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NanoImpact 33 (2024) 100499

Contents lists available at ScienceDirect

NanoImpact

journal homepage: www.elsevier.com/locate/nanoimpact

Elemental carbon - An efficient method to measure occupational exposure from materials in the graphene family

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ARTICLE INFO

Editor: Bernd Nowack

Keywords:
Occupational health
Elemental carbon
Thermal optical analysis
Graphene
Exposure measurement
Risk assessment

ABSTRACT

Graphene is a 2D-material with many useful properties such as flexibility, elasticity, and conductivity among others. Graphene could therefore become a material used in many occupational fields in the future, which can give rise to occupational exposure. Today, exposure is unknown, due to the lack of efficient measuring techniques for occupational exposure to graphene. Readily available screening techniques for air sampling and -analysis are either nonspecific or nonquantitative. Quantifying materials from the broad graphene family by an easy-to-use method is important for the large-scale industrial application of graphene, especially when for the safety of working environment. Graphene consists primarily of elemental carbon, and the present study evaluates the organic carbon/elemental carbon (OC/EC)-technique for exposure assessment. The purpose of this work is to evaluate the OC/EC analysis technique as an efficient and easy-to-use method for quantification of occupational exposure to graphene. Methods that can identify graphene would be preferable for screening, but they are time consuming and semi-quantitative and therefore not suited for quantitative work environment assessments. The OC/EC-technique is a thermal optical analysis (TOA), that quantitively determines the amount of and distinguishes between two different types of carbon, organic and elemental. The technique is standardised, well-established and among other things used for diesel exposure measurements (ref standard). OC/EC could therefore be a feasible measuring technique to quantitively determine occupational exposure to graphene. The present evaluation of the technique provides an analytical method that works quantitatively for graphene, graphene oxide and reduced graphene oxide. Interestingly, the TOA technique makes it possible to distinguish between the three graphene forms used in this study. The technique was tested in an industrial setting and the outcome suggests that the technique is an efficient monitoring technique to be used in combination with characterisation techniques like for example Raman spectroscopy, scanning electron microscopy and atomic force microscopy.

1. Introduction

With an increased use of a new material, questions arise concerning the material's potential hazardousness, and thereby risk at exposure. Both producers of the materials and users will be concerned (Laux et al., 2018). Graphene as one new type of material with extraordinary properties, has been intensively studied for different applications. The focus has started to shift from gram scale in laboratory research to kilograms mass production and large-scale applications. This is for example evidenced by the progress of the Graphene Flagship at a European level, but also by different national initiatives. One example is the "SIO grafen" which is a strategic innovation programme supporting

Abbreviation: BLG, Bi layered graphene; CNT, Carbon nanotubes; EC, elemental carbon; FID, flame ionization detector; FLG, Few layered graphene; GNF, Graphene nano family; GNP, Graphite nano platelets; GO, Graphene oxide; OC, organic carbon; PC, pyrolytic carbon; rGO, reduced graphene oxide; SLG, Single layered graphene; TC, Total carbon; TOA, Thermal optical analysis.

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https://doi.org/10.1016/j.impact.2024.100499
Received 11 October 2023; Received in revised form 9 February 2024; Accepted 16 February 2024
Available online 17 February 2024

the industrial graphene and 2D material development in Sweden (SIO-Grafen, 2024). In the last nine years "SIO grafen" has had over 200 projects involving over 200 organisations working on innovations of graphene. Along with the success of graphene-related research and applications, standards for the vocabulary and how to characterize graphene have been and are being developed in international standardisation bodies (ISO, 2023; IEC, 2023). However, the development of a feasible method to measure the occupational exposure to graphene is sought after.

Graphene's toxicity is still being investigated and researchers are therefore not sure how to judge graphene's hazardousness (Bianco et al., 2022). Also, the occupational exposure to graphene is to a large extent unknown, since only a few studies have been performed (Spinazzè et al., 2016; Spinazzè et al., 2018; Vaquero et al., 2019; Boccuni et al., 2020; Bellagamba et al., 2020; Lovén et al., 2021). Further, there exists no standardised method for quantitative exposure assessment to graphene in the work environment, rather, there are a multitude of characterisation methods for the material. Measurements have been performed with set ups comprising many qualitative techniques (Lovén et al., 2021).

Graphene is the building block of a group of different materials by convention named "the graphene nano family" (GNF) (ISO, 2017). The graphene structure is made up of sp2 hybridised carbon atoms in hexagonal units bounded in a single atom layer (Bianco et al., 2013). A material with this structure is named single layer graphene (SLG). It has a thickness of about 0,335 nm and a planar 2D structure, with a size usually between 100 nm and 100 μm. Multiple layers of SLG can be bounded on top of each other to form bi-layered graphene (BLG), consisting of two layers or few layered graphene (FLG), consisting of three to ten layers (ISO, 2021). A common form of graphene is graphene nanoplatelets (GNP) which consists of short stacks of platelet-shaped graphene sheets (Bianco et al., 2013). When using the term graphene, it mostly refers to a material consisting of one to ten graphene layers. When ten or more graphene layers have bounded on top of each other, the electrical structure changes and the material is referred to as graphite (Bianco et al., 2013). The GNF comprises the before mentioned graphene materials but also chemically modified forms of graphene. Some of the most common are graphene oxide (GO) which is oxidized graphene, and reduced graphene oxide (rGO) the reduced form of GO.

A large hurdle to overcome when it comes to the study the toxicity of graphene, is the question of which material to investigate. Properties such as lateral size and number of layers, are factors that have been observed to affect the toxicity (Bianco et al., 2022). Many studies have been performed in this area, and many review articles of the area have been published in recent years (Domenech et al., 2022; Cebadero-Domínguez et al., 2022; Ghazimoradi et al., 2022; Xiaoli et al., 2020). It appears that graphene on a cellular level might be able to cause some adverse toxic effects. The longest duration of graphene exposure was merely a couple of months, which is not directly transferable to prolonged occupational exposure (Bianco et al., 2022). Therefore, in addition to toxicity risk assessment, the exposure needs to be assessed, especially when toxicity evaluation related to human exposure is scarce. Traditional occupational hygiene measurement methods cannot be applied for several of these new materials, due to the lack of specificity and sensitivity for nanomaterials such as nano carbon tubes (CNT) or 2D-materials like graphene. There is a need to evaluate available technologies and identify methods that can be used as standards for measuring carbon-based nanomaterials for risk assessment in working environments.

An established method used for air-quality measurements quantifies elemental carbon (EC). Air samples are pumped onto quartz fibre filters and this is now a standardised technique used for occupational measurements of diesel exhaust (*Directive (EU)* 2019/130 Of the European Parliament and of the Council of 16 January 2019 Amending Directive 2004/37/EC on the Protection of Workers from the Risks Related to Exposure to Carcinogens or Mutagens at Work, 2019). The instrument used is a dedicated thermal optical analyser (TOA). The basis for the method is that EC needs oxygen to be combusted, while organic carbon (OC) can be combusted in an oxygen-free environment (Birch and Cary, 1996). First, the OC is separated from the filter by heating in a helium atmosphere and in a second step the EC is combusted in a helium-oxygen atmosphere. The carbon released from the filter is reduced to methane and detected with a flame ionization detector (FID), thereby measuring the mass of carbon that was collected on the filter. The technique is readily available and will provide an exposure-measure in μg EC/m^3. OC/EC-analysis has further been used multiple times to study exposure to CNT, a material with similar composition as graphene but shaped like a small tube (Birch et al., 2011; Hedmer et al., 2014; Guseva Canu et al., 2020). NIOSH has acknowledged OC/EC as a standard technique for measuring air concentrations of CNT and has also proposed an occupational exposure limit of 1 μg EC/m^3 for CNT (Guseva Canu et al., 2020).

Basically, sampled filters are heated following a pre-set protocol for temperature increase. The protocol determines a stepwise temperature increase in each phase (OC or EC) and for how long the temperature should be held. Many different protocols exist, and any labs can easily produce their own protocols.

