (CO<sub>2</sub>, hydrocarbons) or biowaste are emerging in recent years.<sup>11-13</sup> GR2Ms produced by different methods exhibit considerable variation in physical properties and compositions such as the number of layers, lateral particle size, defects of sp<sup>2</sup> carbon structure, crystallinity, oxygen level and presence of impurities. This diversity is causing a significant challenge for the industrial implementation and applications of manufactured GR2Ms.<sup>18</sup> Variations in GR2Ms properties from manufacturer-to-manufacturer and batch to batch production could have a significant impact on the consistency and quality of graphene based products. The developers of these products need to carefully select appropriate graphene materials and suppliers who are able to provide consistent quality of graphene materials with properties that match their requirements for specific applications. Lack of proper quality standards, characterization methods, and certification procedures for GR2Ms is a serious barrier in this process and could impact the progression of a multi-billion graphene industry. To make this problem even more challenging, recent studies have revealed that most of the industrially manufactured graphene materials currently available on the market are not graphene by ISO definition and contain a large amount of graphite, which has raised worldwide concerns.<sup>11,15</sup> That is another important reason why the standardization of GR2Ms supported by reliable characterization and quality control methods is urgently needed.

**International Standardization and Characterization of GR2Ms.** To address the standardization challenges of GR2Ms, the international standardization organizations (ISO 229 and IEC 113 committees) with the support of scientific communities have devoted huge efforts to develop several standards on graphene terminology (ISO/TS 80004-13:2017) describing graphene and related 2D materials, their properties, associated measurement techniques (ISO/TR 19733:2019) and technical specification (ISO/TS 21356-1:2021) detailing measurement protocols to determine their structural properties.<sup>15-18</sup> In addition, several other supporting documents and guidance related to graphene standards and characterization methods were published by the European Graphene Flagship, national standardization bodies (e.g. British Standards Institution, BSI) and national metrology institutes (e.g. National Physical Laboratory, NPL, UK).<sup>19-21</sup> Based on these standards, a carbon particle is considered as graphene if the majority number of graphene layers is < 10. Other types of graphene depending on the number of layers of graphene particles are defined as single-layer graphene (1LG), bilayer graphene (2LG), and “few-layer graphene” (FLG), usually referred as graphene nanoplatelets.

ISO characterization techniques recommended for the determination key properties of graphene such as the number of layers, defects, crystal structure, and chemical compositions are transmission electron microscopy (TEM), Raman spectroscopy, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). These methods can be classified as localized or “spot” characterization methods,

probing the properties of GR2Ms at only a single or few graphene particles or their parts at nano or micron scale. Their disadvantages are high cost of these instruments, needs for skilled operators, long testing time, and high operational cost, which are unaffordable for industry and typical graphene and graphene products manufacturers. To have other complementary analytical methods which are low-cost, simple, and able to provide reliable information on the “bulk” properties of produced powder materials rather than localized spots are highly desirable. To know these “bulk” or average properties of manufactured GR2Ms produced at large batches (e.g. 10 to 100 kg) are equally important for manufacturers and the end-users. Methods such as light microscopy (number of layers), the gas adsorption analysis by Brunauer–Emmett–Teller method (specific surface area), pH titration (acids and oxygen groups), TGA (qualitative and quantitative determination of components, thermal properties), laser diffraction or dynamic light scattering (particle size distribution, PSD) have been successfully used and recommended for simple and low-cost characterizations of GR2Ms.<sup>22-27</sup> Some of these methods are currently under evaluation to assess their characterization capability, uncertainties and limitations needed to developing reliable ISO standards.

**Thermogravimetric Analysis (TGA) of GR2Ms.** TGA is commonly used analytical method in research and industry labs, offering a rapid and simple qualitative and quantitative analysis of raw materials and products such as minerals, additives, plastics, paints, adhesives, rubber etc.<sup>28,29</sup> In the case of GR2Ms, the TGA method has been explored to determine their thermal properties, elemental composition (carbon, oxygen groups) and impurities such as contents of water, acids, oxidants, solvents, and non-combustible inorganics (silica, metal oxides and etc.).<sup>30,31</sup> Most recent TGA studies reveal that different GR2Ms such as GO, rGO and FLG have distinctive thermal decomposition signatures, presented by their TGA, the first (DTG) and the second derivatives (d<sup>2</sup>TG) graphs.<sup>23</sup> The number of peaks, their peak shapes, and the peak or maximum mass change rate temperature (T<sub>p</sub>) are demonstrated to distinguish these different types of GR2Ms.<sup>22-23</sup> Representative TG graphs for GO, rGO, FLG and graphite, powders are presented in **Figure S1**. By using these TG-graphs, it was shown that it is possible to successfully discriminate FLG powders from ‘fake’ graphene powders containing graphite, GO or other carbon particles, confirming that TGA as a very useful complementary method for characterization and quality control of bulk GR2Ms.<sup>22-24</sup> However, to make TGA a standard method for GR2Ms, it is important to confirm its reliability and confidence.

**International Interlaboratory Comparison (ILC).** This paper presents the results from an International Interlaboratory Comparison (ILC) study of the TGA method for chemical characterization of GR2Ms that is coordinated through the Versailles Project on Advanced Materials and Standards (VAMAS) program, Technical Working Area (TWA) 41 ‘Graphene and Related 2D Materials’. The aim of the study is to evaluate the reliability and measurement uncertainty of the TGA method for the characterization of GR2Ms, and its ability to be implemented for a new ISO

standard for TGA based chemical characterization of GR2Ms. The method performance was evaluated by series of TGA measurements of five selected parameters using three different types of GR2Ms (GO, rGO and FLG). These parameters are: (1) number of mass loss steps, (2) thermal stability, (3) temperature of maximum mass change rate ( $T_p$ ) for each decomposition step, (4) the mass contents (%) of moisture, oxygen groups, carbon, combustible organic impurities and (5) the mass content (%) of non-combustible residue. These parameters have been selected to combine the measurement of physical, and qualitative and quantitative chemical properties of GR2Ms based on their practical relevance, complementarity with other ISO characterization methods and the developed procedures from both the authors and in the literature.<sup>22-24,32</sup>

TGA measurements on representative samples of three types of GR2Ms using provided protocol were performed by 12 ILC participants from 5 continents and different institutions (metrology, academia and industry). Specifically, this study was focused to answer the following questions about: (1) the reproducibility of the proposed TGA method for selected parameters, (2) the discrepancies between obtained results performed by international laboratories around the world, (3) the impact of different TGA instrumentation, their software and processing of acquired data, (4) influence of the operators performing measurements and (5) influence from the stability of commercial GR2M samples used in the study. The collected and processed data of TGA measurements reported by all participants were compared and used to evaluate performance statistics by the lead participant (LP) using the distribution of the Mandel's  $k$  (within participants' consistency) and  $h$  (between participants' consistency) with overall summary on the statistical conformity of these values. The obtained results and learnings from this ILC study and recommendations for the improvement of the TGA method will be made herein and implemented in a new ISO standard for chemical characterization of GR2Ms.

