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Nanotechnol Russ. Author manuscript; available in PMC 2017 June 08.

Published in final edited form as:

Nanotechnol Russ. 2016 January ; 11(1): 110–116. doi:10.1134/S1995078016010055.

Assessment of Airborn Multiwalled Carbon Nanotubes in a Manufactoring Environment

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Abstract

This study was carried out in a factory producing multiwalled carbon nanotubes (MWCNTs) by the catalytic chemical vapor deposition method in a pyrolysis reactor. Air samples of the personal breathing areas were collected simultaneously on mixed cellulose ester filters, for analysis by transmission electron microscopy (TEM), and on high-purity quartz filters for thermal-optical analysis of elemental carbon (EC). It is found that the production of MWCNTs is accompanied by the release of the MWCNT structures in the air of different working zones. The concentration of respirable aerosol in the personal breathing areas, averaged over an 8-hour period, ranges from 0.54 to 6.11 μg/m^3 based on EC. Airborne MWCNTs were found in the form of agglomerates that range in size from about 1 to 10 μm. These data are consistent with measurements in different plants by two other international groups (from the United States and Sweden) using similar methodology (TEM in combination with EC analysis). In the absence of convincing data on the potential health risks of MWCNTs, and following the principle of reasonable precautions, preventive measures should be taken to minimize exposure to these materials.

Introduction

The number of companies producing or using carbon nanotubes (CNTs) and other types of carbon nanomaterials is growing, but there are relatively few published studies of occupational exposure. Exposure to carbon nanotubes, both multiwalled (MWCNTs) and single-walled (SWCNTs), and to carbon nanofibers (CNFs), continues to be a health concern [1]. Different approaches to the determination of workplace CNT/CNF have been proposed, and several methods for workplace monitoring have been applied by research groups and some larger companies [2–17].

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The problem of quantitative analysis of airborne CNTs/CNFs can be addressed in different ways. In the case of CNTs, determination of the mass concentration via the content of the accompanying metals catalysts [2–4, 9] is an indirect method, but the concentrations of CNT-associated metals may be too low to quantify, or the background interface may be too high [12, 18]. Also, the relationship between the metal and CNT mass may be variable. Thermal-optical analysis allows one to determine directly the content of elemental carbon (EC), of which CNTs consist, in an air sample taken from the workplace. An EC method, Method 5040, was developed by the National Institute for Occupational Safety and Health (NIOSH). The method was initially developed for occupational monitoring of diesel particulate matter (DPM) [18], but the thermal-optical technique on which 5040 is based has application to other types of carbonaceous aerosols [1, 18]. Dr. Birch et al. proposed its application to carbon nanomaterials and applied it in preliminary field study, for both surface and air sampling [5, 6]. In that initial survey, total carbon (TC) was reported as a measure of airborne carbon nanomaterials because both composite and bulk CNT dusts were present. Depending on the task, TC gave a measure of unbound CNT or composite dust in air samples collected in separate areas of the facility. However, the results were corrected for organic carbon (OC) background due to adsorbed vapor, and other OC interferences were absent [1]. In general, TC is not an accurate measure of CNT/CNF because of the many potential OC interferences in the workplace [1, 18]. Results of subsequent, multi-site screening surveys that induced different types of carbon nanomaterials have been reported [11], but for those surveys, the TC concentrations were not corrected for OC interference, and thus represent a worst-case scenario [19].

Based on results of laboratory and field tests, NIOSH recommended Method 5040 (with modification) for monitoring CNT and CNF, as EC [1]. Thermal-optical analysis was employed in a comprehensive study at a CNF manufacturing facility [12, 13], and in an industry-wide exposure study of workers exposed to CNTs/CNFs [17], both by NIOSH investigators. In these studies [12, 13, 17], transmission electron microscopy (TEM) and other methods (e.g., direct-reading) were applied to characterize workers' exposures. A direct counting of individual nanotubes sampled into liquid medium (distilled water) from a certain volume of the air also has been suggested [20].

Characterization of exposures is important for planning toxicological experiments, including those intended to validate the maximum allowable exposure levels. However, there are relatively few data on the content of carbon nanomaterials in workplace air. The paper reports the first study of MWCNT exposure at a domestic manufacturing facility in Russia.

