THE EMISSION OF ULTRAFINE PARTICLES IN THE MANUFACTURE OF FIREPLACE CERAMIC TILES

KAREL LACH & IVONA SMOLOVÁ
Institute of Public Health Ostrava, Czech Republic

ABSTRACT

Studies in the field of the adverse effect of inhaled particles show that not only particle mass is crucial but also particle size and specific surface are. The main objective of this study was to investigate and characterise ultrafine particle (UFP) emissions on workplace in the manufacture of ceramic tiles at two problematic places - at ceramic tiles kiln and spraying glazing suspension. The process of creating of glaze on the surface of stove tiles is performed at temperatures reaching up to 1,100°C. At this high temperature occurs fugitive emissions from glaze and ceramic consist of vapours and UFP containing various heavy metals such as Pb, Cr, Cu, Mo, Zr, etc. from glaze and ceramic, respectively. The data obtained from the measurements confirmed the significant emissions of UFP at the two chosen workplaces, but the composition of particles, their size distribution and other parameters differed from one to another. In case of the workplace near the kiln, the following parameters were noted: total concentration of particles ranging from 5.6 nm to 560 nm is 2×10^5–4×10^5 N/cm^3; median of size distribution is 37 nm, median of mass distribution is 153 nm, particle surface deposited in tracheobronchial (TB) part of lungs is 200 μm^2/cm^3, particle surface deposited in alveolar (A) part of lungs is 450 μm^2/cm^3 and the concentration of Pb is 3,744 μg/m^3. In the case of the manual spraying of the glaze suspension on tiles, the following parameters were noted: total concentration of particles is 2×10^5 N/cm^3; median of size distribution is 11 nm, median of mass distribution is 177 nm, particle surface deposited in TB part of lungs is 50 μm^2/cm^3, particle surface deposited in A part of lungs is 170 μm^2/cm^3 and the concentration of Pb is 1.9 μg/m^3. It can be concluded from the data above that both the measured workplaces meet the permissible exposure limit for lead, which is 50 μg/m^3. It is important to note that, in this study, the health impacts of UFP on staff and employees were not studied.

Keywords: air emission, heavy metals, lead, pottery kiln emissions, scanning electron microscopy, size resolved sampling, solid aerosols, ultrafine particles.

1 INTRODUCTION

The modern ceramic and pottery industry is subject to extensive health, safety and environmental regulations. The issue of unintentional emissions of ultrafine particles (UFPs) in the working environment has been in the spotlight in recent years due to the potential adverse effects on humans.

Specialized literary sources mostly focus on characterization of nano-aerosol present during production of nanoproducts (especially nanopowders) such as TiO_2, SiO_2, CeO_2, ZnO, fullerenes, carbon nanotubes, colloidal metals and certain low tonnage nanoproducts [1–4]. Incidence of the unintentionally emitted UFP and their toxicity to the human body [5–9] has been unfairly neglected. However, they can present a much more serious impact. Nanoparticles get into the body mainly through inhalation, with penetration of the skin or via the gastrointestinal tract being less common. Their ability to penetrate is related mainly to their small size. This enables them to pass the physiological barriers and enter the bloodstream, which then distributes them to other organs and cells as such. Presence of the secondary UFP emissions is often not taken into account, and therefore, they may present one of the significant factors endangering the employees' health. Some of the sources emitting solid aerosol containing high proportion of UFP into the atmosphere at the workplace are, among others, the technologies involving heating of material to a high temperature, or working with

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metal melts, their oxides, silicates and the related compounds, while generating nanoparticles containing heavy metals presents a risk to human health. In general, these mostly include metallurgical plants of all kinds, either those that produce metals or their alloys, or plants for high-temperature treatment of waste materials, foundries and others. Arc welding of metallic materials is also very hazardous, especially if they contain certain toxic components, such as nickel or chromium. Fortunately, when it comes to these activities, there are measures in place today which prevent UFP from penetrating the human body. However, less attention is paid to work processes and technologies such as production of ceramic products by firing, or surface treatment by enamelling in electric kilns. One of the few published studies [10] that discusses quality of air during the process of ceramic firing in a small pottery studio describes certain differences in the number and sizes of UFP depending on the technique used – i.e. if the so-called bisque technique (first ceramic firing) was in process, or the second firing, after the application of glaze. Various oxides or silicates of metals are part of the raw material used for manufacturing and shaping of the ceramic products but metals are also contained in the coloured pigments used for production of suspensions to be coated on the ceramic surface for decoration purposes or in order to improve the surface characteristics. Other components present in such suspensions are materials designed to lower the melting point, or possibly to ease the surface tension of the melt and thus ensure faultless coverage of the surface and pores on the fired ceramic.

