Graphene detection in air: a proposal based on thermogravimetric behaviour

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Abstract. Graphene’s production and application are growing in accelerated speed. In this scenario, it is imperative to guarantee the healthy and safe conditions to producers and consumers along the graphene value chain. Due to the unique characteristics of graphene, its characterization in complex matrices is still a challenging endeavour. In this work, we show an ongoing methodology that aims to assess the exposition to nanomaterials inside a graphene pilot plant by adapting the current particulate matter sampling methodologies. A systematic study was performed by preparing different graphene dispersions which were deposited on clean quartz filters and on filters exposed to an outdoor environment. Real samples, containing indoor airborne material were also analyzed. Thermogravimetric analysis was performed in all samples and revealed that the thermal decomposition of the deposited graphene was detectable and occurred around 635 °C. The presence of a thermal decomposition event within the typical temperature range of graphene was also detectable in the real indoor sample. These results pointed out that thermogravimetric analysis can be used to detect small amounts of graphene suspended in air, and the key factor is the with graphene's high thermal stability being the key factor. The methodology provides a robust way to improve air quality surveillance and exposure evaluation.

1. Introduction

Although the graphene market has not yet reached its true potential, the number of graphene suppliers is still increasing, with more than 35 companies with graphene-based products around the world1. The safe development of this new industry is non-trivial and must be supported by the development of reliable risk assessment methods1,2,3.

In this scenario, airborne exposure represents one of the major concerns in an occupational risk approach. It is already known that inhalation is a preferential and the most common route of exposure in workplaces4,5,6. In these facilities, the uptake of airborne nanoparticles can occur during processing to obtain the nanomaterial dry powder, packaging and general handling to product’s characterization.
Recently, the World Health Organization have published a guideline on protecting workers from potential risks of manufactured nanomaterials\(^1\). In case of no OEL (occupational exposure limit) available, a qualitative assessment is recommended as a first step in order to check the presence or absence of exposure. The following steps will comprise the quantitative assessment, to measure the exposure concentration, and the comprehensive measurement, that includes a more complete characterization of the nanomaterial, with size distribution, morphology, and chemical composition assessments\(^2\).

One of the major challenges for nanomaterials is its detection and quantification in complexes matrices – such as organisms, waters, and soil. Regarding the graphene family of nanomaterials (GFN), as recently reported by Goodwin and co-workers, “one key factor related to GFN detection and/or quantification is that various environmentally and biologically relevant matrices may impact the type of techniques used”\(^3\).

Due to graphene consisting of a monolayer or few layers carbon atoms, it has novel and unique structural and thermal properties (to name a few). Its detection is possible through different types of techniques: spectroscopic, microscopic, and thermal analysis. The techniques usually applied for graphene characterization includes spectroscopic methods - such as Raman and X-ray photoelectron spectroscopy - microscopic methods as atomic force microscopy, transmission electron microscopy, and scanning electron microscopy, and thermal methods like differential scanning calorimetry and thermal gravimetric analysis\(^4-10\).

However, the environmental matrices complexity might create interferences, like background fluorescence or deposition bias, thus making graphene detection a challenging task. In a realistic exposure scenario, the co-existence of other carbonaceous materials and/or nanomaterials and its possible interaction with other environmental compounds can even intensify these methodological difficulties\(^7\).

In industrial settings, the workplace environment is usually assessed by the use of gravimetric methods of sampling and analysis. The airborne particulate matter is collected in pre-weighed air filters\(^11,12\). These methodologies, which are conceptually uncomplicated, give, by weight difference, the concentration of the total particulate matter, an information that can be used to estimate occupational exposures to airborne particles and/or to evaluate the efficacy of air pollution control technologies\(^13\).

In this work, we developed a new method to assess the workplace atmosphere in terms of graphene materials exposition. This is achieved by adapting the current standardized methodology and using the nanomaterials unique thermal properties.