Experimental

The present study was carried out in a company where a catalytic hydrocarbon pyrolysis reactor is used for the synthesis of MWCNTs [21]. In addition to MWCNTs, the company produces graphene and its modifications, nanosized carbon black, and other carbonaceous materials. It also supplies catalytic hydrocarbon pyrolysis reactors for the production of MWCNTs. The company's production capacity is over 2 tons per year. The produced MWCNTs have the trade name “Taunit”, and the main properties are given in Table 1.

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Employee exposure to CNT aerosol is possible in different production and handling processes. During the early pilot studies [4–6], material handling was found to pose the highest exposure risk for CNTs/CNFs. Subsequent studies also found manual handling as the main cause of CNT/CNF exposure. The investigators also found exposure to byproduct emissions and identified emission sources [8, 12, 13, 15 , 17] .

Identification of process areas where exposure to MWCNT aerosol is most likely to occur was accomplished through a site inspection, and by taking into account the technical documentation and consultations with the shop floor specialists. The MWCNT production was observed directly, and interviews were conducted with workers using a time card system. The data were registered in the workplace evaluation records. As a result, the following critical areas/processes were selected (Fig. 1) for monitoring:

—unloading the finished product from the reactor,

—mechanical grinding of the product,

—weighing and packaging of the finished product,

—ultrasonic dispersion in an aqueous suspension (in adjacent room),

—weighing and packaging of the finished product,

—the laboratory work area of the chemical analysis assistant (separate laboratory room).

Air samples of the worker's breathing zone were taken simultaneously on mixed cellulose ester (MCE) filters, with a diameter of 37 millimeters (mm) and pore size of 0.8 micrometers (μm) (for TEM), and on high-purity quartz filters with a diameter of 25 mm (for thermal-optical analysis). Filter cassettes were pined to the upper portion of the individual's work attire (chest pocket etc.), no further than 20 cm from oronasal area, during the main technological processes. The use of open-faced filters cassettes may result in partial loss of the sampled material due to mechanical collisions, but this is a possible issue for larger (non-respirable) agglomerates and was not a concern for this study. Leaks due to hand-assembly of the cassettes are a concern, as is sample contamination, but the latter problem is usually associated with OC rather than EC. Therefore, to avoid air leaks and filter contamination, preloaded filter cassettes, with seals at the joints of the cassette pieces, were purchased commercially.

Observation of individual nanotubes and their agglomerates in air samples by TEM, in combination with energy-dispersive X-ray spectroscopy (EDS), served as a criterion for confirming the presence of MWCNT aerosol in the workplace. High-resolution TEM analysis can provided images of individual CNT fibers and agglomerates in the sample, to estimate roughly the content of CNT structures, and to determine their morphological characteristics. The MCE filters were analyzed by a modified NMAM 7402 TEM method [16] on a JEOL 2100F transmission electron microscope.

Air sampling on the MCE filters was performed in the worker's breathing zone of the technological processing areas identified by the site inspection. At least 400 L of air was taken at each area at a rate of 7 to 16 liters per minute (L/min). The sample set included one

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blank cassette that was placed in an open area (with filter facing upward) in a lounge room. The sampling time for the blank was the same as that for the process samples. Six samples in total were taken on the MCE filters, including the air samples in the lounge room and one sample taken during nonworking hours in the middle of workroom. After sample collection, the filters were packaged in an upright position and shipped to the analytical laboratory. Bulk samples of the products, from different stages of the production process, also were provided to the laboratory for thermal-optical and TEM analyses.

For the TEM analysis, three roughly circular filter portions (with a diameter of about 8 mm) were taken from each of the sample and blank filters. The portions were covered with a graphite film and prepared for transfer to a 3-mm copper TEM grid with 200 grid openings. The grids were observed in the TEM at a magnification of 20,000×.

The TEM images of MWCNT particles in the filter samples were examined for the following structural and morphological characteristics: size, particle shape, and degree of aggregation. Depending on the number of identified fibers and MWCNT agglomerates, up to 15 grid openings per grid were inspected on a random basis, counting all of the MWCNT-containing structures, which included: matrix particles consisting mainly of amorphous carbon, with associated MWCNT and trace metals; MWCNT agglomerates; and separate fibers, which were uncommon. Up to 100 MWCNT structures were counted.