Ceramic pigments are made of crystalline structure with high temperature resistance into which a certain chromophore is properly integrated. They are used mostly for colouring the ceramic glazes and enamel, as well as for manufacturing colours for tiles, glass, porcelain and ceramic. Ceramic mixed pigments can solve some of the issues that occur when using pure oxides. For example, when a pure chromium (III) oxide is used as a colourant in order to acquire a green hue, when in the kiln, it evaporates, sublimates and is released into the air of the kiln, and if the conditions are favourable, also to the air at the workplace. Lead is also very often included in the glaze, which has been used in ceramic products for a long time, both in the glazes and in decorations. When used in the glaze, lead provides a smooth, glass-like surface, making the colours and decorative patterns brighter. More often than not, use of the lead-based fluxes is connected to the rich or intense colouring.

Based on the temperature and vapour tensions, the melted glazes are evaporated into the atmosphere when they are being fired in the kiln. A very fine solid aerosol with a high percentage of UFP is formed due to quick condensation of the above-mentioned vapours. Therefore, it is mandatory to have a well-ventilated workspace where the ceramic is being fired or the enamel suspension is being sprayed. The employees need to be submitted to regular medical examinations focusing on identification of intoxication by heavy metals, namely lead.

The goal of this study was to verify the state of workplace atmosphere during the process of manufacturing stove tiles in a plant where a high-quality ventilation system has already been installed at all critical production places, and where fluxes and pigments not containing lead, or with significantly low percentage of the lead component, are used.

Measurements and collecting samples of dust emissions were executed at the ceramic stove tiles production workshop. Five large-capacity electric kilns are available in total for the given technology. All the kilns are working concurrently, maximum temperature can reach up to 1,050°C and the firing time including cool-down is approximately 27 hours. The kilns are being loaded as the firing goes along, and therefore, they are in different stages of the ceramic firing process. Since this is a plant producing quite a large number of tiles with glazes of various colours, which are changing from time to time with the situation on the market, the collected findings are connected to the actual status at the time of the measuring and may not represent long-time average numbers or any potential short-term deviations in the UFP concentration. A similar situation was found at the other place of measurement, which was the manual application of glazing suspension by spraying it on in small exhaust ventilated covered boxes. New air-handling system was quite recently installed in the whole production plant. It provides perfect exchange of air, thus lowering contamination of the environment by UFP to a minimum and, together with the use of lead-free enamels, this is a condition for reaching a relatively clean working environment.

2 MEASUREMENT AND SAMPLING

The proposed measurement was focused mainly on the assessment of the most complex characteristics of the UFP present in the tiles manufacturing working environment. This assessment entails as much as possible the determination of the number of the particles present, the size and weight distribution of the particulate matter and assessing whether any toxic metals are present, and if yes, what is their size-dependent weight distribution within the collected airborne dust. When assessing the technologies, the space surrounding the firing kilns was found to be the most polluted, followed by the location where the glaze suspension was applied by a "spray gun" to the surface of the tiles after the first firing. There are historical cases that have proven that higher lead concentrations are observed in the atmosphere when spraying and using the pigments containing lead.

At the first location, the measuring apparatus was placed in the immediate vicinity of the kilns. For the second case, the glaze-spraying boxes were placed about 4 m away from measuring point. In both cases, the space was intensively suction ventilated, providing a perfect exchange of air and thus minimizing the emission of UFP to the working environment.