Graphene mainly consists of EC and the OC/EC instrument has been used to determine occupational exposure (Vaquero et al., 2019; Lovén et al., 2021; Lee et al., 2016). However, neither of these have specifically investigated how OC/EC-analysis works with different materials from the GNF and the interpretation of the resulting signal. NIOSH states in the standard procedure for diesel exhaust NIOSH5040, that the technique can be used to measure different carbon nanomaterials (*NIOSH Manual of Analytical Methods (NMAM)*, 2017). In such cases, it is recommended to also analyse the bulk material in order to be able to identify the material of interest.

The aim of this research was therefore to investigate how OC/EC measurements can be used for quantification of graphene and its derivatives as a standardised tool in occupational exposure measurements of graphene.

2. Material and method

2.1. Material

The graphene materials studied in this article can be found in Table 1. The GNPs, GO and rGO () powders were obtained from Abalonyx (Norway) (now LayerOne), Nanesa (Italy), Graphenea (Spain) and Sigma Aldrich (US) respectively. The rGO1 was prepared in-house by reducing water-dispersed GO from Layer One using hydrazine hydrate as reduction reagent. GO was reduced under relatively low temperature (60 °C) and adjust pH (pH = 11) in order to prepare the well-dispersed single layer rGO in water, instead of the aggregated rGO large particles. Graphene oxide (GO) can be well dispersed in water after sonication, while the graphite nano platelets (GNP) and heavily reduced graphene oxide (rGO) do not form a stable dispersion in water due to agglomeration and hydrophobic surface. While rGO can be suspended in water long enough (minutes) to extract reproducible amounts of material, GNP will agglomerate. Graphene 1–3 and graphite were obtained from industrial scale commercial graphene producer 2D-FAB. These materials contain significant amounts of graphite due to the production process and were obtained in powder form. The graphite arrives to the factory in an expanded form and consists of large particles (Table 1).

2.2. Method

2.2.1. SEM- analysis

All graphene materials were spread over conducting carbon tape before the analysis in the SEM. To make GO conductive it was treated in a LEICA EM ACE600 for 6 min producing a 4 nm thick layer of gold coating over the carbon tape and the material. The SEM-analysis was performed using JEOL 7800F prime under 5 kV at different

Table 1
Short summary of the different graphene and graphite materials studied in this article. The form mentioned in the table, is the form the material was in when it was transferred onto the quartz fibre filter for the OC/EC-analysis.

Name of material Producer	Abbreviations	Form	Average thickness	Lateral size (d_{50})
Graphite nano platelets 1 Graphmatech AB	GNP 1	Water dispersion	1–20 nm	< 5 μm
Graphite nano platelets 2 Nanesa	GNP 2	Water dispersion	1–20 nm	< 5 μm
Graphene oxide Layer One	GO	Water dispersion	1 nm	1–3 μm
Reduced graphene oxide 1 Chalmers university	rGO 1	Water dispersion	1–30 nm	10–20 μm
Reduced graphene oxide 2 Graphmatech AB	rGO 2	Water dispersion	1–30 nm	10–20 μm
Reduced graphene oxide 3 Layer One	rGO 3	Water dispersion	1–30 nm	10–20 μm
Graphene 1 2D-fab		Powder	4 nm	8 μm
Graphene 2 2D-fab		Powder	4 nm	14 μm
Graphene 3 2D-fab		Powder	4 nm	24 μm
Expanded graphite Proprietary information		Powder	250 nm	250 μm

magnifications.

2.2.2. OC/EC-technique

Analysis of graphene and graphite were performed with a thermal-optical analyser for organic- and elemental carbon (Sunset laboratory inc., Parsippany, NJ, USA).

Samples are collected onto, or materials are placed on quartz fibre filters and analysed in the instrument. The filter is first heated in a He atmosphere, where the organic carbon is desorbed from the filter, followed by heating in a He—O_2 atmosphere where the elemental carbon leaves the filter, see Fig. 1. The carbon compounds that leave the filter are oxidized to CO_2 in a manganese oxide oven and then reduced to CH_4 before being detected with an FID. The combined amount of OC and EC is categorized as the total carbon (TC), which is the total amount of carbon present on the sample. The analysis makes it possible to quantitatively determine the amount of carbon present in the sample, even if the amount is very low (μg). The cut-off point between the OC and the EC is determined by light-transmittance. The analysis protocol used is based on the NIOSH5040 method described in NIOSH manual of analytical methods (*NIOSH Manual of Analytical Methods (NMAM)*, 2017). The instrument detection limit is 0.20 μg/cm^2.

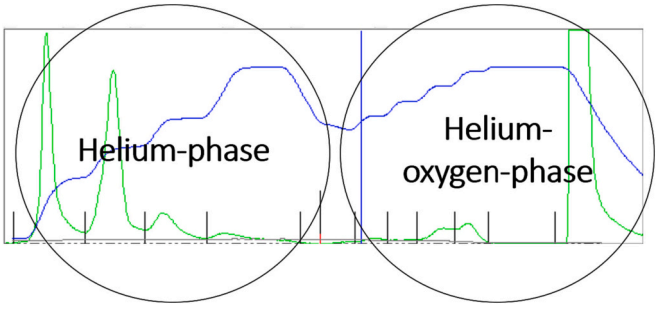

Fig. 1. Curves from OC/EC-analysis of carbonaceous samples on quartz-fibre filter. OC is emitted and detected during the helium phase and EC is emitted and detected during the helium-oxygen phase. The blue line represents the temperature of the sample during the analysis, the green line is the carbon detection by the FID during the analysis. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

During the helium atmosphere phase some of the OC is charred to the filter and is converted into pyrolytic carbon (PC) due to the fast-rising temperature (Cavalli et al., 2010). PC is very similar to EC and will also be desorbed in the He—O_2 atmosphere, which would give an incorrectly high EC-signal. To account for the produced PC a laser is used, either measuring the transmission or the reflectance of the filter. Both PC and EC absorb the laser at 810 nm, while OC does not. Therefore, when the PC is produced a decrease in laser signal is detected. This difference is then used during the He—O_2 atmosphere to correct for the produced PC, making it possible to estimate the original amount of EC on the filter (Cavalli et al., 2010).

2.2.3. Procedure for graphene analysis

Quartz fibre filters were heat treated in a muffle furnace at 900 °C for 2 h. A 1.5 cm^2 piece was cut out from a quartz fibre filter (Merck Millipore) and was placed on the quartz glass spoon in the Sunset OC/EC-instrument (*Sunset-Laboratory-Inc. Organic Carbon / Elemental Carbon (OCEC)Laboratory Instrument Manual*, 2024). Each sample in Table 1 was analysed. The sample was placed onto a piece of quartz fibre filter, either by pipetting or by weighing the powder. For the samples diluted in water with a concentration of 1 mg/mL (see Table 1) a pipette was used to transfer different amounts of the solution onto the quartz fibre filter. The filter was inserted into the oven of the Sunset instrument which then was used to dry the filter. The graphene samples in powder form, see Table 1, were weighed using a Mettler Toledo analytic scale. A piece of quartz fibre filter was placed on the scale, and the graphene or graphite samples were added to this filter and the weight was noted. This filter was then inserted into the OC/EC-instrument for analysis. Data from the analysis was analysed using Sunset's calculating software Calc451 and Calc453 to determine the OC, EC and TC of each sample.

In NIOSH5040 no temperature program is specified (*NIOSH Manual of Analytical Methods (NMAM)*, 2017). In the present study, samples were analysed using a protocol specified by the instrument vendor called NIOSH930 setting (Panteliadis et al., 2015), see Table A1 in appendix A for specifications. The two highest temperature steps were maintained for a longer time, compared to the original instrument setting, to ensure that graphene samples were desorbed from the filter.