The number of MWCNT structures per mm^2 of the filter area was determined by the following formula:

$$N_{MWCNT} = N_{CS} / (N_C \times 0.01), \quad (1)$$

where N_{MWCNT} is the number of MWCNT structures per mm^2, N_{CS} is the number of counted structures, N_C is the number of inspected cells, and 0.01 is the area of one grid opening in mm^2.

The quantitative analysis was carried by determining the EC content of the quartz filters samples (Pallflex Tissuquartz®, USA) by thermal-optical analysis, using a NIOSH 5040 modified method [1, 17].

As mentioned, collection of air samples for thermal-optical analysis was performed concurrently with sampling for TEM analysis. The EC samples were collected on high-purity, 25-mm quartz fiber filters, both without and with a cyclone (GS-3 conductive plastic respirable dust cyclone, SKC Inc.). It was used to select the respirable aerosol fractions, i.e., particles penetrating into the deeper parts of the respiratory tract, to the alveolar region. Ten air samples were collected on the quartz filters, i.e., five using a cyclone for the respirable dust fraction and five without a cyclone, to approximate the inhalable fraction. In CIB 65, NIOSH (United States) set a permissible exposure limit (PEL) for CNT/CNF at 1 $\mu g/m^3$ as EC, which is above the estimated limit of detection (LOD range: 0.42 to 0.82 $\mu g/m^3$, depending on blank variability) for an air volume of about 500 L (i.e., 0.5 m^3) [1]. In our study, we took at least 270 L of air at each area sampled, with a sampling rate of 3 L/min

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and sampling period of 90 min. In addition, background (non-process areas) were collected in a worker's lounge room. No combustion engines, open flames, or smokers were present near the sampling points.

The carbon content in a sample was determined by thermal-optical analysis. As described in NIOSH 5040, OC and EC are removed, respectively, by heating the sample in inert and oxidizing atmospheres. The evolved carbon undergoes oxidation in a heated bed of manganese dioxide (850°C), subsequent reduction to methane (by a heated nickel catalyst), and measurement of methane by a flame ionization detector (FID) [22]. As applied to DPM and other ultrafine, carbonaceous aerosols, the split between OC and EC is based on the filter transmittance (or reflectance) signal, which is continuously monitored (using a pulsed diode laser and photodetector). The filter transmittance (reflectance) decreases when samples contain materials that carbonize, forming a light-absorbing “char.” In such cases, an optical correctionis automatically made by the data analysis software to reduce positive bias due to char. As char is oxidized from the sample filter, the filter transmittance (reflectance) increases and approaches its initial value, which is designated as the OC-EC split. All carbon evolving prior to the split is defined as OC, while that evolving after the split is considered EC [18].

NIOSH also recommended application of the thermal-optical method for occupational monitoring of carbon nanomaterials, CNTs and CNFs in particular. Because of the larger particle size of these powders relative to DPM (micrometer-sized CNT agglomerates versus ultrafine DPM), a manual split is usually necessary [1, 17]. In addition, some CNTs may require minor adjustments to the temperature program (e.g., Mitsui MWCNT-7 requires a longer period and higher maximum temperature, e.g., 920°C, for oxidation [1]). Analysis of the bulk CNTs/CNFs (e.g., 10–20 μg) is recommended to examine their thermal profiles, to determine the onset of oxidation and maximum temperature required [1]. This information also is useful in setting (manually) the OC-EC split [1].

The quartz filters were carefully removed from the cassettes and transferred to a clean aluminum foil surface. Using a metal punch, a 1.5 cm^2 sample portion was removed from the filter and placed into the analyzer furnace compartment, and the elemental and organic carbon was determined in $\mu g/cm^2$. The obtained EC value was multiplied by the sample deposit area (3.46 cm^2 for the 25-mm filter) to calculate the total EC in each sample. The calculations were carried out also for the control (clean filters) samples.

The concentration of EC in the air of the working zone was calculated from the sampled air volume according to the following formula:

$$C_{\mathrm{EC}} = \frac{\left(M_{\mathrm{EC}} - M_0\right)}{V}, \quad \mu\mathrm{g/m}^3 \ , \qquad (3)$$

where C_{EC} is the concentration of EC in $\mu g/m^3$, M_{EC} is the sample mass in μg, M_0 is the mass of EC for a control sample in μg, and V is the sampled air volume in m^3.