1.1. Instruments used

Electrostatic classification using the Fast-Mobility Particle Sizer (FMPS, Model 3091, TSI Inc., St. Paul, MN, USA) was used for particle size distribution and total number concentration measurements. Size distributions were measured from 5.6 to 560 nm (16 channels per decade with 1-s shortest scan time). Size-dependent sampling was carried out by means of a wide-range aerosol sampling system – Nano-ID® Select, (Naneum Ltd., Canterbury, UK). The samples of all 12 stages collected by the Nano-ID® Select were analysed both for heavy metal content by ICP-MS (Perkin Elmer, model NexION 350D, Waltham, MA, USA) and also SEM (FEI QUANTA 450 FEG, FEI Company, Hillsboro, OR, USA) was used for observing the morphology of particles, equipped with BSE, LF and Everhardt Thornley (ETD) detectors with EDS and WDS modules for energy-dispersion element analysis and wave-dispersion element analysis, respectively. Accessories to this SEM include the module for the so-called "scanning transmission electron microscopy" (STEM). In order to determine the surface area of deposited particles in the tracheobronchial (TB) and alveolar (A) part of the respiratory tract, the mobile equipment Aerotrak 9000 (TSI Inc., St. Paul, MN, USA) was used. Wide range measurement of the solid aerosol particles concentration utilizing the synergic connection of NanoScan (SMPS) Nanoparticle Sizer 3910 and Optical Particle Sizer 3330 (OPS) (both TSI Inc., St. Paul, MN, USA) was carried out to compare the results with FMPS. The indicated simultaneous deployment of the two instruments made it possible, through the sophisticated software MULTI-INSTRUMENT MANAGER (MIM-2™), to link the measured distribution values from both instruments in the size range from 10 nm to 10 μm.

1.2. Results from FMPS

1.2.1. Measuring point I – ceramic kiln

The very quick response (1 s) of a measured signal allows for the display of even short transition states during the UFP concentration change.

Quite significant fluctuation was recorded during the measurements when it comes to the overall number of the present UFP, as well as short episodes (sudden changes) of emission of nanoparticles smaller than 10 nm. These turbulences are probably caused by the workers' movements and distribution of materials for firing to the adjacent kilns, by opening of the kilns, or possibly by fluctuation in the suction-ventilation efficiency. An average number of particles measured by the FMPS ranged from 2×10^5 to 4×10^5 N/cm^3. Changes in concentration of the total particle count ranging from 5.6 to 560 nm are shown in Fig. 1 and variations in size distribution during the measurement period are shown in Fig. 2 in the form of the 3D

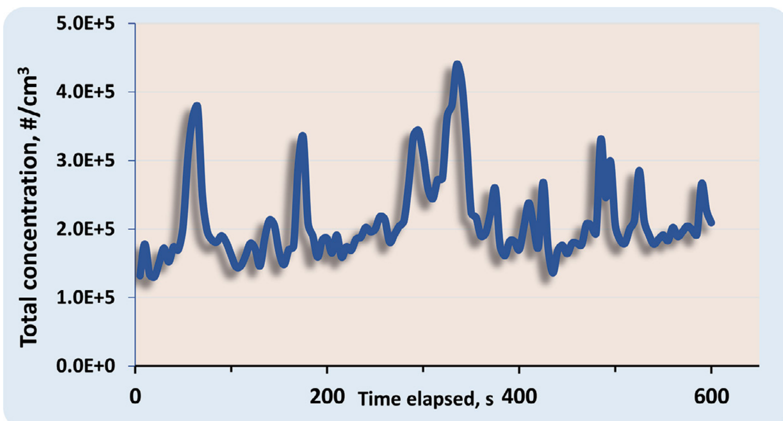


Figure 1: Point I – pottery kiln. Total concentration of UFP measured by FMPS (1-s averaging).

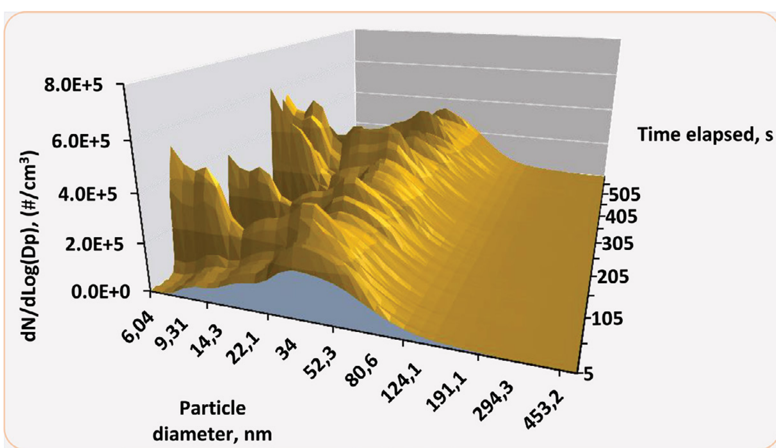


Figure 2: Point I – pottery kiln. 3D – time-dependent size distribution.

graph where 30 nm nanoparticles prevail. We can conclude from the results that the total concentration is not very stable and that it fluctuates, possibly due to changes in the firing technology.