2.2.4. Calibration

The instrument was calibrated with sucrose solutions according to the manufacturer's instructions. Different amounts of graphene materials were analysed in order to determine the linearity of the method. Three different amounts, 5, 7.5 and 10 μL, of a 1 mg/mL solution of the GO and rGO materials were pipetted on to a quartz fibre filter for analysis.

2.3. Measurements in the work environment

The technique was applied in a production facility, where graphite is reshaped into graphene. The sampling presented in this manuscript was sampled when the workers were mixing the produced graphene powder in a small container 50x25x20 cm^3, half full of graphene powder. The raw graphene obtained from the production process, was mechanically converted to specified powders, and the procedure lasted for a couple of hours. The process was performed in a small room, 4 × 2 meter, with no other EC-sources. Air samples were collected by connecting an air pump (Gillian 5000XR) to a sample holder (Millipore monitoring cassette 37 mm) holding a 37 mm quartz fibre filter, with an air flow of 4.0 L per minute. The filter was placed in the breathing zone of two workers for personal sampling, and the stationary sampling was placed in the other side of the room, 1.5 m away.

Person 2 was the worker that handled the graphene material and converted the raw graphene material to specified powders. Person 1 was standing in the background and observed the process. During the graphene handling, graphene material 1, 2 and 3 presented in Table 1 were handled. Samples of these materials were obtained during the visit and brought back to lab for analysis.

2.4. Data presentation

In all attached figures from the OC/EC-analysis the data curves have been normalized for easier comparison.

2.5. Material characterisations

A JEOL JSM-7800F Prime scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) was used to analyse the morphology and particles size.

The materials graphene 1, 2 and 3 and graphite were analysed with UV–vis by the producer 2D-fab, to determine the thickness of the materials. SEM was used to study the size and morphology of these materials.

3. Results

3.1. Graphene analyses

The commercial GO, rGO, and GNP were selected as testing materials to evaluate OC/EC for different materials, and their morphology and nanostructure were examined by SEM (Fig. 2). The GNP flakes with large lateral size (up to 5 μm) are composed of multilayer graphene. Graphene can be also observed, but most abundant are the graphite nanoplates. The GO powders are micrometer sized particles. In the GO dispersion, GO appears as exfoliated nanosheets. After drying they show the typical feature of graphene wrinkles. In contrast to GO, rGO in dispersion aggregates, with a size in the tens of micrometers range due to interactions.

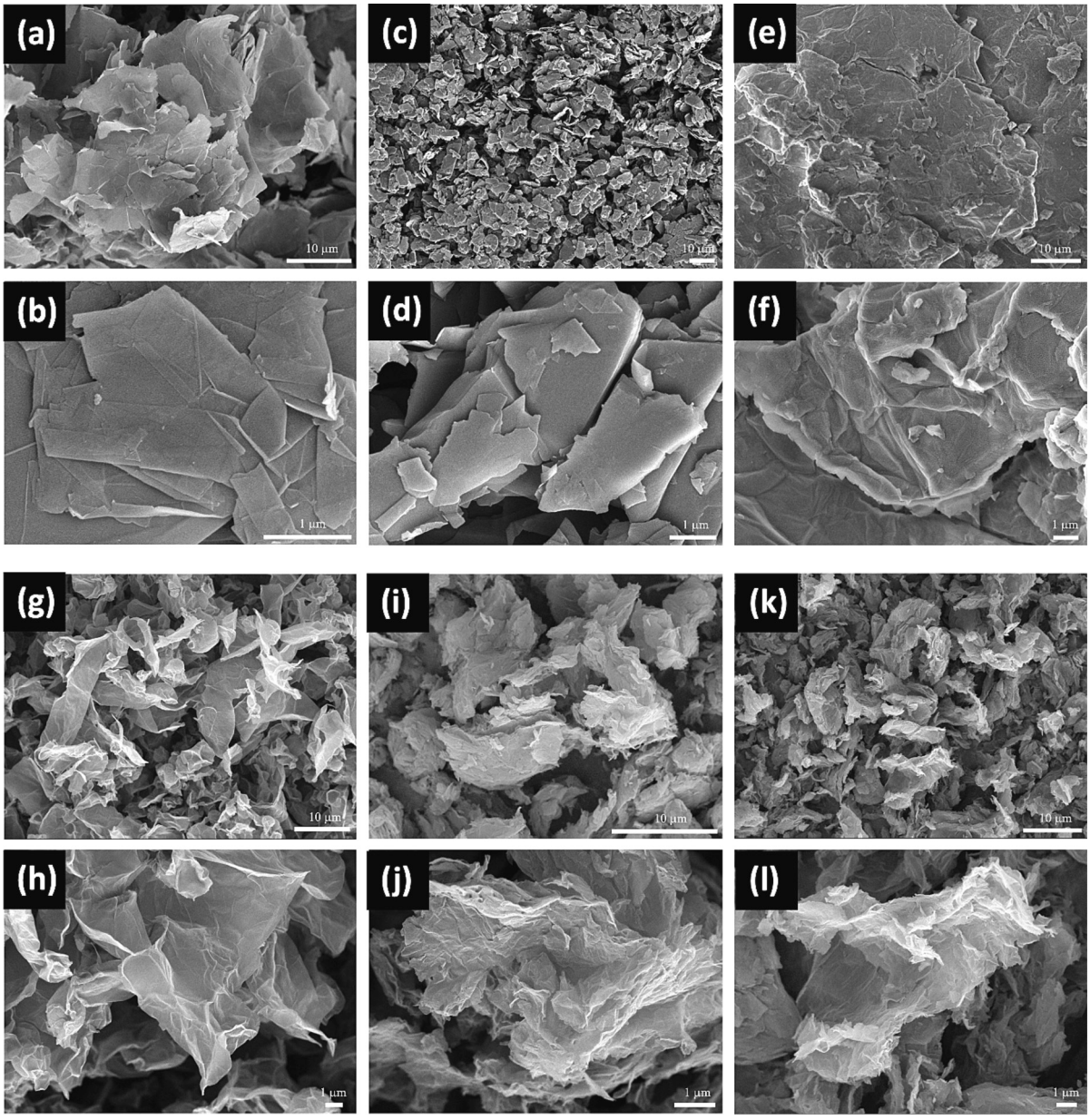

Fig. 2. SEM images of the graphene and graphite materials studied in this article. (a) and (b) are GNP 1, (c) and (d) are GNP 2, (e) and (f) are GO, (g) and (h) are rGO1, (i) and (j) are rGO2 and (k) and (l) are rGO3.

The graphene 1, 2 and 3 varied in lateral size as presented in Table 1, from 8 μm to 24 μm. The material contained a mix of graphite and graphene particles with an average thickness around six graphene layers measured with UV–vis. The expanded graphite consisted of many hundreds of layers of graphene and had a varying lateral size, with an average around 250 μm. SEM images of all materials can be found in Fig. 3.

The curves from GO, rGO and GNP display visible differences regarding their emissions from the filter, with increasing temperature (Fig. 4). Overlap can be seen between all the materials, but there are differences in their peak emission temperature.

In Fig. 5, the results from four different materials obtained from a graphene producer can be observed. The three different graphene materials were produced using the graphite material as raw material. Data shows that there is a large overlap in emission. The graphite material seems to be emitted from the filter earlier than two of the graphene materials and have a narrower emission temperature.

Fig. 6 presents how the emission peak varies due to the amount of material added to the filter. As can be seen, when increasing the amount of graphite on the filter from 110 μg to 180 μg, the emission peak is broadened.

Fig. 7 shows a comparison between three different rGO materials and one GO material. GO can be observed to have a visibly earlier emission time than the rGO materials. This is because of the removal of the oxygen containing functional groups (e.g., hydroxal, epoxy, carboxylic groups) (Sun et al., 2023; Sun et al., 2018). A large overlap between rGO2 and rGO3 can be seen, the materials were bought from different producers, which might explain the difference in emission time. rGO1 leaves the filter earlier than the other two, due to the presence of residues of carboxylic functional groups (Sun et al., 2021). This material was produced in the university laboratory, which might have led to some deformities compared to the industry produced material and thereby a different emission temperature.