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The results of the thermal-optical measurements of EC were taken into account only if the presence of CNTs was confirmed in the parallel TEM sample. For these samples, the obtained EC concentrations were recalculated as an 8-h time weighed average (TWA) for the shift (8-h) according to the following formula:

$$C_{\text{cc}}=\frac{C_i \times T_i}{T_0}, \quad (3)$$

where C_{cc} is the average concentration of EC for an 8-h period in μg/m^3, C_i is the concentration of EC during the ith technological operation, T_i is the sampling time in hours, and T_0 is 8 h.

Results and Discussion

Through an industrial hygiene assessment, the following work areas and tasks were identified as having the greatest potential for employee exposure to aerosolized MWCNTs: 1) unloading/collection of the synthesized MWCNTs from the reactor, 2) area for mechanical disintegration of MWCNTs in an electric mill, 3) area for packaging of the finished product, and 4) laboratory work with MWCNTs.

In all of the test samples, TEM revealed MWCNT agglomerates with the sizes ranging from 0.5 to 10 μm (Figs. 2–3). The agglomerates were either interwined nanotubes and amorphous carbon or solely nanotubes. Individual nanotubes were not observed. Cobalt and nickel, serving as catalysts in the MWCNT synthesis, were found in the agglomerates by energy-dispersive X-ray spectroscopy (EDS).

The number of particles per 1 mm^2 of the MCE filter was also calculated. The number of MWCNTs determined by TEM was the highest for the samples collected near the reactor, giving 526 particles per mm^2 of the filter (Table 2).

The results of the evaluation of the MWCNT aerosol content in the air of different workplace zones are shown in the Table 3.

In the absence of the MWCNT exposure standards in Russia, the obtained concentrations, calculated as 8-h TWAs, were compared with the U.S. NIOSH REL for CNT/CNFs, 1 μg/m^3 as EC [1]. The respirable aerosol fraction in the worker's breathing zone, averaged over 8-h, reached 6.11 μg/m^3 during unloading of the finished product from the reactor, which significantly exceeds the recommended level.

Both the EC and the TEM data indicate the presence of airborne MWCNT within the facility during production and processing of MWCNT. In addition, MWCNT particles were detected in the air of working areas even during nonworking hours with the equipment shut down, which means the possibility of exposure of the service personnel, company managers, and others (customers, etc.).

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It was also found that the method of counting the number of individual MWCNTs sampled from the air to distilled water [20], as recommended by the Russian MR 1.2.2639-10 standard, is difficult to apply because airborne MWCNTs are present in the form of agglomerates with a size of 0.5 to 10 μm.

As expected, the maximum MWCNT (as EC) concentrations in the working areas were detected during manual unloading of the finished product from the reactor, while laboratory work was accompanied by the lowest MWCNT aerosol mass concentrations.

A comparison of estimated MWCNT concentrations found by different researchers is shown in Table 4. Indirect (from residual amounts of catalysts) or inaccurate (simple gravimetry) methods of evaluation of the MWCNT content in air were used in the early stages. The EC method, which allows one to measure the concentration of CNTs and CNFs with greater selectivity, precision, and sensitivity, to ensure the consistency of the results obtained by different groups, was put into practice progressively starting in 2011 [1, 12, 16, 17]. The accumulation of exposure data by accurate and consistent methodology, in a variety of workplaces internationally, is necessary for planning and carrying out toxicological and epidemiological studies that will eventually help to establish science-based exposure standards to protect worker health.

Despite differences in the floor plans and technological processes used for CNT/CNF production by different companies, the EC results (respirable fraction) found in this study, generally agree with the results obtained by two other research groups, at NIOSH (USA) [12, 17] and Lundt University (Sweden) [16], although the NIOSH studies have generally found results below the NIOSH REL of 1 $\mu g/m^3$.

A concentration of 6.11 $\mu g/m^3$ of respirable MWCNT aerosol averaged over 8 h, as estimated in the present study, indicates the need to implement engineering solutions to reduce health risks to the personnel. It is necessary to organize systematic monitoring of MWCNT at different stages of the technological process. To screen the premises and identify the main points of MWCNT aerosol release, an approach utilizing simple, direct-reading instruments was proposed [11, 14]; but the instruments applied are not selective for nanomaterials, and they are not sufficiently sensitive for low-level detection [8, 12]. Nevertheless, direct-reading instruments, for both aerosols and gases, can be useful in identifying background and byproduct emissions [8, 12, 15, 17] in the workplace.