2. Materials and Methods

2.1 Graphene's obtention and characterization

At MGgrafeno pilot plant, natural graphite was converted in graphene by using the liquid-phase-exfoliation method\(^14\). By the end of the process, the produced dispersion was characterized using Raman spectroscopy, transmission electron microscopy (TEM) and thermogravimetric analysis (TG).

Raman spectra were obtained using the Witec Alpha 300 RA equipment, with 532 nm as laser line; each spectrum was measured by 10 accumulations with an integration time of 20 seconds using a 10x objective. Transmission Electron Microscopy images were taken using a Tecnai G2-20 SuperTwin FEI microscope with 200 kV.

And, the thermogravimetric analysis was performed in a TGAQ5000 equipment under the following conditions: temperature range between 40 °C and 1000 °C, heating rate of 5 °C/min, in sample port of alumina of 100 μL, air atmosphere synthetic high purity. The measurement uncertainty in relation to the mass is 0.3 mg and the uncertainty in relation to the temperature is 2.5 °C. The pre-purging time was 20 minutes.

2.2 Samples preparation
Air samples were collected during the routine monitoring activities at MGGrafeno project using a High-Volume Air Sampler (Hi-Vol) equipment with high purity quartz filters. Samplings were performed inside and outside of the pilot production plant in compliance with the Brazilian standard (NBR9547) for total suspended particulate matter\textsuperscript{12,15}. As described in 2.2.1 section, a standard experiment was executed using filters containing a known amount of graphene – clean filters and sampled filters (after Hi-Vol sampling outside graphene pilot plant) were used. Real samples (indoor air collecting filters during graphene production) were also analyzed (detailed in 2.2.2 section). All samples were analyzed by thermogravimetry as described below.

2.2.1 Standard study/Filter’s graphene deposition

A dried few-layer graphene sample was used in the preparation of standard dispersions. The solid material was redispersed in ethanol (reagent grade). A stock dispersion at 1 mg/mL concentration was prepared and then diluted to give a 0.1 mg/mL and 0.01 mg/mL dispersions.

Brand new quartz filters circles, having an approximate diameter of 1.2 cm, were cut and 3 mL of each dispersion was deposited via filtration (using a syringe) on its surface. In this way, samples containing graphene with different amounts deposited - maximum 3 mg, 0.3 mg, 0.03 mg - were obtained. Control samples, without graphene, were also analysed.

Sampled filters containing environmental airborne material, collected outside the pilot plant, were also prepared as described above. One sample was used as control and in the other, 3 mL of the 0.01 mg/mL graphene dispersion was deposited via filtration.

2.2.2 Real indoor samples/Filter’s air collecting

Filters containing the airborne material collected during graphene production were also analyzed by thermogravimetry. Additional characterization such as Raman spectroscopy, X-Ray analysis and Scanning Electron Microscopy were performed directly on the sampled filter. Raman spectroscopy was performed as described previously and used to evaluate the presence or absence of the D, G and 2D bands. To observe the presence of crystalline planes of graphite and/or graphene, a 3.5 cm diameter circle was cut for analysis by X-ray diffraction in a PANalytical Empyrean-branded equipment. The following experimental conditions were applied: Cu (45 kV/40 mA) X-ray tube with a pitch of 0.0525° (2θ), counting time of 33 minutes using the PIXcel3D model detector and automatic slit, in the range of 4° to 90° (2θ). Also, Scanning Electron Microscopy (SEM) were performed using a FEI Quanta 200 FEG microscope.

2.2.3 Thermogravimetric Analysis

The thermogravimetric analysis was performed in all filter samples with the same parameters described for the graphene characterization.