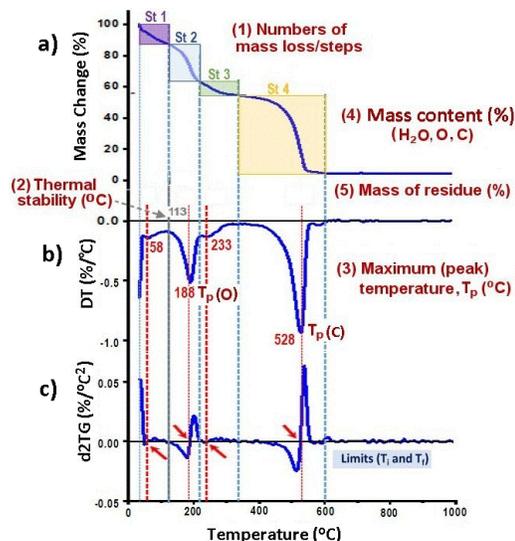
## EXPERIMENTAL DETAILS

**ILC study:** The process of ILC study is illustrated in **Scheme S1**. After the TGA measurements on provided GR2Ms samples using provided TGA protocol were completed, the participants provided a report (labeled as PM-PP) containing measurement details, the results for five requested parameters collected from TG, DTG and d2TG graphs, including the raw unprocessed TG data/graphs. The lead participant (LP) analyzed the participants' raw data using the same data processing step and generated the PM-LP results. For each parameter, two datasets were created and compared: participant-measured and participant-processed (PM-PP), and participant-measured and lead-participant-processed (PM-LP). The details for the sample preparation, TGA protocol, the measurements of specific parameters, data processing and statistical analysis are presented in the [Supporting Information](#).<sup>33-35</sup> Representative TG-DTG-d2TG graphs used for the determination of five TGA parameters, with representative examples, are presented in **Figure 1 and Figure S1**.

## RESULTS AND DISCUSSIONS

**Background characterization.** Characterization results for all representative GR2Ms samples (GO, rGO and FLG) used in this study performed by SEM, TEM, Raman spectroscopy, XRD, FTIR PSD, and XPS analyses are presented in **Figure S2** and **Table S1**. These results confirmed that the samples have expected properties as reported in the literature.<sup>11,15,23</sup> The representative TG-DTG-d2TG graphs of GO, rGO, FLG samples with extracted TGA parameters presented in **Figure S3 and Table S2** also confirmed their distinct thermal characteristics.

**The number of mass loss or decomposition steps (parameter 1).** The aim of this assessment was to evaluate the ability of TGA method to detect temperature induced mass changes in GR2Ms samples related to (1) the presence of additional components (*e.g.*, water, organic/inorganic



**Figure 1:** Representative thermograms (TG) used for the determination of five TGA parameters showing: a) TG, b) DTG and c) d2TG graphs of GO (used as the example). The grey dashed line and grey arrow indicate the thermal stability using DTG and d2TG plots. Blue dashed lines indicate how temperature limits ( $T_i$  and  $T_f$ ) were determined from DTG and d2TG graphs used to determine mass change (%  $H_2O, O, C$ ) and red arrows and red dashed lines show how the  $T_p$  was

impurities), (2) additional components in graphene structure (*e.g.*, oxygen, nitrogen groups) and (3) difference in carbon structure ( $sp^2$  and  $sp^3$ ). Because each of GR2Ms has defined number of steps (GO-3, rGO-1 and FLG-1), this parameter can provide qualitative information about the presence of other components. Results reported by the participants (PM-PP) and their PM-LP analyses for characterized GR2Ms are summarized in **Figure S4 and S5**.

For GO sample, 8 participants reported correctly the four mass loss steps that agrees with PM-LP analysis. It is important to state that these participants correctly found additional small peak (after 200 °C) that is related to organic impurities that were decomposed after oxygen. This unexpected result for GO is confirmed by XPS analysis showing presence of N and S groups (ca 2%) showing this commercial GO sample has some impurities (**Table S1**). These consistency in results by 8 participants is a strong demonstration of the ability of TGA method to provide qualitative information and detect the presence of organic

impurities in GR2Ms. In the PM-LP analysis of the data, an inconsistency of PM-PP results was observed from the participants 3 and 5 showing three and five mass loss steps. The difference in number of steps was due to a difference in how the temperature limits were determined. Participant 3 combined both mass loss events in the first (moisture) and second steps (oxygen groups) as a single mass loss step with only a set of temperature limits ( $T_i$  and  $T_f$ ) reported. Participant 5 reported five steps with additional mass loss step (accompanied by a pair of temperature limits) recorded after 550 °C, showing a very small shoulder peak. After consultation with this participant and analysis of the raw TGA data, this additional peak shown in **Figure SA1** is likely resulted from the instrument instability and the baseline drifting during measurements. This problem can be linked to many reasons such as electronics, the balance quality or buoyancy effect. Participants 8 and 10 incorrectly used nitrogen gas as sample gas, instead of air as specified in the protocol, which resulted in a limited carbon combustion with only three mass transition steps in their thermal profiles.

For rGO sample, nine participants in the PM-PP analysis reported two mass loss steps while two participants recorded one mass loss step and one participant for four mass loss steps indicating high inconsistency. PM-LP analysis of the raw TG data showed that observable moisture peak (below 100 °C) in the DTG and d2TG plots of rGO was only found for participants 1, 5 and 8 and the rest have only one mass loss step. The observed presence of moisture peaks for rGO can be explained by exposure of sample to the humidity after the opening and long testing time. The recorded humidity level in their labs was between 40 % and 58 %, and sample could adsorb moisture if kept open at ambient for a longer time. This problem was caused by a lack of following the proposed protocol specifying strict sample storage requirements with minimal time of exposure to air between sample preparation and testing.

For FLG, nine participants reported in their PM-PP analysis that only one mass loss step as expected. Two participants (4 and 5) observed two and participant 1 four mass loss steps. The PM-LP analysis showed that the number of mass loss steps for the FLG sample for each participant has only one mass loss step, except for participant 1 where an unusual shoulder peak was observed at 700 °C. Participant 1 also observed this peak on high resolution DTG- d2TG graphs showing small peaks at 25 °C -100 °C (correspond to moisture) and 200 °C - 300 °C (corresponds to oxygen groups), bringing the total to four in the PM-PP data. The observed small shoulder peak in the carbon decomposition step that was found in both the PM-PP and PM-LP data (all repeated FLG samples) can be linked to traces of carbon contamination in the crucible, that was not thoroughly removed during crucible cleaning process. The positive side of this result showed: (1) high sensitivity and ability of TGA method to distinguish other carbon materials from GR2Ms and (2) to improve the crucible cleaning protocol by removing all remaining impurities.