1.2.2. Measuring point II – spraying glaze suspension

The second measurement took place at the location, where manual application of enamel suspensions by spraying is performed. This technology presents an increased risk of inhalation of fine aerosol that more often than not contains inorganic metal compounds, including lead. The spraying takes place in small exhaust-ventilated boxes. In order to prevent inhalation of the emitted aerosol, the spray pistol operators have to use respiratory system protection in the form of a suitable respirator (protective respirator mask). Unlike near the kilns, the concentration and size distribution of particles was very stable over the whole measuring period, as presented in Figs. 3 and 4. However, the prevailing number of fine nanoparticles below 10 nm was surprising.

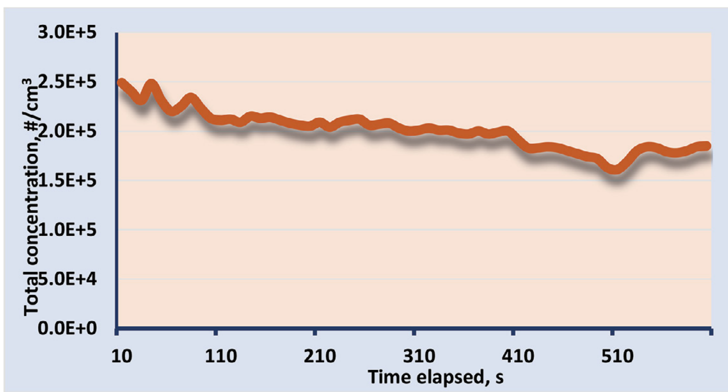


Figure 3: Point II – spraying glaze suspension. Total concentration of UFP measured by FMPS (5 sec averaging).

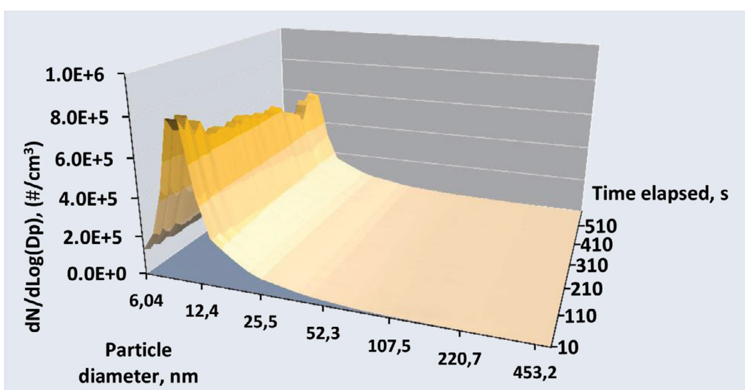


Figure 4: Point II – spraying glaze suspension. Size-resolved distribution 3D plot during measuring period measured by FMPS, 5-s averaging.

1.3. Results from Nanoscan and Optical Particle Sizer

As already mentioned above, both appliances are commonly used for measuring the numbers and size distribution of particles ranging from 10 nm to 10 µm. Nanoscan provides information regarding concentration of nanoparticles ranging from 10 nm to 300 nm, while OPS is measuring the same parameters but within the range from 300 nm to 10 µm. It is possible to follow-up with mathematical combination of both recordings (Nanoscan+OPS), which results in creation of a distribution profile covering the full measurement scope. However, in most cases, the concentration of particles under 300 nm is much higher and so the possible upper limits of the particle size distribution within the airborne dust for particles over 300 nm can disappear within the graph. Figure 5 shows an example of measurement result from position I at the kilns calculated by combination of the measured data from both appliances. The mode of distribution can be found approximately at the 35nm particle size, which matches very well the FMPS data (Fig. 2). The distribution curve shows that there is no significant presence of particles larger than 300 nm in the air. Total number of particles expressed in the PM10 format reaches the value of 1×10^5 N/cm^3.

