Ultrafine industrial aerosol as a risk factor for the health of smelting shop workers at a machine-building enterprise

L. P. Sharavara*, N. M. Dmytrukha, I. M. Andrusyshyna

1Zaporizhzhia State Medical and Pharmaceutical University, Ukraine; 2State Institution "Kundiev Institute of Occupational Health of the National Academy of Medical Sciences of Ukraine", Kyiv

Aim. To evaluate the amount and physicochemical properties of ultrafine industrial aerosol (UIA) in the work zone air (WZA) of smelting shop workers at a machine-building enterprise under various technological processes (melting, welding, and metal machining).

Materials and methods. The physical properties of UIA particles were evaluated with NanoScan 3910 scanning spectrometer: the number of particles (number/cm³), particle surface volume (nm³/cm³), particle surface area (nm²/cm²), and nanoparticle mass concentration (μg/cm³) in the WZA of a furnace operator (n = 416), a welder (n = 315), a cutter (n = 286), a grinder (n = 286), and workers of the control group (n = 315). The chemical composition of the air samples was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using an Optima 2100 DV device.

Results. It has been found that the highest concentration of UIA nanoparticles was recorded during metal melting at the workplaces (WP) of furnace operators (4.28 × 10⁴ to 2.41 × 10⁵ particles/cm³) and welders (3.01 × 10⁴ to 3.14 × 10⁵ particles/cm³). During mechanical metal processing, a much smaller number of nanoparticles was produced (for grinders, the number varied from 9.81 × 10³ to 1.44 × 10⁵ particles/cm³; for cutters, it varied from 2.71 × 10³ to 1.94 × 10⁵ particles/cm³). Indicators of surface area, volume, and mass concentration at the WP of furnace operators, welders, grinders, and cutters exceeded the corresponding indicators of the control group for almost all sizes of suspended particles with statistically significant differences (p ≤ 0.05). It has been estimated that such metals as Al, Cu, Mg, Mo, Fe, and Ni were present in the workers’ WZA but their content did not exceed the current maximum permissible concentrations.

Conclusions. The presence of suspended particles of UIA with a maximum concentration in the range from 20 nm to 70 nm has been confirmed in the WZA during melting, welding of metals and machining. Indicators of concentration, surface area, surface volume, and mass concentration at the workplaces of melting shop workers at the machine-building enterprise significantly exceeded the corresponding indicators in the control group without dust formation processes, showing statistically significant differences (p ≤ 0.05). The evidence of metals in the WZA has suggested their presence in the form of nanoparticles, which are more active and dangerous, thus increasing the risk of their adverse effects on the workers.
In recent years, scientists from different countries have demonstrated increased interest in assessing the content of respirable dust fractions in atmospheric air and work zone air (WZA), namely ultrafine particles or suspended particles smaller than 100 nm (nanoparticles). This interest is due to the risk of their negative impact on the health of workers and the population. Today it is known that nanoparticles have completely different physical and chemical properties that cause different toxic and biological effects compared to larger ones. The ultra-small size and large surface area enable the penetration of nanoparticles deep into the lungs and the blood flow overcoming biobarriers (hematoencephalic, histohematological, placental), their translocation to target organs, as well as access to intracellular structures such as mitochondria and nucleus, etc. [1,2,3,4,5,6]. It is believed that workers’ contact with nanoparticles can cause specific adverse health effects, namely the development of oxidative stress and inflammatory processes, damage to organelles and DNA, as well as apoptosis in cells and tissue necrosis [5,7,8,9,10].

While conducting hygienic studies of working conditions in Ukraine, only suspended particles of large dust fractions (PM, PM,.) are currently identified and evaluated in the WZA. In contrast, particles of the ultrafine range (nanoparticles) are neither monitored nor considered as a high-risk factor that may impact workers’ health. At the same time, it is the nanoparticles formed during various technological processes [11] that can contribute to various negative health effects on workers, depending on their physical and chemical properties. According to modern studies, when assessing the hazards from exposure to ultra-dispersed particles of industrial aerosol, NIOSH (National Institute for Occupational Safety and Health) suggests considering the following physical characteristics: size, shape, chemical composition, mass concentration and surface area of suspended particles [10,12]. Today, many scientists confirm that suspended nanoscale particles have the greatest toxic effect due to their larger surface area, which allows them to actively adsorb and transfer harmful chemicals, increasing their degree of toxicity depending on the adsorbed material [11,12,13,14,15,16,17].