In summary, the main reason for the observed variations in determining the mass loss steps between the participants and the lead participant can be explained by the non-adherence of the participants to strictly follow the provided

protocol. Two participants used incorrectly  $N_2$  instead of air as sample gas, as previously described. Other participants did not perform testing immediately after opening the samples and left them in the lab to be exposed to the moisture. This also could include a lack of proper cleaning of the crucible that creates false results. The influence of environmental conditions could lead to the adsorption of the water, which was reflected by an additional mass loss at temperature below 100 °C. These results indicate a sensitivity to environmental conditions for some GR2Ms and it is recommended to improve the protocol with highlights on how to avoid the influence of moisture. The subjectivity in selecting very small temperature changes as peaks, when they are in the range of noise (participant 1) was also noticed. To avoid this source of errors, it is important to define the threshold of signal (peak/step) vs noise in the protocol.

**Thermal stability (parameter 2).** The aim of assessing this parameter was to confirm the consistency of the TGA method to determine the thermal stability of GR2Ms, which is an important physical parameter defining their properties.<sup>22-23</sup>

Results reported by participants (PP) and their LP analysis for all GR2Ms samples are summarized in **Figure S6 and S7 and Tables S3 and S4**. The results showed that 10 participants reported the thermal stability of GO in the expected range of 100 °C - 150 °C, while two participants (3 and 7) showed higher thermal stability between 180 °C - 250 °C. LP processing of these data were in a good agreement with the expected values. Eight participants reported the thermal stability of sample rGO between 110 °C - 250 °C, while four participants showed that it extended to around 500 °C. The LP analysis found that the thermal stability of sample rGO was between 300 °C - 500 °C for all the participants, showing consistently higher values compared with PP results.

A significant variation of PP results on thermal stability for FLG was observed with higher temperatures of 500-800 °C. These results were narrowed to 400 °C-500 °C with significantly lower variations when these data were analyzed by lead participant (PM-LP). The observed discrepancy of thermal stability parameters between PM-PP reports and PM-LP analysis is explained by the negligence to follow provided protocol to correctly determine requested temperature points. Some participants likely used the TG curve without considering the DTG and d2TG graphs as requested in the protocol, where these points can be determined with better precision. Higher variations in results were observed for rGO and FLG compared to GO, because practical examples for the determination of thermal stability for rGO and FLG were not provided in the protocol.

Statistical consistency tests using Mandel's  $h$  and  $k$  analysis to evaluate the precision and accuracy of obtained results within and between the participating laboratories are presented in **Figure S6 a-b**. The Mandel's  $k$  statistic plot showed that no laboratory has a thermal stability value beyond the critical values for all the three samples under both PM-PP and PM-LP analyses, indicating a good repeatability within the same laboratory. The  $h$  statistic Mandel's plots revealed that the thermal stability values were consistent for all the samples based on PM-PP and PM-LP analyses, except for GO reported by participants 3 (187.6 °C),

7 (222.5 °C), and 8 (124.3 °C). These values for thermal stability were significantly greater than the 5 % and 1 % critical values ( $h$ -crit) in PM-PP analysis and deviated from the group mean value (117.1 °C). Based on PM-LP analysis, the overall thermal stability value was 116.7 °C and most participants reported these values below  $h$ -crit $_{\alpha=1\%}$  value for all the tested samples, except for participant 3 that exhibited a  $h$  value (2.66) exceeding the  $h$ -crit $_{\alpha=1\%}$  value (2.22) for sample GO.

In summary, by excluding the outliers, a satisfactory outcome (100 %) was achieved on the statistical tests (Mandel's  $h$ , and  $k$ ) for the thermal stability parameter of all GR2M samples in both PM-PP and PM-LP analyses. To address the noted inconsistency problems and outliers, it is suggested to further improve the TGA protocol by providing practical examples for all GR2M samples with the DTG and d2TG graphs showing the first limit at zero crossover and instruction how to determine this parameter.

### The peak or maximum mass change rate temperature ( $T_p$ ) for each step (parameter 3): $T_p$ of Oxygen groups.

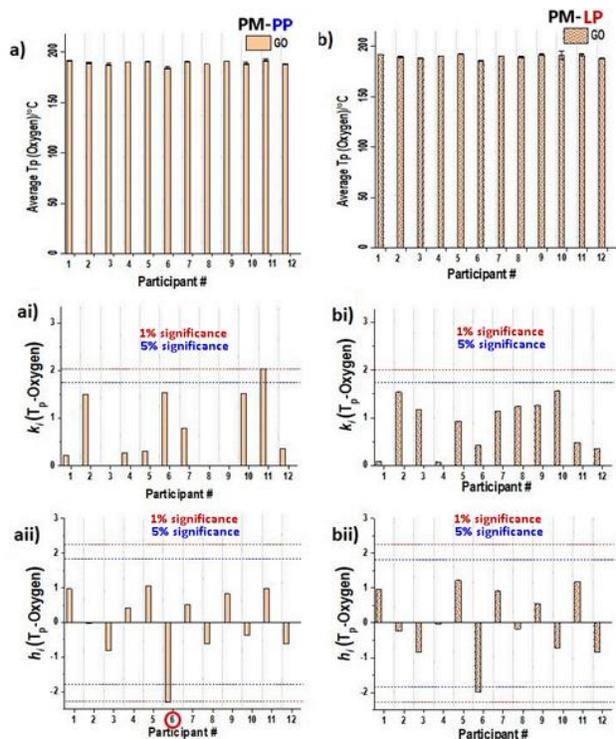
The aim of evaluating this parameter was to confirm the ability and consistency of the TGA method to determine the temperature of the maximum mass change rate ( $T_p$ ) related to the thermal decomposition of oxygen groups if present in GR2Ms. Oxygen containing groups are only present in GO, where the  $T_p$  related to oxygen containing groups bonded to carbon and  $T_p$  (O), can be determined in Step 2 on the thermogram. However, lower level of oxygen can be present as impurities in rGO and FLG from their production process (GO reduction, or graphene oxidation). Therefore, the  $T_p$  parameter is important because it can provide qualitative information to confirm the presence of oxygen groups in GO as expected and their absence in rGO and FLG where they can be considered as no wanted impurities.

Results from this study reported by participants (PP) and their LP analysis for all the samples are summarized in **Figure 2, Figure S8 and Table S5-S6**. The obtained results for GO are consistent showing as a minimum peak at temperature ranges between 185 °C - 195 °C in both the PM-PP and PM-LP analyses.

The Mandel's  $k$  plots (**Figure 2ai, Table S5**) revealed that the calculated  $k$  values from all the participants fall below  $k$ -crit $_{\alpha=1\%}$  (2.03) with similar observation in PM-LP analysis (**Figure 2bi, Table S6**), suggesting high repeatability of this TGA parameter. The plots showing Mandel's  $h$  statistic (**Figure 2aii, Table S5**) implied that satisfactory values derived from the results of all participants. Participant 6 with reported  $T_p$  (O) at 184.5 °C ( $h_i = -2.30$ ) deviated from the group mean value of 189.3 °C ( $h$ -crit $_{\alpha=1\%} = 2.25$ ) under the PM-PP analysis. However, all the  $T_p$  (O) from the participants examined by the lead participant (**Figure 2 bii, Table S6**) fall within the  $h$ -crit $_{\alpha=1\%}$  value, indicating high reliability and consistency of this measurement among the participating laboratories.