Conclusions

MWCNT production and processing is accompanied by the release of MWCNT in air. Operations such as unloading of the finished product from the reactor, packaging of the product in bags and containers, mechanical treatment of the finished product, and laboratory testing are the most significant in terms of aerosol formation and potential exposure. The concentration of the respirable aerosol fractions in the worker's breathing zone, averaged over an 8-hour period, varies in the range from 0.54 to 6.11 $\mu g/m^3$, with EC as the exposure measure. In addition, MWCNT particles in the air of working zones are detected even during nonworking hours with the equipment shut down. MWCNTs are present in the air in the

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form of agglomerates with the size ranging from about 1 to 10 μm. The obtained data are consistent with the measurements carried out in different companies by two other international groups (from the United States and Sweden) using similar methodology (a TEM method in combination with the thermal-optical analysis). In the absence of convincing data on the safety of MWCNTs for human health, and following the principle of reasonable precautions, it is necessary to introduce a system of preventive measures at manufacturing sites. Exposure can be minimized by several means such as use of closed-system designs for all operations involving MWCNTs, monitoring MWCNT in the facilities and worker's breathing zone, good industrial hygiene practice, and use of personal protective equipment (PPE). Biological monitoring and medical examinations of potentially exposed personnel also are suggested.

Acknowledgments

This work was supported by NTRC 939011K and Grant of the Government of Republic of Tatarstan “Algarysh” for prospective area “Nanotechnology” (2008–2009).

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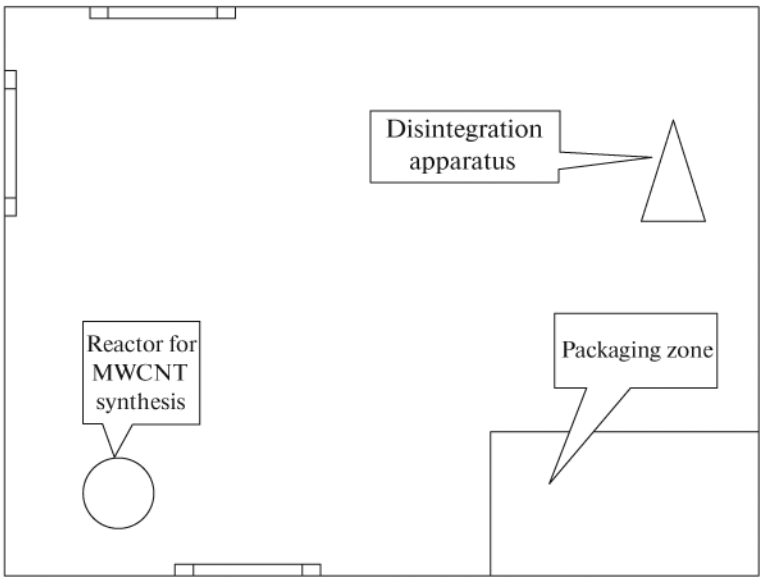

Fig. 1. Layout of MWCNT production

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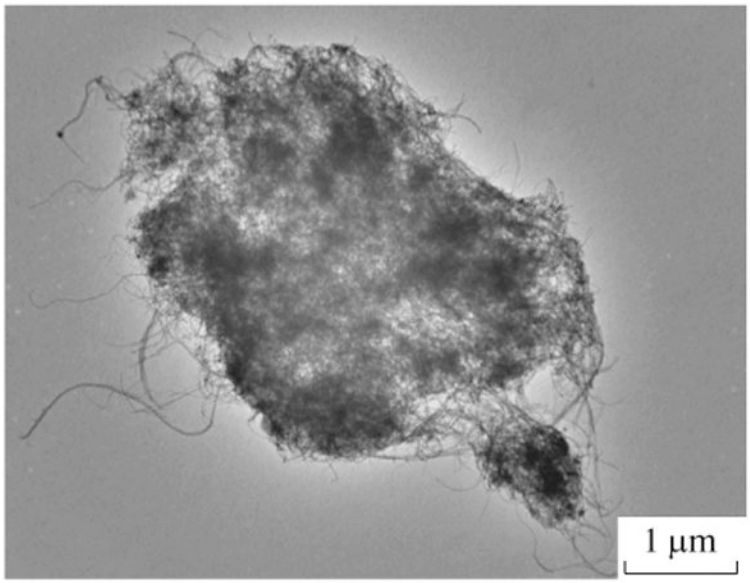