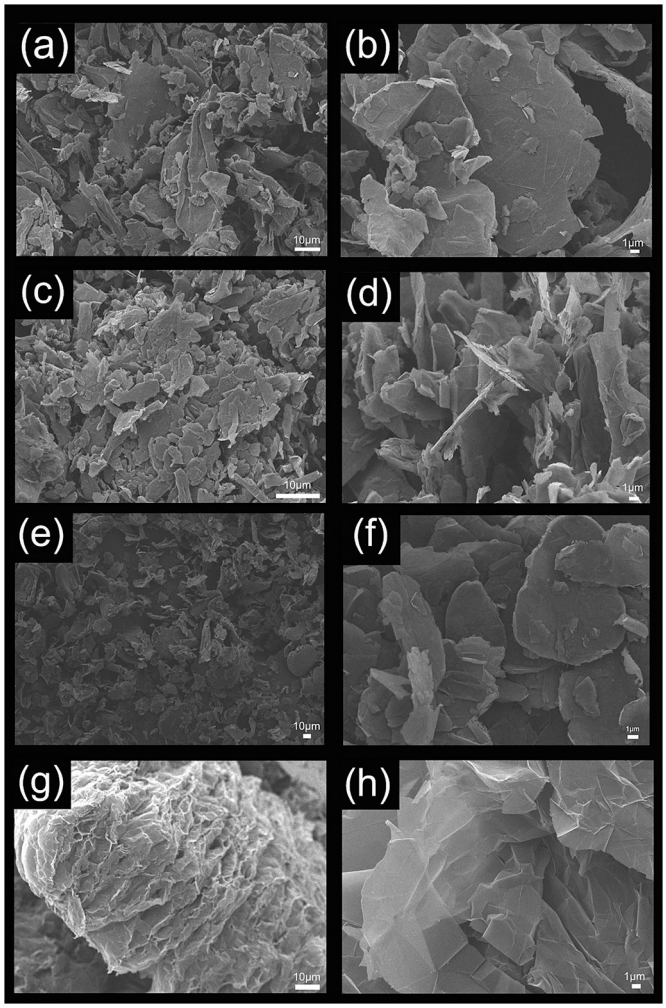

Fig. 3. SEM images of the graphene and graphite materials studied in this article. (a) and (b) are Graphene 1, (c) and (d) are Graphene 2, (e) and (f) are Graphene 3 and (g) and (h) are graphite.

3.2. Calibration

The results from the calibration curve can be seen in Figs. 8 and 9. All signals received from the FID has been normalized to a 0 to 1 scale to easier be able to compare the different graphene materials. As can be seen the graphene derivatives has a linear correlation between amount of sample added to the filter and the signal received from the FID.

In Figs. 8 and 9 the analysis of graphene materials of different amounts can be observed, it can also be seen that the TC signal received matches well with the amount of GO and rGO added to the quartz fibre filter. The OC and EC signal for both materials are quite different, a show different ratio of OC and EC in GO and rGO. The signal received appears to be related to the total amount of carbon added to the filter.

3.3. Results from in the field measurements

Measurable levels of elemental carbon were found in the air during the in-field measurement at the graphene producer. The quantification limit of 0.20 μg/cm^2 for EC gives with 15 min of sampling a quantification limit 29 μg/m^3 and the detection limit for an entire workday (8 h) was 0.9 μg/m^3. The duration of measurement in the current study was 110 min which gives a detection limit of 3.9 μg EC/m^3.

The signals received from the filters sampled in the personal breathing zone matches well with the graphene materials that were handled during the measurement see Fig. 10, where graphene 3 is presented. Graphene 1 and 2 were also handled and can be seen in Fig. 5.

Air measurement of person 2 that worked the graphene material showed a concentration of around 60 μg EC/m^3. For person 1, who observed the process in the background, a concentration of about 20 μg EC/m^3 was recorded. The stationary measurement, 1.5 m from the handling area, showed 15 μg EC/m^3. The EC-concentration was measured during the handling of all three materials and the air samples collected are therefore a combination from handling all three graphene materials.

4. Discussion

New and promising materials, their production, use and recirculation might impose new health risks and therefore exposure assessments are needed. Assessment of airborne exposure in the work environment relies on appropriate measurement techniques and when it comes to materials in the graphene family, no single measurement technique has yet been made available for efficient quantification of airborne exposure.

In this exploratory study we have done measurements and exposure screening. The results from the present study show EC-analysis as a feasible tool that can be used for screening of airborne exposure to materials in the graphene family. Analysis of known amounts of graphene derivatives, gives a linear response to mass, verifying that the signal received matches well with the amount of graphene (Figs. 8 and 9). The OC/EC-analysis can therefore be used for graphene quantification.

Interestingly, the thermo-optical analyses of different graphene derivatives, result in different emission patterns from oxygen-containing derivatives on one side, and graphene and graphite on the other side. GNP and graphite show quite similar emission patterns, which can be explained by the high content of graphite in the graphene materials included in this study. Field measurements performed at a graphene

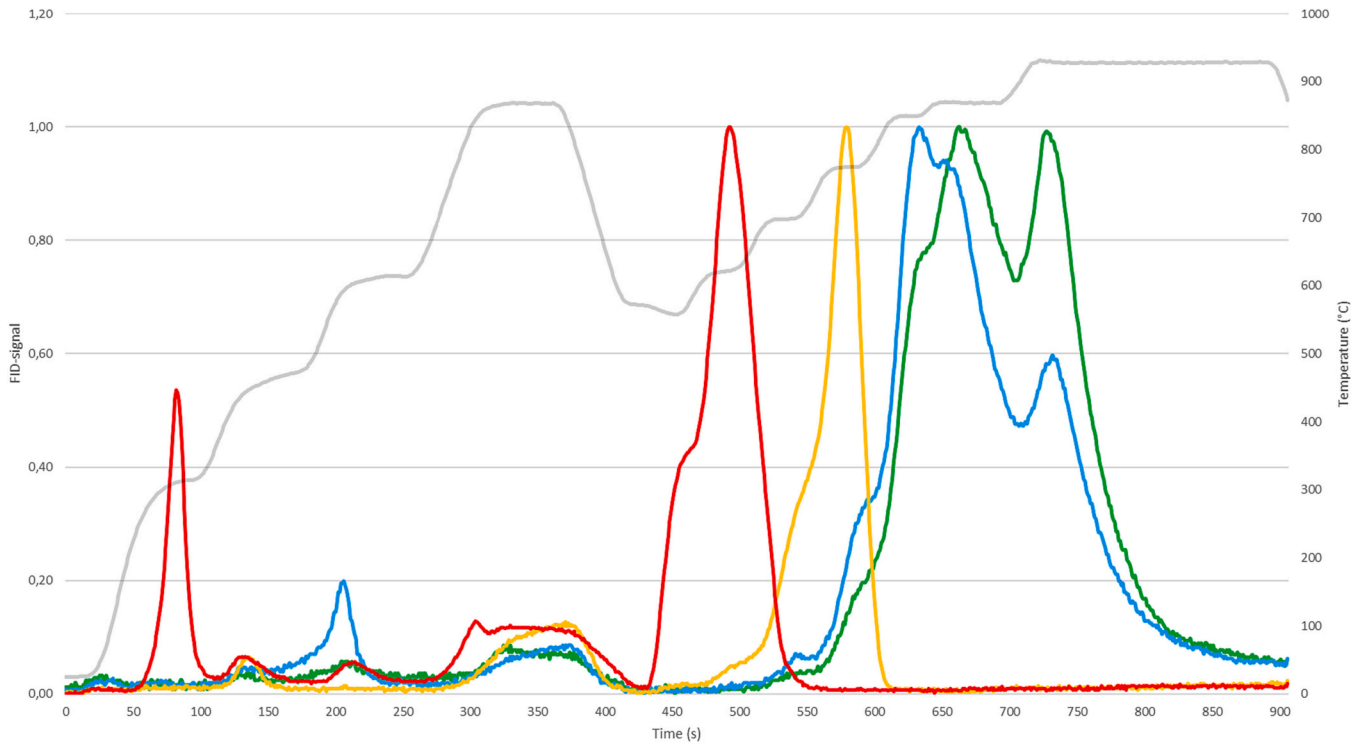

Fig. 4. GO and rGO characteristics are easy to distinguish from graphite, though there are some overlaps. (—)-GO, (—) rGO2, (—) GNP 2 and (—) GNP 1 and (—) is the temperature, as has been presented in Table 1. All signals received from the FID has been normalized to a 0 to 1 scale to easier be able to compare the different materials.