ILC results of the TGA method for this parameter showed good consistency between both the participants data and the lead participant analysis with only a slight difference (0.1) of overall standard deviation ( $s_i$ ) between PM-PP (2.1) and PM-LP (2.0) analyses. The Mandel's  $k$  and  $h$  results showed statistical conformity for both the analyses, except for results

from one out of 12 participants (91.7 %), which did not fulfill the statistical criteria of Mandel's  $h$  in PM-PP analysis.



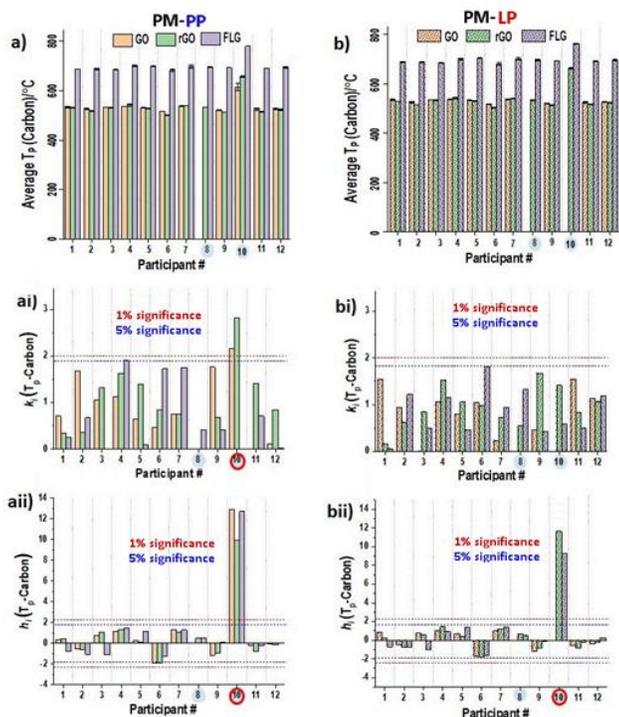
**Figure 2.** The peak or maximum temperature  $T_p$  of oxygen-containing groups results based on a) PM-PP and b) PM-LP analyses on GO. Statistical Mandel's  $k$  analysis to evaluate the consistency for ai) PM-PP and bi) PM-LP results. Statistical Mandel's  $h$  analysis to evaluate the consistency between laboratory for aii) PM-PP and bii) PM-LP results. Participants circled in red if  $h$  or  $k$  value  $>$   $h$ -crit and  $k$ -crit at 1%. Further information is available in SI (**Table S5 and S6**).

### The peak or maximum mass change rate temperature ( $T_p$ ) for each step (parameter 3): $T_p$ of Carbon.

The aim of assessing this TGA parameter was to confirm the ability and consistency of the TGA method to determine the temperature of maximum mass change rate related to the carbon thermal decomposition step in GR2Ms. The  $T_p$  (C), of carbon component is correlated to the carbon combustion and varies between the GR2Ms depending on the differences and defects in their  $sp^2$  carbon framework. The  $T_p$  (C) is determined in the final step as a minimum peak in the DTG at temperature beyond 360 °C. This TGA parameter can be used for the qualitative analysis of GR2Ms to identify if the material is GO, rGO, FLG, graphite or other carbon material as it was demonstrated in a recent study.<sup>23</sup> The  $T_p$  (C) parameter also can be used as an indication of level of defects in  $sp^2$  graphene structure and determine graphene with  $>>10$  number of layers.

Reported results from this study by participants (PP) and their LP analysis for all samples are summarized in **Figure 3, Figure S9 and Table S7-S8**. These results show a good consistency between PM-PP and PM-LP analyses for all samples. The results from two participants (8 for GO and 10 for rGO and FLG) varied considerably from the rest of participants. As already noted, these results were defined as erroneous, and not considered in the statistical analyses, due to incorrect use of nitrogen gas during TGA analysis causing an incomplete carbon combustion.

Apart from the results of participants 8 and 10, the consistency test (Mandel's  $k$  plots), as depicted in **Figure 3ai-bi** and **Table S7- S8**, showed that the calculated  $k$  values of this thermal metric from all the laboratories were below  $k\text{-crit}\alpha=1\%$  in both PM-PP and PM-LP analyses, implying relatively good precision of this parameter. Mandel's  $h$  indicators of  $T_p$  (C) in **Figure 3aii-bii** and **Table S7-S8** indicate no significant variation from the mean  $T_p$  (C) values (GO: 528.4 °C, rGO: 525.9 °C, FLG: 692.8 °C) and (GO: 528.7 °C, rGO: 525.3 °C, FLG: 693.0 °C) in PM-PP and PM-LP



**Figure 3:** The peak or maximum temperature  $T_p$  of carbon results on GO, rGO and FLG samples based on a) PM-PP and b) PM-LP analyses. Statistical Mandel's  $k$  on  $T_p$  (C) to evaluate consistency for ai) PM-PP and bi) PM-LP results. Statistical Mandel's  $h$  on  $T_p$  (C) of GO, rGO and FLG to evaluate the consistency for aii) PM-PP and bii) PM-LP results. Participants circled in red if  $h$  or  $k$  value  $> h\text{-crit}$  and  $k\text{-crit}$  at 1%. Participant shaded in blue are identified as outliers (missing data, inconsistent sampling conditions, or data misinterpretation) and removed from statistical analysis. Further information is available in SI (**Table S7 and S8**).

analyses, respectively. These statistical analyses (Mandel's  $k$  and  $h$ ) showcased that high accuracy and precision within and between laboratories were accomplished on this TGA parameter with 100 % statistical conformity (**Table S7 and S8**) for all the tested samples in both PM-PP and PM-LP analyses.

**Mass Contents (parameter 4).** The aim of assessment of this characterization metric was to confirm the ability and consistency of TGA method to provide the quantitative information about GR2Ms and determination of their chemical compositional components such as % carbon, oxygen and associated impurities such as % of moisture, organics and non-combustible residues. Results from PM-PP and PP-LP analysis, showing the TGA results, including all these components (moisture, oxygen functional groups,

carbon and residue) for three GR2M samples are summarized in the following figures and tables.

**Mass Contents (parameter 4): % of Moisture.** Quantitative determination of moisture content in GR2Ms is critical for many applications as it could affect their properties (conductivity, processability and etc). The mass loss observed from TGA measurements is due to the evaporation of adsorbed moisture in GR2Ms upon heating of sample. This parameter is a characteristic for GO samples having significant water content. The presence of water is not expected in rGO and FLG samples, as described previously and this is confirmed by measurements by the LP before sending the samples to the participants.

