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Airborne nanomaterials in the workplace: graphene exposure characterization and risk mitigation measures

Exposure characterization (1) during the production phases (freeze-drying of graphene ink obtained by liquid phase exfoliation of graphite layered crystals (2)) of few layers graphene (FLG) was carried out in a Research and Development (R&D) laboratory, following a multiparametric tired approach based on the Organization for Economic Cooperation and Development (OECD) harmonized guidelines (3). Real-time measurements of particle number concentration (PNC), average diameter and lung deposited surface area, were performed. Time-integrated measurements were also achieved using inertial impactors for offline analytical characterization by Scanning (SEM) and Transmission Electron Microscopy (TEM) and Raman spectroscopy. Simultaneously to the exposure scenario measurements and samplings, biological monitoring was performed on workers involved in FLG production (4).

Results obtained from real time measurements could not exclude the FLG spillage in the air, especially when workers handled graphene in powder form, during the phase of produced materials storage and subsequent cleaning of surfaces and equipment (STOCLE). During STOCLE, FLG projected diameter (dproj) was obtained by SEM images, and it was compared with the corresponding calculated aerodynamic diameter (dae): because of the unusual aerodynamic property of platelet-like particles, FLG could penetrate and settle in a deeper region of the respiratory tract if dae is lower than dproj, as the electron microscopy evidence suggest. Raman spectroscopy and SEM analysis highlighted that the collected material was most likely FLG (i.e. morphology of flat carbon layers); finally, selected area electron diffraction (SAED) with TEM (i.e. SAED patterns related to both single and stacked graphene layers), allowed to definitively confirm the presence of airborne FLG in the workplace.

One year later in the same R&D laboratory, real time measurement and offline characterization analysis were performed again during the STOCLE, after the introduction of mitigation measures including a new fume hood and ventilated glove boxes to reduce the workers exposure to FLG in powder form, during the handling task (5). PNC time series, before and after the introduction of such mitigation measures, were compared using the non-parametric paired Wilcoxon Test (0.05 significance level) and their PNC mean values were respectively 3530 (std. dev. 1126) part/cm3 and 2914 (std. dev. 1380) part/cm3. Although a lowering of PNC values, SEM analysis revealed only one graphene aggregate, after scanning several fields, highlighting the presence of rare and residual airborne FLG. Workers were recommended to continue using respiratory personal protective equipment during the STOCLE phase.

Based on the previous results obtained in the R&D laboratory , the exposure in the scaling up of FLG production in a pilot plant has been investigated, following a prevention-through-design approach (6): the amount of FLG produced increased by ca. 20 times compared to the R&D laboratory(2 kg per cycle vs 100g per cycle) and the STOCLE phase, placed in a room separated from the other workplace areas, is confirmed to be the most critical work task.

In conclusion, the strategy applied, by the integration of real-time measurements and off-line characterization techniques, to characterize a complex exposure scenario such as the FLG manufacturing process, can provide a valid basis for both the risk assessment and management but also it can give valuable information for a prevention-through-design approach in scaling up the production from R&D laboratory to the pilot plant.

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