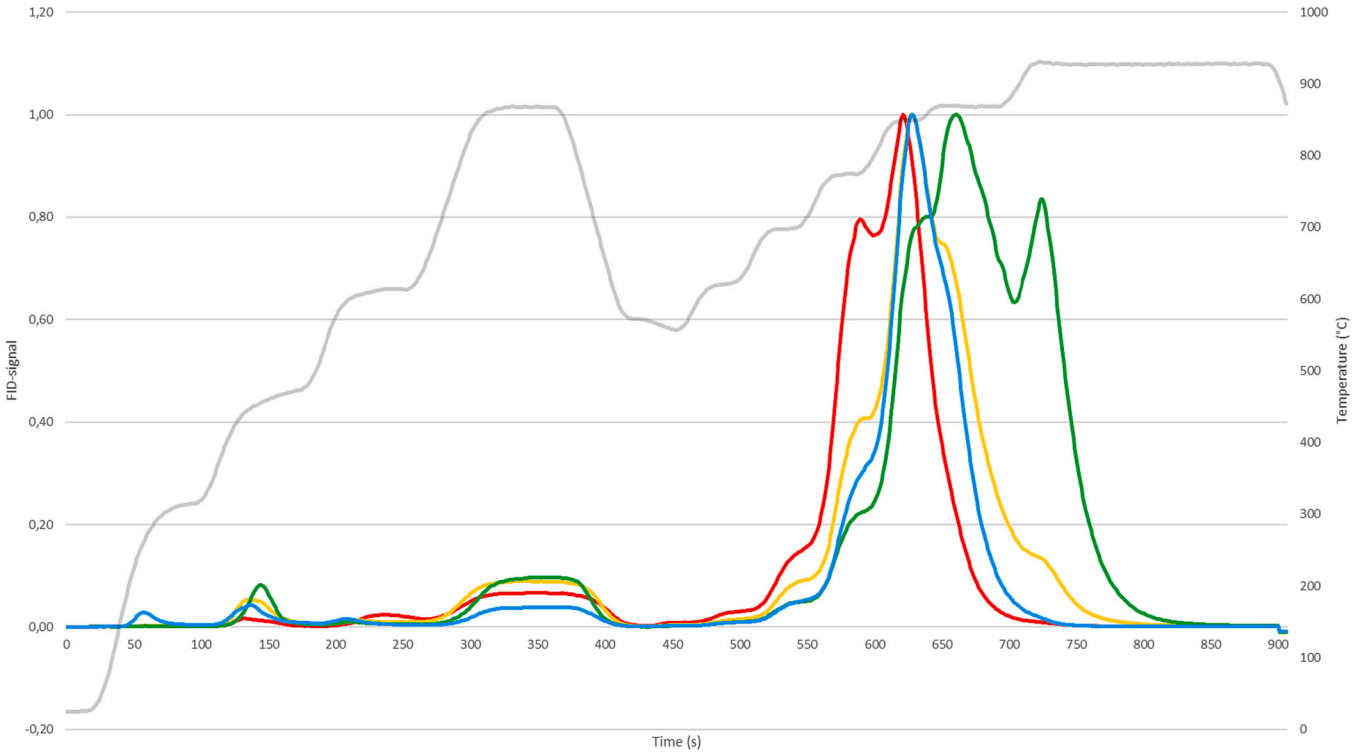

Fig. 5. Analysis of three types of graphene and the graphite raw material used to produce the graphene materials. (—) graphene 1, (—) graphene 2, (—) graphene 3 (—) Graphite and (—) is the temperature, as has been presented in Table 1. The three graphene materials were handled during the work environment measurement. All materials were obtained from a graphene producer. All signals received from the FID has been normalized to a 0 to 1 scale to easier be able to compare the different materials. Large overall between all the signals can be observed. One of the graphene materials can be observed to be the material that leaves the filter last. Similar amounts of the different materials were analysed, graphene 1130 µg, graphene 2100 µg, graphene 3110 µg and graphite 110 µg.

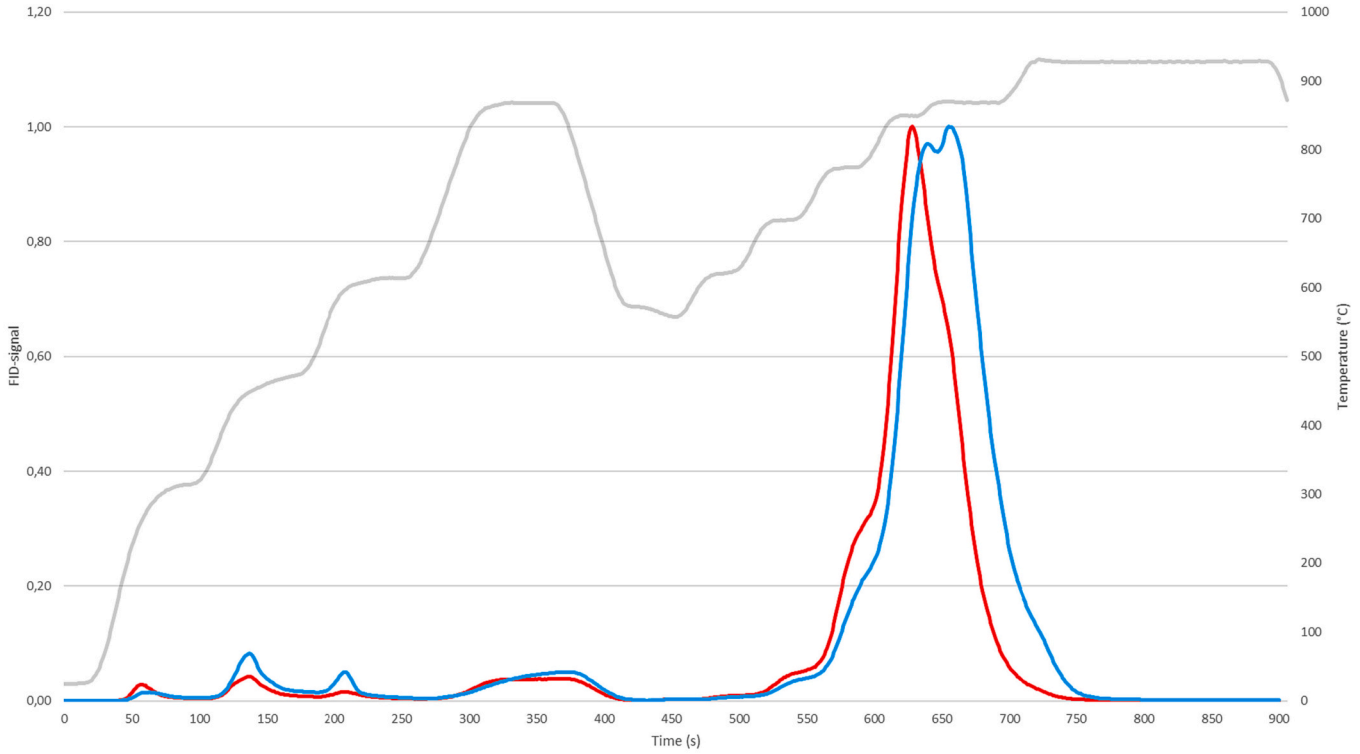

Fig. 6. Influence on filter load on emission temperature. Analysis of the same graphite material, but to different amounts. (—) 110 μg graphite, (—) 180 μg graphite and (—) is the temperature, as has been presented in Table 1. All signals received from the FID has been normalized to a 0 to 1 scale to easier be able to compare the different materials.