Results reported by the participants are summarized in **Figure S10a** with their LP analysis as shown in **Figure S10b and Figure S11**. The average mass content of moisture for GO was reported as  $(15 \pm 3)$  % in PM-PP analysis (**Table S9**), which is consistent with PP-LP analysis as  $(15 \pm 2)$  % (**Table S10**). However, in the case of the rGO sample, a significant inconsistency was observed between PM-PP and PP-LP measurements as depicted in **Figures S10a-b and Figure S11**. Eight participants reported moisture contents in rGO samples (an average of 4.6 %) (**Figure S10a**) despite that moisture content was not expected in this sample. Reassessment of the raw TG data from PM-LP analysis confirmed the presence of water content only for 3 participants (1, 5, and 8). The reasons for this discrepancy are explained as a result of their non-adherence to the provided experimental TGA protocol and instruction on how to perform data processing. These participants determined the temperature limits (initial  $T_i$  and final  $T_f$ ) directly from TG graphs and did not use DTG and d2TG plots for this step as specified in the protocol. The observed difference in identifying  $T_i$  and  $T_f$  values used for moisture calculation was the main source of discrepancy between PM-PP and PM-LP analyses. The water content confirmed by LP analysis from 3 participants was attributed to the presence of moisture in rGO. Further investigation with the participants found that this was likely caused by extended sample exposure to humid ambient lab environments for participants 1, 5, and 8 (average maximum lab humidity 51.2%) resulting in notable water adsorption.

The statistical evaluation of these results using Mandel's  $k$  and  $h$  plots presented in **Figure S10ai, Figure S10 aii, Figure S11, Table S9 and S10** showed a good consistency for GO moisture results within the participants (PM-PP) and between PM-PP and PM-LP analysis. Regarding the Mandel's  $k$  and  $h$  plots analysis for rGO samples, one outlier (Participant 5) was identified by both PM-PP and PM-LP analyses showing large variation. This variation of moisture content found in rGO in all three runs, could be attributed to different amount of moisture adsorbed by sample from air during measurements.

In summary, all the participants demonstrated high consistency and high statistical conformity for the mass % of water determination in GO in both PM-PP and PM-LP analyses. The discrepancy in results was observed for rGO samples due to lack of adherence to provided TGA protocol in calculation of this parameter. The influence of moisture adsorption by exposed samples was identified and shown

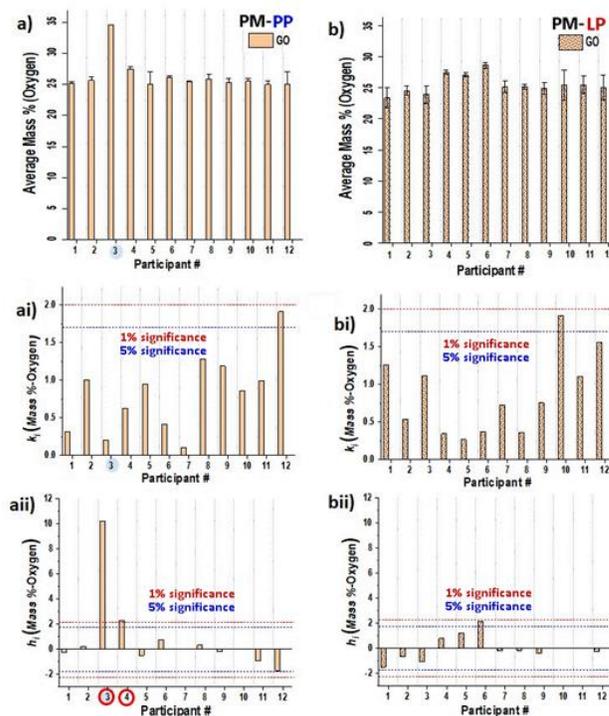
again for this parameter to be another source of the variation that needs to be considered. The influence of both factors can be successfully mitigated by the improvement of TGA protocol and training to operators to strictly follow the protocol. These results also indicated high sensitivity of GR2Ms to moisture adsorption that needs to be addressed. To avoid this problem, it is important to improve the handling these samples during all steps from packaging, storage and in the lab during measurements. It is suggested that GO powder samples are packed in a vacuum sealed and gas impermeable bags. For rGO and FLG powder samples, it is recommended to include a desiccant in a vacuum sealed bag to minimize moisture adsorption during sample transport. Samples should be stored and not exposed to the ambient environment for longer than one hour prior to TGA testing.

**Mass Contents (parameter 4): % of Oxygen Groups.** The mass loss attributed to the decomposition of oxygen functional groups bonded to the carbon framework of graphene is relevant only for the GO sample which contains different oxygen group types (*e.g.*, carboxyl, hydroxyl, epoxy, phenolic and etc).<sup>23</sup> Determination of this parameter is valuable information as it could provide quantitative information of % of O in GO that is critical for many applications. This TGA parameter was determined from the second mass loss step from the TGA curve as described in the TGA protocol. Reported results on this parameter by participants (PP) and their LP analysis for all the samples are summarized in **Figure 4, Figure S11 and Table S11-S12**. The average mass content of oxygen for GO was reported as a mass fraction of  $26 \pm 1$  % by PM-PP (**Table S11**) which is consistent with PP-LP analysis mass fraction of  $25 \pm 1$  % (**Table S12**). Deviation from these results was noted by participant 3, showing the mass content of oxygen at mass fraction of 35 %. However, when the raw data results were analyzed by the lead participant (PM-LP), these results were consistent with other participants (**Figure 4a-b and S11**). This discrepancy can be explained by the subjectivity in identifying the temperature limits ( $T_i$  and  $T_f$  values) where both mass loss steps (1<sup>st</sup> and 2<sup>nd</sup>) were identified as a single mass loss event by participant 3.

Statistical evaluation using Mandel's  $k$  plot on this thermal metric showed no significant variability within the laboratory based on the calculated  $k$  values, which were below 1 %  $k$ -crit ( $k$  crit <sub>$\alpha=1\%$</sub>  = 2.01 and 2.03) in both PM-PP and PM-LP analyses as depicted in **Figures 4ai-4bi and Table S11-S12**. However, calculated  $h$  values for participant 3 ( $h_i$  = 10.22; mass % of O = 34.5 %) and participant 4 ( $h_i$  = 2.27; mass % of O = 27.5 %) demonstrate variabilities from the overall mean value ( $h$ -crit <sub>$\alpha=1\%$</sub>  = 2.22; average mass % of O = 25.5 %) in PM-PP analysis (**Figure 4aii and Table S11**), while no visible variation was observed on the Mandel's  $h$  plot after data evaluation in PM-LP analysis (**Figure 4bii and Table S12**).