On the contrary, Fig. 6 shows very fine particles, with the maximum presence of those ranging from 10 to 20 nm in size, are predominant in the air near the suspension application. Yet again, it corresponds with the FMPS data (Fig. 4). Total number of particles expressed in

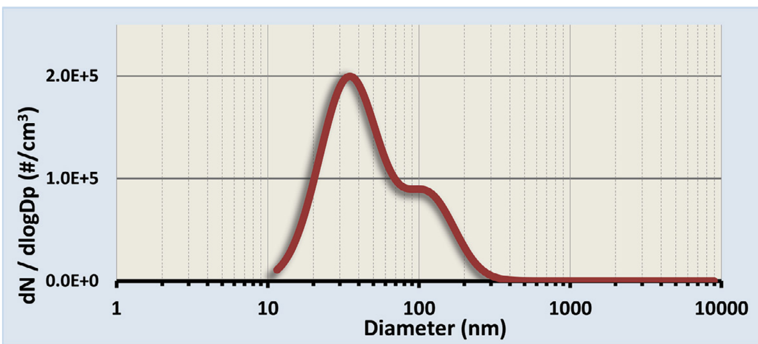


Figure 5: Point I – pottery kiln. OPS + Nanoscan composite curve size-resolving distribution.

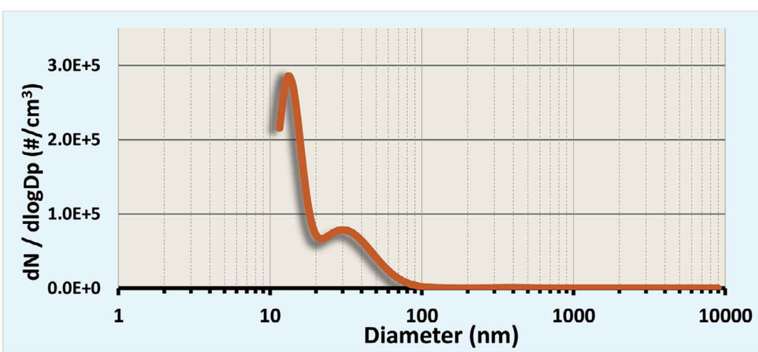


Figure 6: Point II – spraying glaze suspension. OPS + Nanoscan composite curve size-resolving distribution.

the PM10 format reaches the value of 8×10^4 particles/cm^3, which is an insignificant decrease when compared to the concentration measured near the kilns.

1.4. Results Aerotrak 9000

Determining the total surface area of particles deposited in the respiratory system is becoming a very important parameter when it comes to assessment of the particle toxicity. It is based on a logical assessment that all biochemical processes occur when the nanoparticles come into contact with the relevant cell structure. Data for A fraction and TB fraction are evaluated separately.

Situation at the position I close to the kilns is shown in Fig. 7. Two curves can be seen at the chart. TB and A deposition is represented. Due to the unstable composition of the airborne dust size distribution at the measuring place, the values for the A and TB deposition are not correlating. Figure 8 demonstrates a very stable UFP distribution and concentration in the case of suspension application. This is clearly evident when determining the surface area deposited by particles in the lungs. The values measured at point II are approximately by an order lower than those by the kilns and are very similar to a typical city environment.

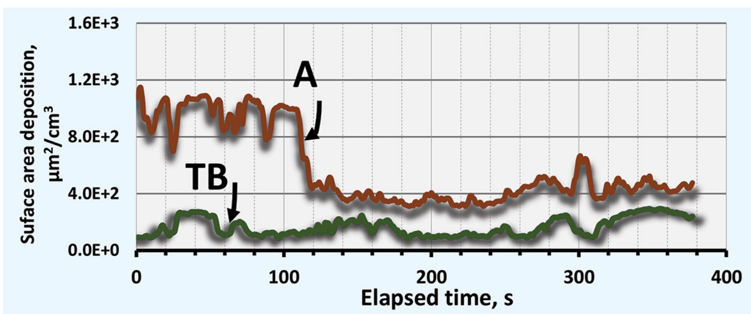


Figure 7: Point I – pottery kiln. Comparison alveolar (A) and tracheobronchial (TB) particle surface area deposition.