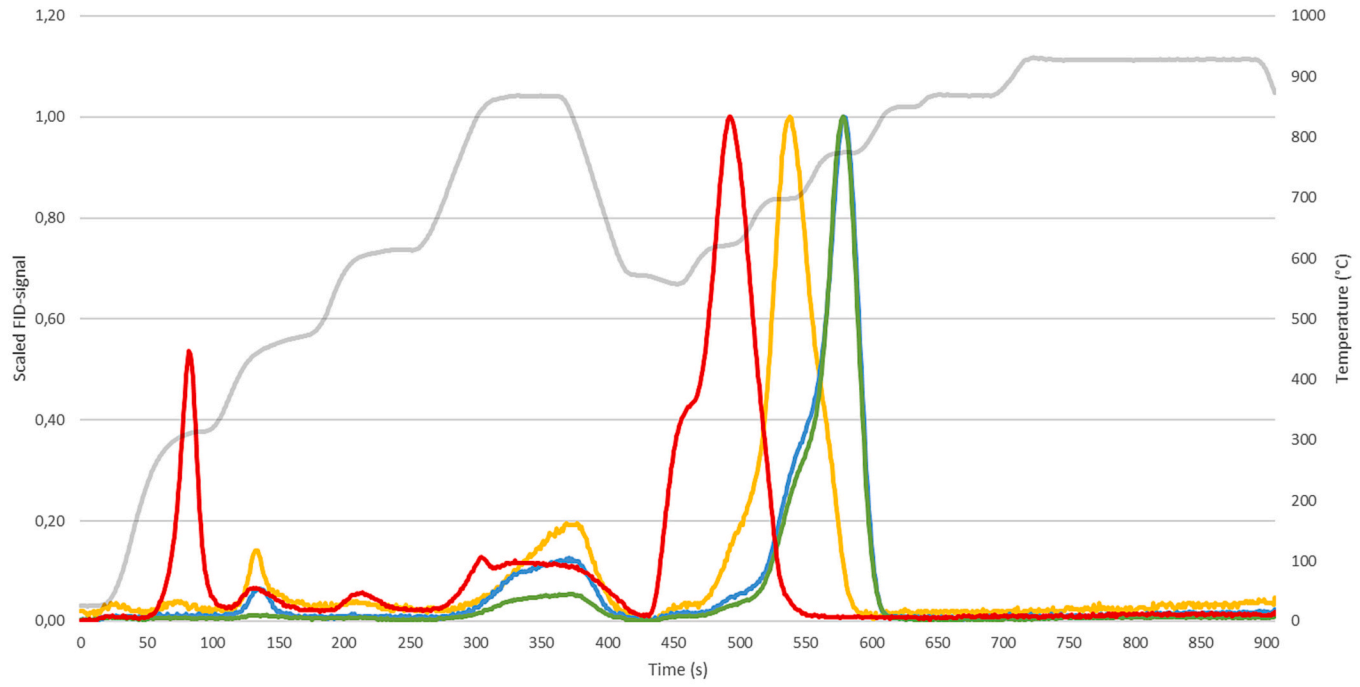

Fig. 7. Comparison of three different rGO materials and a GO. (—)-GO, (—) rGO1, (—) rGO2 and (—) rGO3 and (—) is the temperature, as has been presented in Table 1. Results from the analysis of three different rGO and a GO material. All signals received from the FID has been normalized to a 0 to 1 scale to easier be able to compare the different materials A large overlap in the rGO materials named 4 and 5, both these materials were bought from a producer. rGO 3 was produced in the laboratory where the materials were obtained. GO can be distinguished from the other materials, having a signal earlier.

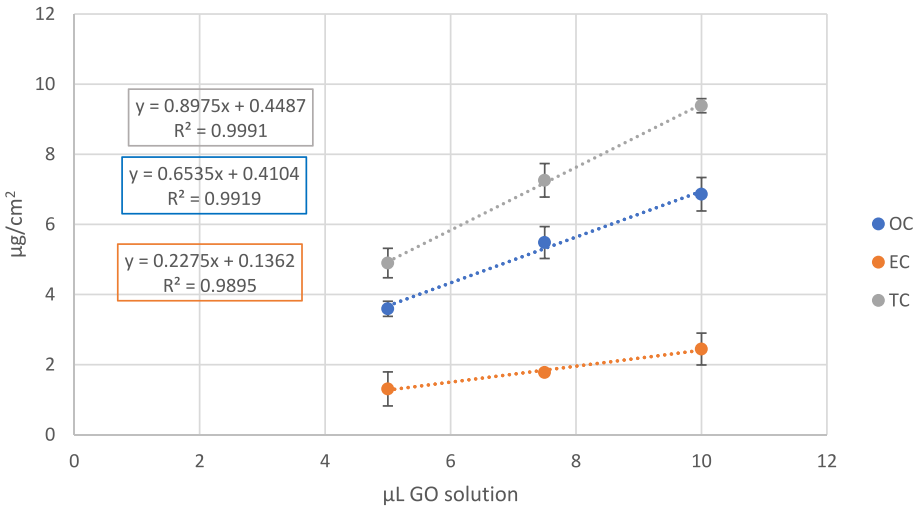

Fig. 8. Calibration curve of the GO, with a concentration of 1 µg/µL, analysed in the OC/EC-instrument. $N = 4$.

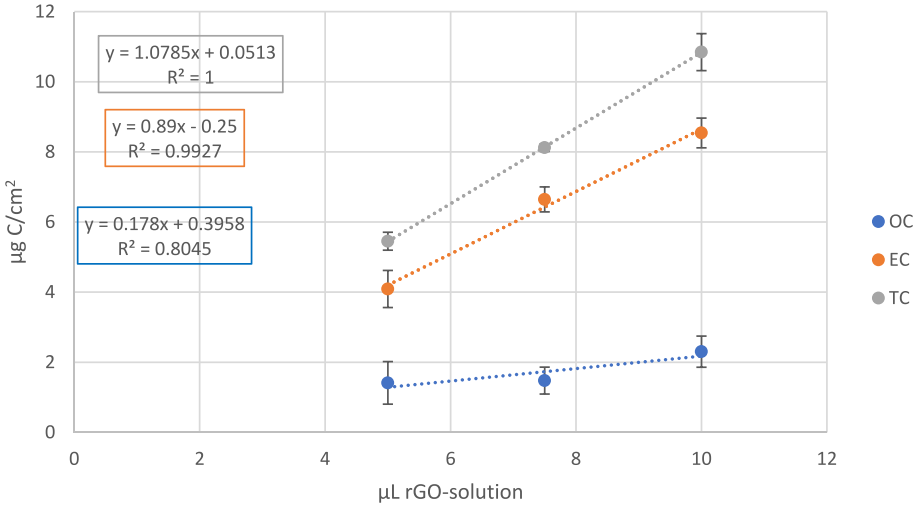

Fig. 9. Calibration curve of one of the rGO (SIO-Grafen, 2024) with a concentration of 1 µg/µL, analysed in the OC/EC-instrument. N = 4.

producer, see Fig. 6, show that collected air samples correlate with the graphene material handled.