According to scientific sources, more than 6 million employees worldwide who work in the field of nanotechnology are exposed to nanoparticles. Employees in other industries may also be exposed to them, provided they are generated during various technological processes [1,18]. High-temperature processes, namely, solid fuel combustion, melting and welding, as well as high-speed mechanical machining processes, various procedures in the construction industry, operation of motor vehicle engines, numerous technological processes in the service industry, etc. present the greatest risks [5,10,15,19].

Detailed research data on the number of industrial aerosol (IA) particles, their physical and chemical properties (surface area and volume, mass concentration, and chemical composition) in the WZA of certain occupational groups (metal melting, welding, high-speed machining) are missing in most sources. Therefore, these data are important for risk assessment and identification of effective preventive measures against their negative impact on the health of workers.

**Aim**

The study aims to evaluate the amount and physicochemical properties of ultrafine particles (nanoparticles) in the composition of IA in the WZA of smelting shop workers at a machine-building enterprise during various technological processes (melting, welding, and metal machining).

**Materials and methods**

The content of nanoparticles was determined and their physical properties in the WZA were estimated with a portable scanning spectrometer NanoScan 3910 (USA), which measures particles in the range from 10 nm to 400 nm in 13 channels depending on the particle size, with a maximum ability to measure the total concentration of up to 1,000,000 particles per cm³.

For each range of nanoparticle sizes, the number (number/cm³), surface volume (nm³/cm³), surface area (nm²/cm³), and mass concentration (μg/cm³) in the WZA were determined. The content of nanoparticles in the air was examined at the workplace of smelting shop workers of the machine-building enterprise during various technological operations accompanied by the formation of condensation aerosol (such occupations as furnace operator (n = 416) and welder (n = 315)) and disintegration aerosol (such occupations as cutter (n = 286) and grinder (n = 78)). The resulting measurements were compared with the control data taken from the workplaces of the factory managerial staff (n = 515).

The study results were calculated mathematically on a PC using the licensed software Statistica version 13 (Copyright 1984–2018 TIBCO Software Inc. All rights reserved. License No. JPZ8041382130ARCH10-J). Quantitative traits were analyzed for normality by the Shapiro–Wilk test. The studied parameters that were not normally distributed, were presented using descriptive statistics in the form of median with an interquartile range – Me (Q₃−Q₁). Statistical differences between the compared values were defined with the Mann–Whitney test. p ≤ 0.05 was considered to indicate statistical significance.

The chemical composition of the air samples was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) using an Optima 2100 DV device (Perkin Elmer, USA) [NIOSH, 2001, National State Standard ISO 15202-2008]. The wavelength for each element was chosen from the WinLab32 library for the Optima 2100 DV device (provided by the manufacturer), and the most sensitive wavelengths for each element were selected.

The measurement bound (LOC, μg/l) for the method was defined as the minimum value that the device can detect in a control sample consisting of a 2.0 % nitric acid solution (HNO₃) and distilled water.

The concentration measurement convergence for each element in two parallel samples was 2.5–3.0 % according to the requirement for measuring by the OEC-IMS method. The convergence of two parallel samples showed that the measurements of toxic metals and essential trace elements were carried out by the metrological requirements for the Optima 2100 DV device and were correct (Table 1).

Obtained results were mathematically proceeded using the software of the OES-ISP WinLab32 device in the Windows XP Prof OS. As a control, the values of maximum permissible concentrations (MPC) for the WZA (based
Results

The hygienic examination has found a high dust content at the workplace to be the main harmful factor of the production environment at the machine-building enterprise. The dust present in the WZA of smelter workers was divided into condensation aerosol and disintegration aerosol by a dusting mechanism. Condensation aerosol was produced from metal melting. As a result, a molten metal evaporated from the surface under the influence of high temperatures, rose into the air, and cooled, generating suspended particles of various diameters. Employees of the machine-building enterprise exposed to condensation aerosol were furnace operators and manual welders who, by their profession character, performed technological operations of melting and welding metals with different elemental compositions.