3. Results and discussion

3.1 Graphene’s characterization

Raman spectroscopy is a technique routinely used to characterize graphene with high precision mainly because of its known sensitivity to different structural and crystalline characteristics of many carbon nanomaterials\textsuperscript{10,16}. The Raman signal of the graphene dispersion is shown in Figure 1(c), where the D, G and 2D bands characteristic of graphitic/graphene materials are present. In addition to the structural information that Raman spectroscopy can measure in graphene, the order of stacking can be estimated using different spectrum features, such as the intensity of the G-band\textsuperscript{17-19}, the shape of the 2D band or
using the resulting peaks of different combinations of other vibration modes. In the present case, the shape of the 2D band was used to perform the classification on the samples, where it was classified as a few-layer graphene dispersion.

In Figure 1(a, b) we present TEM images that confirms the production of few-layer graphene by showing the morphology of a 4-layer graphene flake. TEM is a powerful technique employed for the lateral size measurement and to measure the number of layers by individually counting the number of graphene layers.

![TEM images](image)

**Figure 1.** TEM images (a, b) of one individual flake, Raman spectrum (c) of the graphene dispersion.

In Figure 2 it is shown the TG (blue) and TG derivative (DTG) (dashed) curves for the graphene powder, showing a single thermal event at 620 °C occurring in the 450 - 700 °C temperature range.

![TG and DTG curves](image)

**Figure 2.** TG and DTG curves of the obtained few-layer graphene.

### 3.2 Standard study
Figure 3 presents the TG (a) and TG derivative (DTG) (b) curves obtained for the three filter samples and for a control sample. This experiment resulted in the graphene thermal decomposition in the expected range, typical of few-layer graphene. A thermal decomposition event was observed in all filters containing graphene in the range of 400 - 750 °C. Control filters (0 mg/mL) remained thermally almost stable with a weight loss of 1.5 %. The thermal decomposition of the graphene deposited on the filters varied from 20 % to 1.7 % depending on the amount of material previously deposited (Figure 3-a). As expected, the higher the amount of deposited material, the higher was the observed mass loss for each filter. Even when the amount of deposited material was in the range of tens of micrograms, it was possible to measure the weight loss in the expected temperature range. This shows the high sensitivity of the technique, in the order of 1 microgram. The combustion temperature of the deposited material occurred around 635 °C for all the three filters (Figure 3-b).

**Figure 3.** Thermogravimetric curves [TG (a) and DTG (b)] obtained at 5 °C min⁻¹ in high purity synthetic air environment (99.999 %) for the three filter samples and for a control sample (0 mg).

These results showed the possibility to detect small amounts of graphene deposited on (onto) clean filters. In Figure 4 we have the TG and DTG curves obtained in the second part of the standardization study that aimed to verify the possibility to detect the graphene material in an environmental sample containing ordinary particulate matter collected outdoors.

**Figure 4.** Thermogravimetric curves [TG (a) and DTG (b)] obtained at 5 °C min⁻¹ in air atmosphere synthetic high purity for real environmental sample without and with graphene.
Figure 4 (a) shows the weight loss for a control (black) and an environmental sample (red) acquired during the pilot plant operation. These two curves are drastically different in the 400 °C and 750 °C range, showing a new event that can be more easily visualized in the DTG curve, Figure 4 (b), where a new peak at 650 °C is observed. Below 400 °C both samples behave similarly except that the environmental sample has an additional peak at 310 °C.

3.3 Real indoor samples

Figure 5 shows the TG (b) and DTG (a) curves for a control filter (red) and a filter containing airborne material collected inside the production plant. Two new thermal events are present in the indoor sample with peaks at 590 °C and 760 °C, as shown in Figure 5 (a). As shown in the nanomaterials characterization results, few-layer graphene material produced in the pilot plant has combustion temperature of 620 °C (peak). The onset temperature is 460 °C and endset 780 °C, which can be assigned to the combustion of a mixture of carbonaceous materials: amorphous carbon (between 400-500 °C) and different types of graphene materials (~ 575-750 °C)^1,14. Stein and co-workers also notice sequential thermal events taking place in graphene nanoplatelets TGA profiles, which can be attributed to the a diverse range of dimensions and defect densities^8.

Figure 5. Thermogravimetric curves [DTG (a) and TG (b)] obtained at 5 °C min^-1 in air atmosphere synthetic high purity for real indoor samples.