Studies on the occupational exposure to graphene during the last few years have employed many different measurement techniques (Spinazzè et al., 2016; Spinazzè et al., 2018; Vaquero et al., 2019; Boccuni et al., 2020; Bellagamba et al., 2020; Lovén et al., 2021; Lee et al., 2016; Tombolini et al., 2021). There are a few methods that are in common among the research articles, but many measuring techniques are only used by some of the researchers. What is clear is that there currently does not exist any standardised method of how to quantify graphene and its derivatives in occupational environments. A quite commonly used method to detect graphene in air is collecting samples on filters and analysing the content with scanning electron microscopy (SEM) (Vaquero et al., 2019; Boccuni et al., 2020; Bellagamba et al., 2020; Tombolini et al., 2021; Hedmer et al., 2022). Particle characterisation by SEM is effective for determining the morphology of a material, it is however not a very efficient method to find out the air concentration of a material, due to the time-consuming analyses. The same holds for transmission electron microscopy (TEM), which applied together with a spectroscopic technique such as Raman or energy dispersive spectroscopy (EDS), can be used to identify graphene in air samples (Tombolini et al., 2021). Thus, there is a need for an efficient quantitative method.

A common method for graphene determination in air, is to count the number of nano particles. There are several different instruments that can be used for this purpose, for example condensation particle counter (CPC) (Spinazzè et al., 2016; Spinazzè et al., 2018; Vaquero et al., 2019; Boccuni et al., 2020; Bellagamba et al., 2020; Lovén et al., 2021; Tombolini et al., 2021; Boccuni et al., 2018). This method is effective for counting spherical nanoparticles, it is however uncertain how it works for 2D-materials, having a large surface area and a small volume.

"Black carbon" (BC), measured with an aethalometer, has been used as a marker for graphene (Lovén et al., 2021), and in a study of air distribution of CNT (Hedmer et al., 2022). It is still unclear how well the aethalometer-technique is able to correctly detect graphene and CNT materials. In the study on CNT the author hypothesises that the size of the CNT causes it to get stuck in the tubing of the aethalometer, thereby being undetected (Hedmer et al., 2022).

Important to note is that the EC-technique is carbon specific and not graphene specific. If there is a graphene exposure there will be an EC-signal, but an EC-signal does not mean that there is graphene exposure. Therefore, in an unknown environment, it is important to perform a characterisation of the samples to determine if it is a graphene material, for example using suitable techniques such as Raman, in order to confirm EC-results (Childres et al., 2013).

It was expected that there would be detectable differences in EC vs temperature when comparing GO, rGO and graphene due to the

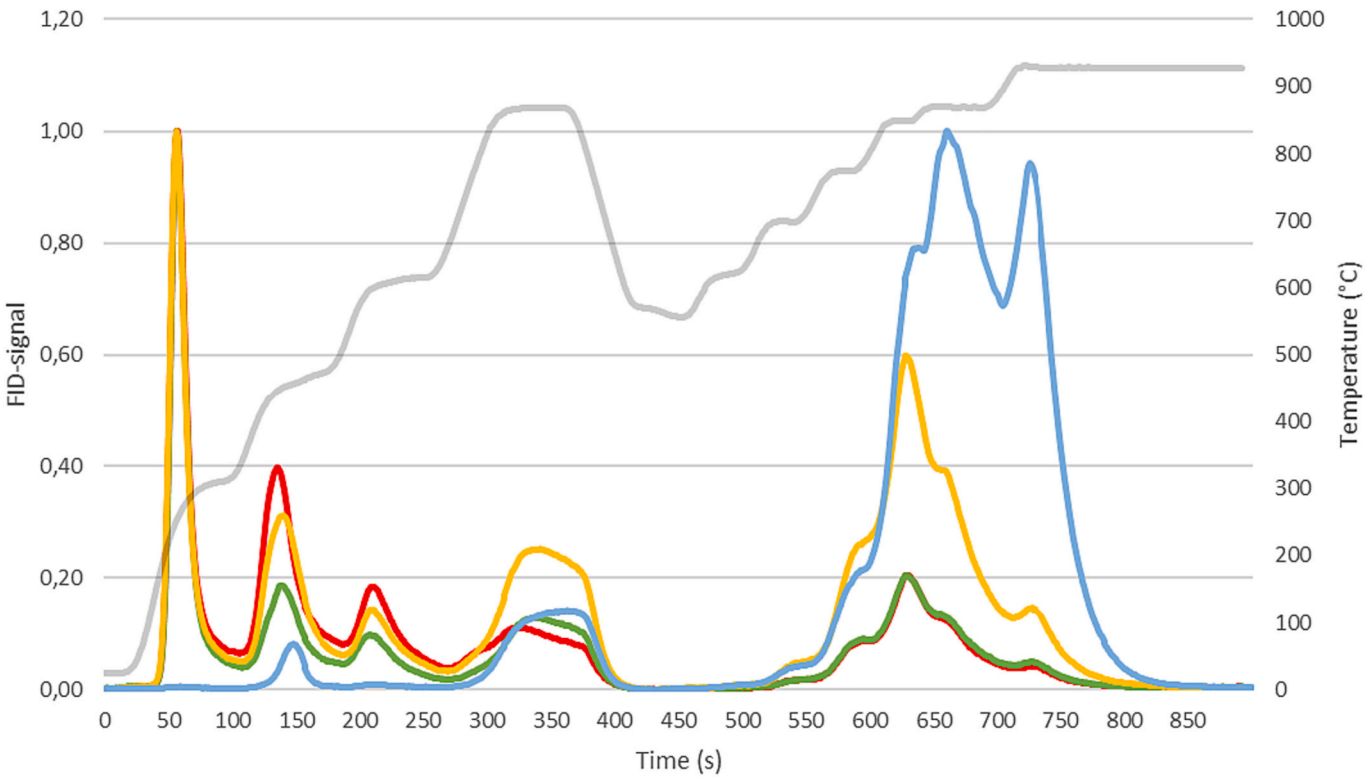

Fig. 10. Air measurements from graphene producer. (—) air measurement person 1, (—) air measurement person 2, (—) graphene material (graphene 3) and (—) stationary measurement and (—) is the temperature. During the work with the produced graphene powder three measurements were made. Two personal measurements and one stationery background measurement, away from the emission zone. During the handling three different graphene materials were handled. In the plot the analysis of one of the materials can be see together with the analysis of the three air measurements, similar outlined curve can be seen on all measurements. Measurements had higher OC-levels due to being air samples, while the graphene sample was pure graphene.

chemical and structural differences related to oxygen content. Also, the chemical similarity between graphene and graphite predicted that selective detection of graphene in presence of graphite would be very difficult given the design of the TOA technique.

4.1. Using thermal optical analysis (OC/EC) to analyse graphene materials in air

The standardised analysis of elemental carbon is complementary to effective characterisation techniques like SEM and TEM and the direct-reading instruments like CPC and aethalometer since the EC-analysis is quantitative and does not rely on the shape of the material. Field-sampling for EC-analysis is similar to sampling for SEM/TEM analysis, but the EC-analysis is extensively less costly and considerably less labour intensive, meaning that occupational exposure can be logged and broadly investigated. In comparison with direct-reading instruments, laboratory EC-analysis of course leads to a time gap from measurement to data reception, but any carbonaceous material will be quantified, regardless of shape and size.

The present study verifies the usefulness of EC-analysis for occupational assessments. As can be seen in Figs. 4 and 5, graphene materials give clear EC-signals when analysed with the OC/EC Sunset instrument. For different graphene materials it can be observed that graphite and graphene need higher temperature, compared to rGO and GO. In addition, there are less pronounced differences between the graphene materials. GO is emitted at a lower temperature than the other materials, and most of the GO has been emitted before any rGO is emitted. Following that, such a finding might allow the identification GO in a mixture, but this has to be further verified. Two of the rGO materials are emitted at about the same temperature, while one of the rGO materials, rGO1, is emitted at a lower temperature see Fig. 4. While rGO1 was produced in a small lab, the other rGO samples were bought from a manufacturer, a fact that can explain this result. The closer similarity of rGO1 to GO is assumed to originate from the characteristics of the oxygen-containing functional groups.