During various types of metal components machining in the smelting shop to shape and size them as needed, workers (grinders, cutters) were exposed to disintegration aerosol containing irregularly shaped particles of various sizes, originated from such technological operations as grinding, cutting, and drilling.

When determining the concentration of ultrafine nanoparticles in the air of the smelting shop, it has been found that their number at the furnace operator workplaces during metal melting ranged from $4.28 \times 10^3$ to $2.41 \times 10^4$ particles/cm$^3$; welder workplaces – from $3.01 \times 10^3$ to $3.34 \times 10^4$ particles/cm$^3$, grinder workplaces – from $9.81 \times 10^3$ to $1.44 \times 10^4$ particles/cm$^3$, and at cutter workplaces – from $2.71 \times 10^3$ to $1.94 \times 10^4$ particles/cm$^3$.

The concentration of nanoparticles with various sizes at the furnace operator workplaces has been revealed to be significantly different from that at the workplaces of the control group employees. So, compared to the control group workplaces, the number of particles was higher by 27.8 times ($p < 0.001$) with a size of 11.5 nm, by 19.1 times ($p < 0.001$) with a size of 15.4 nm, by 10.4 times ($p < 0.001$) with a size of 20.5 nm, by 12.0 times ($p < 0.001$) with a size of 27.4 nm, by 11.5 times ($p < 0.001$) with a size of 36.5 nm, by 11.6 times ($p < 0.001$) with a size of 48.7 nm, by 11.2 times ($p < 0.001$) with a size of 64.9 nm, by 11.1 times ($p < 0.001$) with a size of 86.6 nm, by 11.0 times ($p < 0.001$) with a size of 115.5 nm, by 10.4 times ($p < 0.001$) with a size of 205.4 nm, by 7.3 times ($p < 0.001$) with a size of 273.8 nm, and by 4.7 times ($p \approx 0.002$) with a size of 365.2 nm. By comparing the data on the nanometer-sized particle concentration in condensation and disintegration aerosols at all workplaces of furnace operators, the authors have found that it was statistically significantly higher compared to the control group data ($p \leq 0.05$) (Table 2).

A higher concentration of nanoparticles during metal melting was observed for particles ranging in size from 27.4 nm to 48.7 nm with a peak concentration of 36.5 nm particles – 12945.00 (11031.00; 17648.00) particles/cm$^3$, that was 11.5 times higher than in the control group (Fig. 1a). At workplaces of welders, the maximum concentration was detected for larger particles ranging from 48.7 nm to 86.6 nm in size, with a peak concentration of 64.9 nm – 8782.33 (4655.01; 10980.00) particles/cm$^3$, that was 7.8 times higher than in the control group (Fig. 1b). At the workplaces of workers engaged in machining parts, smaller particles prevailed in terms of concentration. At the workplaces of grinders,
Fig. 1. Concentration of ultrafine IA particles (number/cm$^3$) in the WZA of furnace operators (a), welders (b), grinders (c), cutters (d), and the control group employees (e), Me (Q$_{25}$; Q$_{75}$).
the maximum number of particles was recorded in the size range from 20.5 nm to 36.5 nm, with a peak concentration of 27.4 nm particles – 9408.30 (7808.83; 8048.77) particles/cm²; that was 8.4 times higher than in the control group (Fig. 1c); at the chopper’s workplaces, particles ranged in size from 27.4 nm to 64.9 nm with a peak concentration of 48.7 nm – 6599.98 (3608.83; 8048.77) particles/cm², that was 5.9 times higher than in the control group (Fig. 1d).

At the workplaces of control employees, the concentration of nanoparticles was significantly lower, and the maximal amount was recorded for particles sized from 27.4 nm to 64.9 nm with a peak concentration of 36.5 nm – 1126.61 (870.56; 1404.61) particles/cm³ (Fig. 1e).

Depending on the particle size, the ultrafine aerosol was divided into the nucleation mode (suspended particles ≤50 nm), the Aitken mode (suspended particles sized 50–100 nm) and the accumulation mode (suspended particles ≥100 nm). The analyzed data on the IA concentration have shown that half of the studied aerosol had particles of the nucleation mode, i.e., particles with a diameter of less than 50 nm at all workplaces (Fig. 2).