In summary, 10 out of 11 participants (90.9 %, Mandel's  $h$ ) and 12 out of 12 (100 %, Mandel's  $h$ ) satisfied the statistical criteria for mass % (O) in the PM-PP and PM-LP analyses, respectively. The ILC results on this TGA parameter were acceptable across all the participating laboratories including the PM-LP analysis. It is worth noting that the obtained values of oxygen by TGA method are related to oxygen

content as part of graphene structure in GR2M and not the total elemental value of oxygen that includes moisture and other organic impurities with oxygen and therefore may provide different values from XPS spot analysis considering the total amount of O on the surface of the material. Further



**Figure 4:** Mass content of oxygen-containing groups (% O) based on a) PM-PP and b) PM-LP analyses of GO. Statistical Mandel's  $k$  analysis on mass %-Oxygen to evaluate consistency for ai) PM-PP and bi) PM-LP results. Statistical Mandel's  $h$  to evaluate the consistency for aii) PM-PP and bii) PM-LP results. Participant circled in red if  $h$  or  $k$  value  $>$   $h$ -crit and  $k$ -crit at 1%. Participant shaded in blue are identified as outliers (missing data, using wrong conditions or data misinterpretation) are removed from statistical analysis. Further information is available in SI (**Table S11 and S12**)

studies to compare these oxygen values by TGA and other complementary method are suggested.

**Mass Contents (parameter 4): % of Carbon.** The aim of evaluating this parameter was to confirm the ability and consistency of TGA method to provide quantitative determination of the amount of carbon or graphene component in GR2Ms. To measure this parameter is important because it could provide quantitative information of % of C in GR2Ms that is a critical property related for their practical applications.

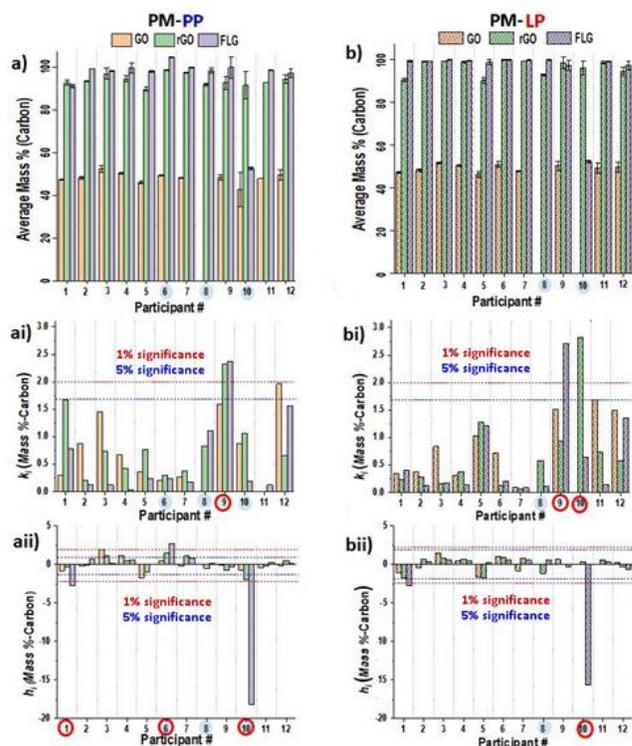
Results reported by the participants with their LP analysis are summarized in **Figure 5, Figure S12 and Table S13-14**. The average mass content of carbon for GO sample was reported as  $49 \pm 2$  %, for rGO as  $94 \pm 3$  %, and FLG as  $98 \pm 3$  %, by PM-PP analysis (**Table S13**) which were consistent with PP-LP analysis showing results of  $49 \pm 2$  % for GO,  $97 \pm 3$  % for rGO and  $98 \pm 3$  % for FLG (**Table S14**). Corresponding histograms from these measurements (**Figure S12**) also demonstrated consistency between PM-PP and PM-LP results. Results of participant 8 (GO) and participant 10 (GO, rGO and FLG) were excluded from the

statistical analyses because nitrogen gas was incorrectly used rather than air as sample gas as specified in the protocol.

Statistical evaluation using Mandel's  $k$  plot on this parameter showed a good consistency within all participants except for participant 9 as presented in **Figure 5ai-5bi** and **Table S13-S14**. The  $k_i$  values exceeded beyond the  $k\text{-crit}_{\alpha=1\%}$  for rGO and FLG in both the PM-PP and PM-LP analyses for participant 9. To understand this discrepancy, the raw data analysis (**Figures SA2 and SA3**) indicated a large deviation between individual TGA measurements and poor repeatability. This was likely caused by the instability of the TGA instrument and can be related to the balance drift due to insufficient time for the stabilization of the thermo balance before the TGA measurement. This specific issue, if occurred can be resolved by allowing adequate time for the stabilization of the thermo balance, *i.e.* until a stable and constant initial sample mass reading is achieved before running the TGA measurement.

Statistical evaluation using Mandel's  $h$  plot on this parameter showed a good consistency for all participants and samples based on the calculated  $h$  values as summarized in **Figure 5aii - 5bii** and **Table S13-S14**. The Mandel's  $h$  plot with the exception of the two missing data points for GO (Participants 8 and 10) showed a good consistency having their  $h$  values below the  $h\text{-crit}_{\alpha=1\%}$  at 2.18 (PM-PP and PM-LP). Similarly,  $h$  values for rGO tabulated within the  $h\text{-crit}_{\alpha=1\%}$  at 2.25, suggesting no significant laboratory variability, confirming that this measurement by TGA was highly reproducible. The Mandel's  $h$  plot established for FLG sample showed higher mass content of carbon by participants 1 (91.3 %), and 6 (104.7 %) that deviated from the group mean value (97.9 %) at  $h\text{-crit}_{\alpha=1\%}$  at 2.18 in PM-PP analysis. However, the  $h$  values in FLG for participant 1 (90.0 %) and participant 6 (99.8 %) fall below  $h\text{-crit}_{\alpha=1\%}$  at 2.19 after PM-LP analysis. Note that the unusual high carbon mass content of 104.7 % of FLG was recorded by participant 6. This artifact could arise from following reasons: 1) the use of contaminated crucible, 2) buoyancy effect, or 3) drift in the TG balance.<sup>36, 37</sup> The participant was unable to rerun the measurement using new and clean crucible and performing a blank baseline curve subtraction due to insufficient sample remaining.

In summary, the ILC results on this TGA parameter were satisfactory across all participating laboratories based on thorough statistical evaluations using Mandel's  $k$  and  $h$  tests confirmed that TGA can be used with high confidence as a method for quantitative determination of carbon or graphene component in GR2M samples. Only 1 participant did not fulfill the statistical criteria for the thermal metrics of mass fraction (C) in both PM-PP and PM-LP analyses, resulting in > 90 % overall statistical conformity with details summarized in **Table S13** and **S14**. The observed few inconsistencies are caused by several avoidable factors such as lack of a strict adherence to TGA protocol, possible contamination of crucibles and instability of the instrument. It is suggested to improve the TGA protocol by extending the time for instrument stabilization and perform an additional cleaning of crucible using a Bunsen burner to remove the impurities that could have potentially left on the crucible.