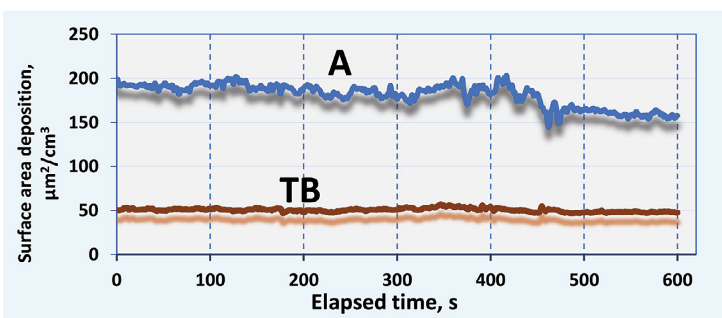


Figure 8: Point II – spraying glaze suspension. Comparison alveolar (A) and tracheobronchial (TB) particle surface area deposition.

1.5. Particle sample collection

The aerosol samples were collected using a wide-range sampler Nano-ID® Select in the size range from 1 nm up to 35 µm. Particles are collected simultaneously due to impact on microscopic slides and diffusion deposition on polymer nets and separated into 12 size channels. This sampler enables sufficient amounts of the nano- and micron-region particulate matter to be collected for further analysis of chemical composition by ICP-MS and scanning electron microscopy. Polished glass microscope slides were used as sampling media for the impactor (0.25–35 µm), while Nylon screens with mesh openings from 20 to 125 per µm were used for diffusion cell (1–250 nm).

1.5.1. Chemical analysis of samples collected

The samples of all 12 stages collected by the Nano-ID® Select were analysed for metal content by ICP-MS method. Prior to analysis, samples were subjected to the mineralization using a microwave system (Milestone MLS 1200 Mega, Milestone Inc., CT). Once the digestion was complete, the samples were allowed to cool and then samples were diluted with high-purity water up to a volume of 50 ml. The analysis by ICP-MS was performed under standard conditions, i.e. without using the so-called collision cells and internal standards. For each element, a five-point calibration curve plus blank were used. Results were corrected by values from the blank samples (slide or net).

More than 10 metals were identified in the collected fractions of the airborne dust, from a toxicological point of view. Lead is the most critical metal. Figure 9 shows that lead is present within the full spectre of the particle sizes, while the three top size areas are present: 1–5 nm, 100–200 nm and 10–20 µm. Based on the mathematical model, the proportion deposited in the lungs can be calculated [11]. Table 1 presents applying this model to the size distribution of aerosol by the kilns. Approximately 13% of the overall amount of lead is deposited in the lungs. This fact, along with low concentration equal to 3.73 µg/m^3, does not pose increased risk to the employees' health. At Point II, spraying the enamel suspension, the content of lead is 1.9 µg/m^3 and the percentage of the lead deposited in the A section of the lungs is 6.3%, which corresponds to 0.2 µg/m^3.

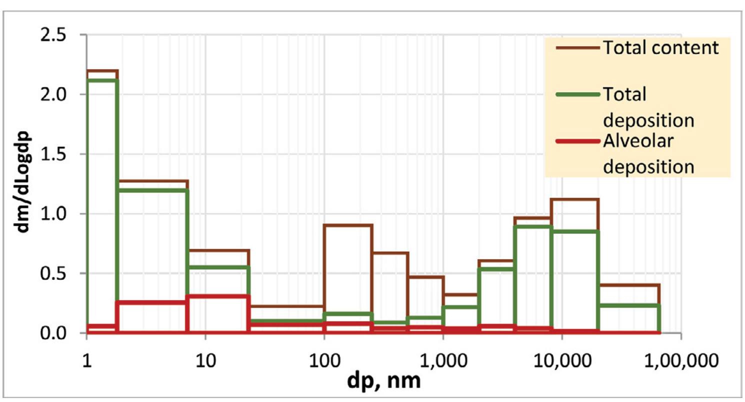


Figure 9: Point I – pottery kiln. Lead aerosol particle mass size distribution, total and alveolar deposition in human respiratory track.