As this sample contains the total particulate matter collected - besides the expected presence of amorphous carbon as a dust ordinary component - different carbon and nanocarbon contributions can be attributed to the workplace processes. At this site, natural graphite, products and subproducts originated from the conversion process are regularly manipulated in different activities - from weighting to drying of nanomaterials small amounts.

Although it is clear the likelihood of airborne exposure, an in-depth filter analysis was performed to confirm the presence of such materials. In Figure 6 we present SEM-EDS mapping, Figure 6 (a) shows that, in addition to the quartz fibers, the sampled filter contains small-sized high contrast particles (aspect of common dust) and larger low contrast and lamellar particles. The last ones are composed essentially
by carbon (Figure 6-c) and its translucid aspect indicates a material with few layers. The filters elemental composition of mainly silicon atoms is showed in Figure 6-b.

Figure 6. SEM image obtained for filter containing airborne material collected inside the production plant. In (a) secondary electrons image and its corresponding silicon (b) and carbon (c) EDS maps.

In Figure 7 are presented the Raman spectra and XRD pattern obtained for filter containing airborne material collected inside the production plant. As shown in Figure 7 (a), the obtained Raman spectrum is typical of a crystalline graphitic material \(^{10,16,20}\). It is possible to notice an intense G-band signal around 1580 cm\(^{-1}\) corresponding to the graphite band, which refers to the sp\(^2\) bonds between carbons in the sp\(^2\) configuration. The disorder induced D-band is located between 1330-1340 cm\(^{-1}\); The relationship between its intensity and the full width at half maximum (FWHM) of the G band can be related to the number of defects presented in the sample, which can be punctual or linear defects or edges. \(^{21}\) The 2D band, around 2700 cm\(^{-1}\), is also present and used to the identification of graphene and/or graphene layers\(^{16}\).

Characteristic peaks of graphite/graphene materials are also observed at the diffractogram (Figure 7-b): at 26.7° (2θ) referring to the plane 002 and at approximately 43,46° (2θ) corresponding to the plane 101 \(^{22-24}\). Narrow peaks indicate the presence of crystalline carbon in the filters.

Figure 7. Raman spectrum (a) and XRD pattern (b) obtained for filter containing airborne material collected inside the production plant.

In summary, we can affirm that the sampled filter is a multicomponent system, having a mixture of different types of carbonaceous materials. The microscopic and spectroscopic results confirm the presence of graphitic materials, although no clear distinction between graphite and graphene could be accomplished in this particular sample through these techniques. In this sense, the differences on the
thermogravimetric behavior can be a useful tool allowing the detection and differentiation of the carbon materials and nanomaterials. High resolution thermogravimetry (HRTG) along with DTG line shape analysis can be used to evaluate multicomponent systems. Trigueiro and co-workers used the HRTG and the theoretical adjustment of DTG with Gaussian function to evaluate the degree of homogeneity and to quantify the fraction of metallic compounds, amorphous carbon and graphite particles present in samples of carbon nanotubes before and after purification process. The authors were able to differentiate thermal events of 3 °C of difference with accuracy of ± 4% of weight loss. The same method was used by Lima and co-workers to evaluate the effect of the addition of single wall carbon nanotube on the thermal stability of nanotube/graphite blends.

4. Conclusions

The results presented here reveal that direct-on-filter TGA of air samples collected inside a graphene pilot plant can provide information regarding graphene materials airborne exposure. The thermogravimetric analysis can be used as a complementary technique to the standard gravimetric methods aiming to assess the graphene materials presence on the collected airborne particulate matter. The continuation of this work will be focused on determining detection limits with regards of total particulate matter weights and on the analysis of filter samples with HRTG in order to identify and quantify the contributions of the different materials in these complexes samples. This will allow a complete evaluation of the airborne exposure inside the workplace environment, including the estimation of the graphene air concentration in the total particulate matter collected.

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