**Figure 5:** Mass content of carbon (%C) based on a) PM-PP and b) PM-LP analyses on GO, rGO and FLG. Statistical Mandel's  $k$  analysis to evaluate the consistency for ai) PM-PP and bi) PM-LP results. Statistical Mandel's  $h$  analysis to evaluate the consistency for aii) PM-PP and bii) PM-LP. Participant are circled in red if  $h$  or  $k$  value >  $h\text{-crit}$  and  $k\text{-crit}$  at 1%. Participant shaded in blue are identified as outliers (missing data, using wrong conditions or data misinterpretation) are removed from statistical analysis. Further information is available in SI (**Table S13 and S14**).

**Mass Content of Non-combustible Residue (parameter 5).** The aim of evaluating this parameter was to confirm the ability and consistency of TGA method to provide quantitative determination of the amount of non-combustible residue in GR2Ms. These residues can be described as the substance remaining after final and high-temperature combustion step (< 1000 °C). Their content could have significant impact on the quality of GR2Ms and critical for many applications. They are often attributed to the presence of inorganic impurities (silica, and metal oxides) resulting from the manufacturing process or in the starting material (graphite). The final temperature of the TGA measurement in this ILC study was set to 1000 °C with air as the sample gas to ensure complete combustion of carbon in GR2Ms and the measurement of contents of remaining residues.

The results on the mass contents of residue (%) for all the samples reported by the participants and compared with LP analysis are summarized in **Figure S13 - S14** and **Table S15-S16**. These results showed a good consistency between all the participants (PM-PP) and PM-LP analysis (**Figure S14**). The average mass content of residue was reported for GO samples as  $2 \pm 2$  %, rGO as  $2 \pm 2$  %, and FLG as  $2 \pm 2$  % by PM-PP, which are consistent with PP-LP analysis showing results of  $1 \pm 1.0$  % for GO,  $(2 \pm 1)$  % for rGO and  $(1 \pm 1)$  % for FLG (**Table S16**). Results of GO from participant 8 (GO) and

participant 10 (GO, rGO and FLG) were identified as erroneous due to incorrect conditions used (thermal decomposition in nitrogen gas not in air) for sample measurement.

Mandel's  $k$  plots presented in **Figure S13ai-bi** and **Table S15-S16** showed satisfied consistency within participants with observed deviations for participants 4 (FLG) and 12 (rGO) in PM-PP analysis and participants 9 (FLG) and 12 (GO and rGO) in PM-LP analysis. Their measured  $k$  values were beyond  $k\text{-crit}_{\alpha=1\%}$  of 2.00 (GO), 2.03 (rGO) and 2.01 (FLG) (**Table S15- S16**). The reasons for these few observed inconsistencies were not conclusive and these discrepancies could arise from many sources as discussed previously for other parameters. The Mandel's  $h$  values on this parameter excluding participant 8 for GO and participant 10 for all the samples demonstrated interlaboratory consistency based on PM-PP and PM-LP analyses (**Figure S13bii, Table S16**). Only participant 12 (GO and FLG) showed  $h$  values beyond the  $h\text{-crit}_{\alpha=1\%}$  at 2.66 (GO), and 2.28 (FLG) in PM-LP analysis, indicating lower consistency for this parameter, that could be linked to potential contamination of the sample.

In summary, overall evaluation from the statistical assessments clearly indicated >90 % and >80 % statistical conformity (Mandel's  $h$  and  $k$ ) was achieved for the mass % (residue) in PM-PP and PM-LP analyses, respectively. Further areas of improvement to minimize the inconsistency for this parameter metric as discussed in the previous sections are: (1) repeating the measurement using the same (clean) crucible from the sample measurement, (2) running the blank under the same condition, (3) performing a blank baseline curve subtraction and (4) performing additional cleaning of crucible by burning on a Bunsen burner (after washing the crucible with water and ethanol) to remove the traces of impurities that could have potentially left on the crucible after each run.

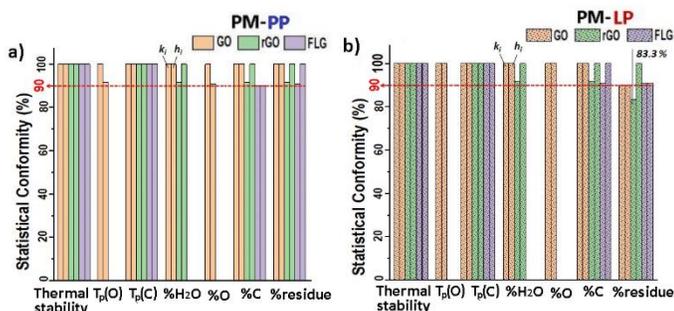
**Overall statistical analysis and key challenges.** Statistical analysis showing standard variation and consistency of TGA measurements presented in previous sections is summarized in **Figure 6, Tables S17-S23 and Appendices SA4-SA35**. **Table S17** presents the overall standard deviation ( $s_i$ ) of assessed five parameters for the three GR2Ms based on

participants PM-PP results and PM-LP analyses after eliminating erroneous results. The  $s_i$  describes the amount of variation of a data set, where a low  $s_i$  number indicates that the values are close to the mean of the data set, while a high  $s_i$  value implies that the value is spread out over a broader range.<sup>38</sup>

In this ILC study, the thermal stability parameter showed the largest  $s_i$  value in both analyses especially for rGO and FLG samples (in red font, **Table S17**). In the case of PM-PP, a very high  $s_i$  for rGO (186.5) and FLG (266.0) was calculated. In the case of PM-LP results, these values were lower, but still high, showing for rGO (42.2) and FLG (21.4), suggesting large variations on this thermal metric. The  $T_p$  (C) parameter also showed a higher  $s_i$  value, when compared to the  $T_p$  (O) variance, with values of 7 °C to 13 °C for all GR2Ms in PM-PP and 7.0 °C to 12.0 °C in PM-LP analysis. Other assessed parameters such as  $T_p$  (O), mass fraction (moisture, O groups, C and residue) showed  $s_i$  values less than 5.0 for all GR2Ms samples and were similar for the PM-PP and PM-LP results. This deviation analysis from ILC study demonstrates low level variations for most evaluated TGA parameters.

The second statistical analysis showing the summary of overall statistical conformity is presented in **Figure 6**. This analysis showed >90 % statistical conformity for all the evaluated parameters, indicating a high performance of TGA method to measure selected characterization parameters of GR2Ms. These results are considered as satisfactory considering the facts that this ILC study (1) did not use reference materials (not established yet for GR2Ms), (2) did not use a standardized TGA method (not established yet) and (3) TGA measurements were performed by operators who did not have previous experience on GR2Ms and used provided protocol for the first time.