As a rule, the accumulation mode particles contributed to the mass concentration of ultrafine aerosol, while the nucleation mode particles did not contribute much to this indicator but had a greater influence on the UIA concentration. The studies have shown the prevalence of the nucleation process, i.e., the formation of a considerable number of nanoparticles at the workplaces of furnace operators, as the difference for all sizes of particles was statistically significant (p ≤ 0.001).

The mass concentration of UIA nanoparticles at the workplaces of furnace operators ranged 3.14 × 10¹⁰ – 6.12 × 10¹⁰ nm³/cm³; welders – 1.68 × 10¹¹ – 2.38 × 10¹¹ nm³/cm³. At workplaces where disintegration aerosol was formed, this indicator was in the range of 2.73 × 10¹⁰ – 3.46 × 10¹⁰ nm³/cm³ for grinders and 9.76 × 10⁹ – 1.27 × 10¹⁰ nm³/cm³ for cutters. The surface volume of ultrafine particles of various sizes at the workplaces, where condensation aerosol (Fig. 5) and disintegration aerosols (Fig. 6) were formed, demonstrated similar trends in the surface area as compared to the control group workplaces, except for furnace operators, as the difference for all sizes of particles was statistically significant (p ≤ 0.001).

The mass concentration of UIA nanoparticles in the WZA of furnace operators ranged from 37.70 μg/m³ to 73.49 μg/m³; welders – from 20.18 μg/m³ to 285.37 μg/m³; grinders – from 32.78 μg/m³ to 41.51 μg/m³; cutters – from 11.71 μg/m³ to 151.96 μg/m³. Mass concentration parameters at the workplaces of the smelting shop and the control group employees are presented in Table 3.

The study results on the content of chemical elements at the machine-building enterprise are presented in Table 4. Chemical elements, Al, Cu, Mg, Mo, Fe, Ni, have been found to be present in the WZA of furnace operators engaged in various technological processes. Although their content did not exceed the current MPC levels, it can still be assumed that these nanoscale metal particles could have an adverse effect on the workers.
Table 3. Mass concentration of ultrafine particles in the working zone air of smelting shop workers, μg/m³ (Me (Q_{25}; Q_{75}))

<table>
<thead>
<tr>
<th>Size</th>
<th>Condensation aerosol</th>
<th>Disintegration aerosol</th>
<th>Control, n = 315</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Furnace operator, n = 416</td>
<td>Welder, n = 315</td>
<td>Cutter, n = 286</td>
</tr>
<tr>
<td>11.5</td>
<td>0.006 (0.004; 0.011)*</td>
<td>0.0014 (0.0010; 0.0019)*</td>
<td>0.001 (0.001; 0.001)*</td>
</tr>
<tr>
<td>15.4</td>
<td>0.022 (0.018; 0.035)*</td>
<td>0.0062 (0.0054; 0.0074)*</td>
<td>0.005 (0.004; 0.006)*</td>
</tr>
<tr>
<td>20.5</td>
<td>0.038 (0.032; 0.068)*</td>
<td>0.0151 (0.0134; 0.0176)*</td>
<td>0.013 (0.011; 0.016)*</td>
</tr>
<tr>
<td>27.4</td>
<td>0.147 (0.109; 0.215)*</td>
<td>0.0574 (0.0454; 0.0689)*</td>
<td>0.056 (0.046; 0.068)*</td>
</tr>
<tr>
<td>36.5</td>
<td>0.393 (0.338; 0.540)*</td>
<td>0.1847 (0.1087; 0.2313)*</td>
<td>0.186 (0.118; 0.220)*</td>
</tr>
<tr>
<td>48.7</td>
<td>0.929 (0.590; 1.362)*</td>
<td>0.5510 (0.2874; 0.6827)*</td>
<td>0.479 (0.262; 0.584)*</td>
</tr>
<tr>
<td>64.9</td>
<td>1.887 (0.946; 3.159)*</td>
<td>1.5111 (0.8009; 1.8893)*</td>
<td>0.719 (0.601; 1.414)*</td>
</tr>
<tr>
<td>86.6</td>
<td>3.760 (2.127; 6.388)*</td>
<td>3.4877 (1.9840; 4.0699)*</td>
<td>1.619 (1.335; 3.333)*</td>
</tr>
<tr>
<td>115.5</td>
<td>6.459 (4.199; 12.408)*</td>
<td>6.6409 (3.9809; 7.7095)*</td>
<td>3.276 (2.950; 3.037)*</td>
</tr>
<tr>
<td>154</td>
<td>11.688 (6.002; 22.104)*</td>
<td>9.5989 (6.0259; 12.0431)*</td>
<td>6.680 (4.945; 10.731)*</td>
</tr>
<tr>
<td>205.4</td>
<td>17.533 (8.982; 30.460)*</td>
<td>10.2532 (8.4740; 14.4820)*</td>
<td>9.722 (5.261; 10.933)*</td>
</tr>
<tr>
<td>273.8</td>
<td>16.561 (4.899; 43.566)*</td>
<td>3.4115 (0.8333; 14.2068)</td>
<td>3.453 (2.257; 4.711)*</td>
</tr>
<tr>
<td>365.2</td>
<td>21.242 (4.611; 58.725)*</td>
<td>5.5125 (0.0000; 22.8845)</td>
<td>4.474 (0.673; 8.854)</td>
</tr>
</tbody>
</table>