Table 1: Measuring at Point I – pottery kiln. Total concentration of lead in environment and the deposited fraction in lungs.

Element	The place of sampling	Airborne mass concentration, μg/m^3	Total deposited mass concentration, μg/m^3 (% of airborne)		Mass concentration deposited in the alveolar range, μg/m^3 (% of airborne)	
Lead	Pottery kilns	3.73	2.67	71.6	0.48	12.8

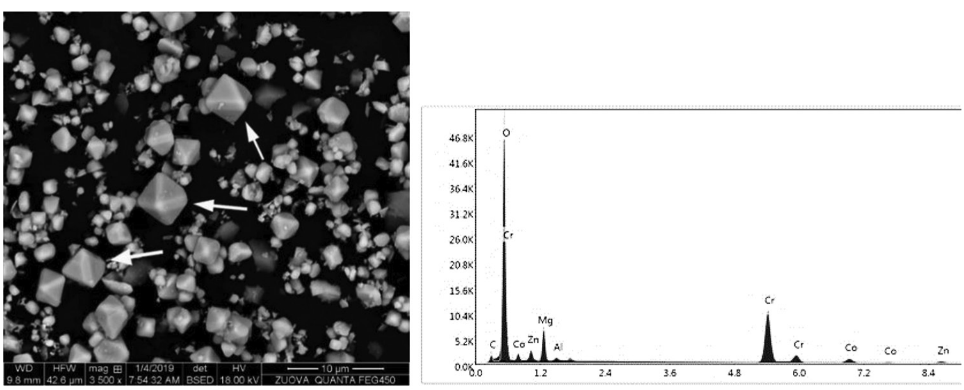
1.6 SEM observation

A fraction sampler was also used at both measuring places to collect samples for observation of morphology and basic composition of the airborne dust particles under a scanning electron microscope. First, some clean pigments were selected for examination. Pigments contain additional matrix elements such as silicon, magnesium, aluminium, sodium and a wide range of other elements mainly in form of oxides or silicates.

Based on the colouring of pigments, the following elements were identified: zirconium, chromium, copper, molybdenum, praseodymium, zinc and barium. Fluorine was confirmed in the yellow pigment. Even though the metals are often contained in the pigments in very small concentrations, the dust emissions created during the firing may present some risk for the employees. Figure 10 shows an example of pigment morphology, in this case of ‘moss green’. The green colour of the glaze is caused by Cr(III) compounds.

Particulate matter collected by the kilns is mostly of irregular shape with sharp edges; their formation due to condensation of volatiles from the melted glaze has thus not been confirmed. They probably originate from various mechanical operations during the tile manufacturing process.

Dust samples collected in the vicinity of the kilns contain a wide spectrum of minerals and compounds. As expected, silicate-based particles prevail. These are predominantly aluminosilicates with a varying ratio of magnesium and potassium. To a lesser extent, some



a) b)

Figure 10: (a) Morphology of a “moss green” pigment. Arrows point to crystals of magnesium chromite (III); (b) EDX spectrum of crystals in question.

compounds were identified among these particles, where copper, zirconium, lead, molybdenum, zinc, antimony, barium, chromium and nickel were identified as the major component. This fact corresponds to the situation when various types of inorganic pigments undergo firing at the same time and they evaporate into the kiln surroundings, or to possible resuspension (rising) of the fine settled dust within the factory hall.

3 CONCLUSIONS

Air quality measurements and sampling of airborne dust were carried out in two locations at the stove tiles manufacturing plant. After taking into consideration the most probable places with the highest concentration of solid aerosol in the working environment, the two following locations were selected as sampling and measuring places. First, the location in the vicinity of the kilns and second, an area where the pigment suspensions are applied by using the spray pistols technology. It can be concluded from the measured data that due to the efficient air-handling system (suction-ventilation) and utilization of new types of pigments with a minimum content of heavy metals, namely lead, the measured values of concentration of heavy metals in the air are several times lower than the permissible exposure limits. The limit for lead in the vicinity of kilns is 3.73 $\mu g/m^3$. Particles smaller than 100 nm were prevailing in both cases. The mode of size distribution is between 30 and 50 nm in the vicinity of the kilns and approximately 10 nm at the suspension spraying place. The average concentration of UFP was about 2×10^5 N/cm^3.

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