Fig. 2. MWCNT agglomerate in the air of working zones; the air sample was taken at the product disintegration site; the TEM image is at magnification of 10,000×

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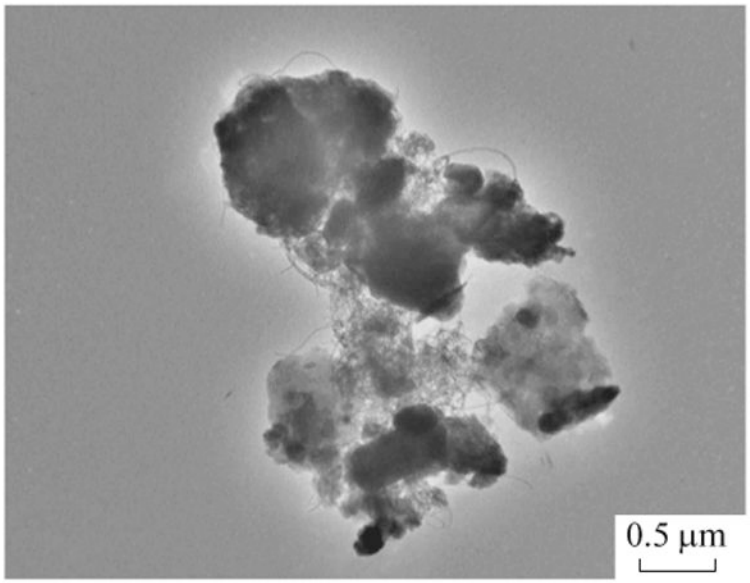

Fig. 3. MWCNT agglomerate in the air of working zones; the air sample was taken in the product packaging zone; the TEM image is at magnification of 20,000×

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Table 1

MWCNT specifications provided by the manufacturer

Physicochemical properties	MWCNT
Outer diameter, nm	8–15
Inner diameter, nm	4–8
Length, μm	2 and over
Total volume of catalyst impurities, %	up to 5
Bulk density, g/cm^3	0.03–0.05
Specific surface area, m^2/g	300–320
Thermal stability, °C	to 600

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Table 2

Number of MWCNTs and their aggregates in three TEM grids

Air sample	MWCNT/Number of observed cells			CNT/mm^2
	Grid 1	Grid 2	Grid 3	
Nonworking hours	15/14	11/13	12/13	95
Disintegration	16/14	17/13	19/13	130
Product packaging	34/8	35/6	32/7	481
Unloading from the reactor	35/6	33/6	32/7	526
Laboratory testing	1/14	1/13	2/13	10
Clean room	0/13	0/14	0/13	None

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Table 3

Elemental carbon content in air samples of working zones at different stages of the technological process

Operation	Cyclone	Short-term C, μg/m^3	TWA 8-h C, μg/m^3
Product collection	+	32.59	6.11
	–	157.77	29.60
Product disintegration	+	10.83	2.03
	–	10.92	2.05
Product packing	+	14.15	2.65
	–	134.85	25.30
Laboratory testing	+	2.87	0.54
	–	3.78	0.71

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Table 4
MWCNT contents in the air of working zones according to the published data

Sampling type	Mass concentration in the breathing zone, μg/m^3	Studies
Breathing fraction (calculated using the indirect method from the amount of a catalyst)	0.7–53	Maynard et al. 2004 [4]
Total powder weight (gravimetrical method)	n/a–331.7	Han et al. 2008 [7]
Total powder weight (gravimetrical method)	7.8–320.8	Lee et al. 2010 [9]
Total carbon in breathing fraction[a]	64–1094	Methner et al. 2010 [11]
Elemental carbon in breathing fraction (4 points)	n/a	Methner et al. 2012 [14]
Elemental carbon in breathing fraction (5 points)	n/a–7.86	Dahm et al. 2013 [15]
Elemental carbon in respirable fraction (4 points)	0.08–7.4	Hedmer 2014 [16]
Elemental carbon in respirable fraction (2 points)	0.41	Dahm et al. 2015 [17]
Elemental carbon in respirable fraction (4 points)	0.54–6.11	Current study

[a]Total carbon not corrected for organic carbon interferences [19]; n/a = not available.