Summary of the key sources of erroneous results, outliers, and their impacts identified in this ILC study with recommendations for further improvement of the TGA protocol is presented in **Table S24**. This analysis identified several common factors that contribute to observed variations with recommendations also provided to eliminate these issues and improve the overall protocol. A major source of variation was found to arise from the non-adherence to provided experimental procedure by the operators that significantly influenced the measurement of all parameters. The subjectivity of data interpretation of obtained raw TGA data by operators is the second common source of variations involving the selection of temperature limits, mass loss steps, and thermal stability. However, when these raw data were processed correctly by the lead participant the results were satisfactory, showing statistical parameters ( $k$ , and  $h$ ) within the acceptable ranges. The third contributing factor was the influence of the laboratory environment, both for stored GR2Ms samples and during TGA measurements (temperature, humidity), which was found in two cases to have impact on the results and needs to be considered in the improved protocol. The fourth contributing factor was the influence of the GR2M samples stability and environmental impact during the sample transport and handling, for example, leading to the reduction of GO and adsorption of moisture or contamination, which has not previously been considered to be a problematic.



**Figure 6:** Summary of overall statistical conformity of selected characterization parameters (thermal stability,  $T_p$  (O and C) and mass loss (% moisture, O, C) performed using TGA method on three GR2M samples (GO, rGO, FLG) by 12 participants showing Mandel's  $k_i$  and  $h_i$  statistical analysis based on a) PM-PP and b) PM-LP results. Further details are in **Table S22 and S23**. The bar charts are displayed in the sequence of  $k_i$  and  $h_i$  values from left to right. Statistical conformity at 90 % was proposed as acceptable percentile level for 5 parameters characterized using TGA method in this ILC study.

## CONCLUSIONS

This ILC study, successfully validated the application of the TGA technique for chemical characterization of GR2Ms demonstrated using three typical types of GR2Ms powder (GO, rGO and FLG) with involvement of 12 international laboratories across 5 continents and different organizations (national measurement institutes, universities, and industry). The study assessed the consistency of a TGA protocol, measuring five parameters, within and between all the participating laboratories. The comprehensive statistical analyses were assessed using Mandel's *h* and *k* analysis confirming that this TGA method is satisfactory for the characterization of these parameters and can be recommended as a quality control process for the chemical characteristics of GR2Ms. The completed objectives of this ILC study and suggested recommendations for improving the TGA protocol are summarized below:

**(1) Reliability, reproducibility and measurement uncertainty of TGA method for characterization of GR2Ms.** This ILC study evidently showed that the optimized TGA method based on the five selected thermal metrics (number of mass loss steps, thermal stability, temperature of maximum mass change rate ( $T_p$ ), mass contents (% of moisture, oxygen groups, carbon) and composition of residues) can be reliably used to identify the three different GR2Ms and quantify their associated components. This conclusion is based on the low standard deviation of obtained results across participants (PM-PP and PM-LP analyses) and the comprehensive statistical analyses of the investigated parameters using Mandel's *h* and *k* analysis, showing > 90 % of the participants achieved satisfactory results.

This objective from the ILC study is successfully completed with recommendation that the optimized TGA method can be used for chemical characterization and the quality control of GR2Ms with high confidence. To be stronger aligned with the chemical characterizations of GR2Ms, it is suggested to improve existing TGA method by excluding a physical parameter (thermal stability) which has limited analytical value.

**(2) Discrepancies between the obtained TGA results performed by international laboratories.** Several common factors that contribute to the observed variations in this ILC study were successfully identified: (a) adherence of operators to the provided experimental protocol, (b) subjectivity in data processing and interpretation, (c) influence of laboratory environment during storage and measurements (temperature, humidity) and d) stability of GR2M samples. The subjectivity of data interpretation by the operators on the manual selection of temperature limits without using DTG/d2TG graphs, appeared to be the common source of variance. These sources of uncertainty were rigorously discussed with a series of recommendations to improve the TGA protocol. To minimize operator subjectivity, a clearer step-by-step explanation is recommended for the TGA procedure, with examples on data collection (TGA graphs), data processing (DTG and d2DTG), selecting parameters, final calculation and interpretation using different GR2Ms. The improved TGA protocol is expected to mitigate these discrepancies and their contributing factors.

**(3) Impacts of different TGA instrumentation.** Measurements performed using TGA instruments from five different manufacturers that have different type of furnaces, balances, sensitivity, software, and sample holder, did not show significant influence on the observed variations of results, indicating a high confidence of this method. One source of potential variance is the use of different types of crucibles (with holes, opened) and using different gas flow systems, thus it is important to define these conditions regardless of the type of TGA instrument.

**(4) Impact of laboratory environment during storage and TGA measurements (temperature, humidity).** The inconsistency (poor repeatability and reproducibility) of TGA results were observed from some participants as a result of changing the properties of GR2Ms samples through exposure to light, temperature, and moisture during TGA measurements. This is particularly critical for GO, which is known to not be very stable with properties that can change on short timescales (oxygen reduction, moisture adsorption). From this learning point, the recommendation was made to minimize exposure of these samples to air during TGA measurements.

**(5) Impact of stability during transport and storages of the GR2M samples** A notable impact on observed variations were found due to changes in the GR2Ms during handling and transport before arriving at the laboratory for testing. Based on this observation, it is recommended to store the prepared GR2Ms samples in vacuum-sealed vials in the dark and at 4 °C before any measurement and with limited exposure to the testing environment. Measurements should be performed as close to the time of samples arrival as possible; it is also recommended to spend specific attention to GO which is the most sensitive to environmental exposure.

Finally, the outcomes of this ILC study and VAMAS project with suggested recommendations for the improvement of TGA method will be implemented in a new standard for characterization of GR2Ms (ISO/IEC standard "NWI 23359 - Nanotechnologies - Chemical characterization of graphene-related two-dimensional materials from powders and dispersions"). In this standard, the TGA method is used in combination with other chemical characterization methods, namely XPS, FTIR and ICP-MS, and will provide greater understanding of the chemical properties of commercially available GR2Ms and their appropriate selection for different application areas.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.analchem.XXXXXX.ht> Experimental section includes: experimental protocols, characterization results of 3 GR2M samples using SEM, TEM, XPS, Raman, FTIR, PSD and TGA, processed TGA results with tables, bar graphs, histograms on testing 5 parameters, their statistical analysis and some raw data and graphs.

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The manuscript was prepared through contributions of all authors and they gave approval to the final version.

#### Notes

The authors declare no competing financial interest

## ACKNOWLEDGMENT

This work was conducted under VAMAS, TWA 41, Project 8 Characterization of bulk graphene materials and its derivatives. The authors thank the ARC Research Hub for Graphene Enabled Industry Transformation, (IH15000003). S.M.L. acknowledges support from MCTI/CNPq (Process 400030/2018-7). E.M acknowledges partial contribution of the U.S. Government (not copy-writable within the U.S.). SG and AJP thank the European Union's Horizon 2020 support, No: 881603 (Graphene Flagship Core 3). Other participants would like to thank their organizations providing technical and financial support for this ILC study.

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