*: statistically significant differences compared to the control group (p ≤ 0.001).
Fig. 5. Surface volume of suspended condensation aerosol particles depending on size, nm³/cm³.

Fig. 6. Surface volume of suspended disintegration aerosol particles depending on size, nm³/cm³.

Table 4. Metal content in the air of the smelter working area under different technological processes, (mg/m³)

<table>
<thead>
<tr>
<th>Technological processes</th>
<th>Al</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Me</td>
<td>min</td>
<td>max</td>
</tr>
<tr>
<td>Metal melting*</td>
<td>0.008</td>
<td>0.0001</td>
<td>0.015</td>
</tr>
<tr>
<td>Metal welding*</td>
<td>0.03</td>
<td>0.0004</td>
<td>0.058</td>
</tr>
<tr>
<td>Mechanical metal processing*</td>
<td>0.006</td>
<td>0.0057</td>
<td>0.0061</td>
</tr>
</tbody>
</table>

MPC, mg/m³

<table>
<thead>
<tr>
<th>Mn</th>
<th>6.0×0.20*</th>
<th>1.0×0.5*</th>
<th>10.0×6.0*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>min</td>
<td>max</td>
<td>Me</td>
</tr>
<tr>
<td>Metal melting*</td>
<td>0.013</td>
<td>0.0002</td>
<td>0.025</td>
</tr>
<tr>
<td>Metal welding*</td>
<td>0.009</td>
<td>0.0001</td>
<td>0.019</td>
</tr>
<tr>
<td>Mechanical metal processing*</td>
<td>0.015</td>
<td>0.014</td>
<td>0.0154</td>
</tr>
</tbody>
</table>

MPC, mg/m³

<table>
<thead>
<tr>
<th>Mo</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>min</td>
</tr>
<tr>
<td>Metal melting*</td>
<td>0.058</td>
</tr>
</tbody>
</table>

*: MPC for condensation aerosol substances; #: MPC for disintegration aerosol substances (according to Order of the Ministry of Health of Ukraine No. 1596 dated 14.07.2020 "On the approval of hygienic regulations on the accessible content of chemical and biological substances in the air of the working area").
Discussion

The results of our study on the content of UIA nanoparticles in the WZA of machine-building suggest that the technological processes of melting, welding, and machining of metal generate suspended nano-sized particles, as evidenced by other studies [11, 19].

According to the literature sources [20,21,22], studies of nanoparticles in WZA are usually based on the determination of the total quantitative concentration (number/cm²) of suspended particles up to 100 nm in size without regard for a number of other essential physical properties of the UIA. Moreover, data on the physical properties of nanoparticles (such as number, surface area, surface volume, and mass concentration) are not available in the literature. Our studies examined these indicators during melting, welding, and metal machining, which is undoubtedly important for assessing the degree of occupational risk. It has been revealed that the toxicity of ultrafine (nano) particles depended not only on their size but also on other physical and chemical properties such as particle shape, surface area, exposure time and dose, chemical composition, etc. [6].