While there exists a clear difference between the oxygen containing forms (GO and rGO) on one side and graphite on the other, (Fig. 4), the difference between graphite and graphene is small with a large overlap between the two materials, (Fig. 5). In Fig. 5 there is a large overlap between graphite and the three types of graphene, with graphene being the material emitted at the highest temperature. Different graphite materials give different emission patterns as can be seen when comparing Figs. 4 and 5, where graphite in Fig. 3 has a much more compact emission phase. The reasons for this can be many, and probably lie in the structure of the materials. The influence of how thickness (number of graphene layers) and lateral sizes affect the emission time is not yet studied. If lateral size is a dominating factor, this could explain why graphene needs higher emission temperature than graphite, due to a portion of the graphene flakes having a larger surface area than average graphite flakes. But lateral size does not seem to be the determining factor that affects the rGO emission. In the analysis of the university graphene and graphite materials, rGO can be seen leaving the filter at a lower temperature than GNP, (Fig. 4), even though the rGO had a larger lateral size. In this case, the most likely explanation is the thickness of the materials, rGO has fewer layers than the graphite and/or damages in the graphene layer left over from the oxidation. This should mean that graphene would be emitted earlier than graphite, but as has already been mentioned this is not always the case, (Fig. 5).

Another factor that plays a key role in the emission of graphene and graphite from the filter, is the amount of material added to the filter, (Fig. 5). An increase of graphite material gives rise to a much different emission pattern. This could make it hard to distinguish different

materials from each other in the OC/EC-analysis. However, the amount investigated in Fig. 5, is almost 10 times higher than the amount normally collected in an air measurement, which usually is in the range of 20 μg or less.

In order to make it possible to draw some conclusions on GNF-materials' structure based on EC-emission, future research could be directed towards analysing multiple graphite and graphene samples with clear differences regarding layer thickness and lateral size. Modification of the OC/EC-analysis NIOSH-protocol might be necessary, for example regarding the duration of the steps in the temperature program. However, if the goal is to quantitate and not differentiate the graphene derivatives, it is most straightforward to use a protocol similar to the one presented in Lovén 2021, a protocol with the sole purpose of oxidating all carbonaceous nanomaterials on the filter (Lovén et al., 2021).

4.2. Calibration curve

As can be seen in the calibration Figs. 8 and 9, there is correlation with amount of added solution and the signal received from the analysis. As can be seen in the graphs there is a strong correlation with the amount of material put into the analysis and the signal that is received from the analysis. Both rGO and GO have low standard deviation between analysis. Which indicate that the OC/EC analysis is a method that is able to quantify small amounts of graphene accurately. A similar calibration curve was attempted for both graphene and graphite, but due to the low solubility in water it was hard to add precise amount of the materials to filter thereby giving the analysis a large error.

4.3. Calibration

The calibration of the OC/EC instrument is checked by analysing an aqueous solution of a carbohydrate (sucrose) before every sample run. Although it was anticipated that the calibration would hold also for GNF materials, the linearity was checked and confirmed (Figs. 8 and 9). Here, both rGO and GO show low standard deviation between repeated analyses, which demonstrates that the OC/EC analysis is an appropriate method for accurate quantification of small amounts (low micrograms) of graphene. A similar calibration curve was attempted for both graphene and graphite, but due to the difficulty of dispersing these nonpolar materials in water, it was hard to add precise amounts of the materials to the filter, thereby producing a large deviation in this case. This was not investigated further.

4.4. OC/EC cut-off point

A reoccurring problem with any protocol for the analysis of graphene materials using OC/EC- instrument is the cut-off point between OC and EC given by the instrument, because the instrument is designed for samples having large amounts of OC.

The cut-off point is determined by a laser signal that detects the transformation of OC to pyrolytic carbon (PC) during the helium-phase of the analysis. This formation of PC affects the laser signal, and the PC will leave the filter together with the EC during the helium-oxygen-phase of the analysis cycle. The laser signal is used in the software to estimate when an amount of carbon proportional to the laser-detected PC has left the filter. This time-point in the analysis will be used as the cut-off point between OC and EC. The cut-off point will differ between samples of different compositions, due to variation in OC-composition and -amount.

This is a problem when graphene is analysed on filters from occupational air sampling because the samples contain minimal amounts of OC, resulting in a lack of response in laser signal during the helium phase. Therefore, the cut-off point will not occur. In cases where the graphene material has manually been added to the filter (for example for calibration), the machine recognises the signal as EC in most cases. With graphene samples from in-field measurements, the amount of graphene on the filter is well distributed over the surface, thereby difficult to detect for the laser signal. In this case, the instrument counts all FID-signal as OC, even though most of it or all of it should be classified as EC. Here, the researchers need to study the result and use their experience and prior knowledge about the samples.

4.5. In field air measurements

Measurable levels of elemental carbon, well above the instrument detection limit, were found in the air during the in-field measurement at a graphene producer.

The possibility that the EC-signal observed during this measurement is due to some outside interference, such as a diesel engine exhausts, is extremely low, why the measured EC very likely corresponds to the material handled by the workers. The similarity is seen when comparing the signals from the graphene material and the material collected on the filters, see Fig. 10. This makes it possible to estimate maximum graphene exposure, thereby making the OC/EC-technique invaluable by filling a gap in the field of occupational assessment of graphene exposure. Of course, material analyses with characterisation-techniques, will still be needed in order to determine that the material is graphene. According to OECD guidelines it is recommended to use a multimetric approach for exposure assessment (Strategies, 2017). This was also done during this and following measurement campaigns, and will be presented elsewhere.

In order to increase the usefulness of the OC/EC-analysis technique for many types of materials in the GNF, further tests will be needed involving different types of graphene in many different occupational settings.

5. Conclusions

The OC/EC-technique is a valuable tool for assessment of airborne occupational exposure to materials in the graphene family. The present study shows that TOA-technique developed for quantification of EC from diesel exhaust works also for graphene. Method calibration shows linearity between amount of graphene analysed and the signal obtained. The thermal analysis curves show some clear differences in emission temperature between the different GNF-derivatives graphene, GO and rGO, but no general differences could be observed comparing graphite and graphene among the materials analysed. The OC/EC technique is an efficient monitoring technique for graphene in occupational settings and should be used with complementary characterisation techniques. Prior knowledge of the material in use is essential and it is emphasised that when there is a graphene exposure to be measured, there is also an EC-signal. But at the same time an EC-signal might not mean that there is graphene exposure.

CRediT authorship contribution statement

Tobias Storsjö: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis. **Håkan Tinnerberg:** Writing – original draft, Resources, Methodology, Funding acquisition, Conceptualization. **Jinhua Sun:** Writing – original draft, Resources, Investigation. **Chen Ruiqi:** Investigation. **Anne Farbrot:** Writing – original draft, Methodology, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

H Tinnerberg reports financial support was provided by Sweden's Innovation Agency. H Tinnerberg reports financial support was provided by Swedish Energy Agency. H Tinnerberg reports was provided by Swedish Research Council Formas.

Data availability

Data will be made available on request.

Acknowledgement

Thanks to Sweden's Innovation Agency, Swedish Energy Agency, Sweden and Swedish Research Council Formas, Sweden for financially sponsoring this project.

Thanks to Britta Andres at 2DFAB for assisting with information of the graphene materials as well as Johnny Johansson for assisting with the exposure measurements.

Appendix A

Tables of the different materials OC/EC analysis with two different "standard protocol".

Table A1
Parameters used for the graphene samples analysis in the Sunset OC/EC-instrument. The parameter file is based on the NIOSH930 program, the 930 °C heating step has been lengthened.

Prolonged NIOSH930		
Temperature (°C)	Time (s)	Atmosphere type
310	80	He
475	80	He
615	80	He
870	110	He
550	45	He
550	45	He/Ox
625	45	He/Ox
700	45	He/Ox
775	45	He/Ox
850	45	He/Ox
870	60	He/Ox
930	200	He/Ox

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