We have found that in hot and cold metalworking processes, the highest concentration was recorded among particles ranging in size from 27 nm to 64 nm. According to various literary sources, the proportion of ultrafine particle concentration of the nucleation mode up to 50 nm in size makes up most of the UIA at different workplaces. For example, during machining, ultrafine particles account for more than 95 %, during welding – for 20–60 %, and during melting – for 90 % [11]. Our studies have confirmed that the suspended particle fraction of the nucleation mode accounted for almost half of the UIA during the technological processes of melting, welding, and machining of metal, which can easily penetrate alveolar compartments of the respiratory system, freely enter the blood flow, and get to various tissues and organs. It is acceptable to assume that the physicochemical properties of UIA in the WZA can be influenced by various factors: types of material being processed, methods of metal welding and melting, the presence or absence of a ventilation system at workplaces, its effectiveness, etc.

It has been found by comparing the data obtained, that the concentration and surface area of nanoparticles was higher in hot metal working processes (metal melting and welding) than in cold ones (cutting and grinding). Other literature sources also confirm the data on high concentrations of particles in the processes of heat metal treatment, such as welding and melting [19].

Scientific studies have emphasized the importance of identifying the chemical composition of UIA at the workplaces of workers occupationally exposed to toxic metals [17]. The WZA of workers engaged in metal melting, welding and machining has been shown to contain the following metals: Al, Cu, Mg, Mo, Fe, and Ni. Although their concentrations did not exceed the established MPCs, their presence in the form of nanoparticles could increase the risk of deep penetration into respiratory organs and deposition in them, causing the development of inflammation and other pathological processes, as well as translocation and accumulation in other organs (liver, heart, kidneys) could have an extremely negative effect on employee health.

Conclusions

1. The processes of melting, welding, and machining of metal at the machine-building enterprise have been defined as a source of suspended nanoscale particles in the ultrafine industrial aerosol composition with the maximum concentration in the range from 20 nm to 70 nm.

2. The concentration of suspended particles of all sizes at the workplaces of smelting shop workers statistically significantly exceeded that of relevant sizes compared to the control group (p ≤ 0.05).

3. The majority of the studied aerosols of disintegration and condensation at all workplaces was represented by particles of the nucleation mode (46.4–63.1 %), i.e. particles less than 50 nm in diameter, indicating a high level of occupational risk.

4. Parameters of surface area, surface volume, and mass concentration at the workplaces of machine-building workers during the technological processes of metal melting, welding, and machining. Their presence even in concentrations not exceeding the established MPC levels may have negative health effects due to their higher activity in the form of nanoparticles.

5. The emission of Al, Cu, Mg, Mo, Fe, Ni has been detected at the workplaces of machine-building workers during the technological processes of metal melting, welding, and machining. Their presence even in concentrations not exceeding the established MPC levels may have negative health effects due to their higher activity in the form of nanoparticles.

6. The study on the UIA physicochemical properties at the workplaces of workers during various technological processes is a crucial step in assessing health risks to workers with further possible use of the data obtained in the implementation of an occupational risk management system at enterprises.

Prospects for further research. In the future, it is planned to continue studying the physicochemical properties of UIA in the WZA during various technological processes at industrial enterprises to further determine their negative impact on the health of employees.

Conflicts of interest: authors have no conflict of interest to declare.

Information about the authors:
Sharavara L. P., MD, PhD, Associate Professor of the Department of General Hygiene, Medical Ecology and Preventive Medicine, Zaporizhzhia State Medical and Pharmaceutical University, Ukraine.

Dmytryshka N. M., PhD, DSc, Senior Researcher, Head of the Laboratory of Industrial Toxicology and Occupational Health in the Use of Chemical Substances, SI “Kundiev Institute of Occupational Health of the National Academy of Medical Sciences of Ukraine”, Kyiv.

Andrusyshyna I. M., PhD, DSc, Senior Researcher, Head of the Sector for the Study of Microelements, SI “Kundiev Institute of Occupational Health of the National Academy of Medical Sciences of Ukraine”, Kyiv.
References


