Chapter 3

# Characterization of Airborne Emission of Nanoparticles from the in the Ceramic Industry in Portugal

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## Abstract

The objective of this study was to evaluate occupational exposure to nanoparticles during some tasks performed in different production processes of different ceramic industries in Portugal, to select the places of greatest occupational exposure through the analysis of the sampled data, to verify what is the pulmonary accumulation in these places, to identify the composition of the released nanoparticles, apply a Control Banding Tool and try to understand which companies require more risk control measures. The study was carried out in three different national ceramics production industries, one for sanitary ceramics production, another for porcelain crockery production and finally another for the

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production of ornamental crockery (red paste). It is concluded that occupational exposure values to nanoparticles are high in all cases and that nanoparticles are very small in size (11.5 to 15.4 nm). Existing risk control measures are insufficient and verified risk levels are high (Risk Level 3 and 4). The chemical composition of the analyzed nanoparticles is similar regardless of the typology of the ceramic production plant and their chemical composition as a percentage of certain materials has a direct influence on crystallinity.



**Keywords:** Nanoparticles; Ceramics; Emissions; Risk Assessment

## 1. Introduction

In 2000, the World Health Organization air quality guidelines [1] listed the two particulate matter indicators ($PM_{10}$ and $PM_{2.5}$), with particulate matter in the range of 10 µm to 2.5 µm corresponds to the coarse fraction and is considered inhalable, thus reaching the thoracic region (trachea and bronchi). Already particulate matter between 2.5 µm and 0.1 µm is designated as the fine fraction and is considered breathable as it can reach the alveolar region (bronchioles and alveoli) [2].

Particulate matter with a diameter of less than 0.1 µm (<100 nm) is referred to as an ultrafine fraction (or nanoparticle) and, like a thin fraction, is considered breathable and can reach the same organs [1, 3]. Thus, the smaller the particle, the more likely it is to penetrate deeper parts of the respiratory tract, thus exposing the individual to higher levels of trace elements and toxins.

Routes of human exposure to nanoparticles may include inhalation through the respiratory tract; absorption through the skin; ingestion through the mouth; or combinations of these pathways [4]. It is very likely that the most important route of human exposure to nanoparticles is inhalation [5]. By this way, and due to their size and other characteristics, nanoparticles may reach the alveolar region and have a behavior similar to that of fine particles, giving rise to inflammatory processes in the lungs and subsequent cardiovascular morbidity and mortality. From the results of pharmaceutical research and toxicological studies, it can be concluded that, depending on the size and surface area characteristics, nanoparticles can enter the human body via lungs and intestines and are able to cross the protective barrier of the epidermis and may even penetrate. beyond the dermis [6].

Some epidemiological studies of the general population have shown associations between particle exposure (air pollution) and increased morbidity and mortality from respiratory and cardiovascular diseases [7-9]. Other studies have also shown adverse health effects associated with exposure to ultrafine particles [10-13]. There are uncertainties about the role of fine and ultra-fine particles (nanoparticles) in relation to other air pollutants that cause adverse health effects. In animal studies it was found that nanoparticles can enter the circulation [14] and translocate to other organs [15-16]. It remains unknown what proportion of particles deposited in the lungs, which is eliminated by the macrophage system and which reaches the circulation [14-17].

Regarding occupational exposure to particles, some studies cited by Schutle [18] have shown adverse effects on the working population both in terms of environmental exposure to inhalable particles and respirable particles.

In the ceramic industry, workers may be exposed to nanomaterials throughout the production process due to involuntary release of nanoparticles, as it is the workplace where there is greater exposure to higher concentrations of nanomaterials, requiring special attention to such occupational exposure [19].

Occupational exposure of workers to ceramic dust leads to chronic obstructive pulmonary disease, reduced pulmonary and respiratory symptoms such as wheezing and shortness of breath, dry cough and chronic bronchitis [20-22]. In this industry, the number of workers with silicosis (progressive disease) is very high. This is an occupational disease caused by respirable particles containing crystalline silica lodged in the lungs, the exposure time is extremely important because it determines its period of manifestation [23].

These occupational exposure situations are of high complexity and involve the inherent component of the individual, working conditions and the activity developed [24]; it is necessary to apply an integrated approach to the process of risk diagnosis, assessment and management, adapted to each specific situation [25].

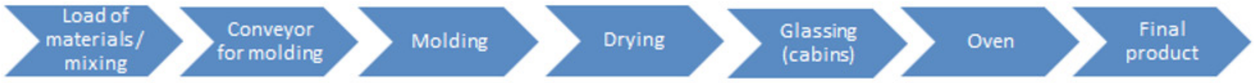
The poor scientific evidence on the effects on human health caused by nanoparticles is paralleled by the lack of information on appropriate parameters for the characterization of nanomaterials and, therefore, for the assessment of the dangers they may pose to the environment and human health. In fact, it is not yet possible to classify nanoparticles according to their health effects, nor to set appropriate benchmarks (for example, mass, particle count, or surface area) to allow comparable assessment of results. This means that, at various levels of the process, the information needed to develop comprehensive and quality risk analysis for nanoparticles is lacking, hence the relevance of developing such studies.

## 2. Materials and Methods

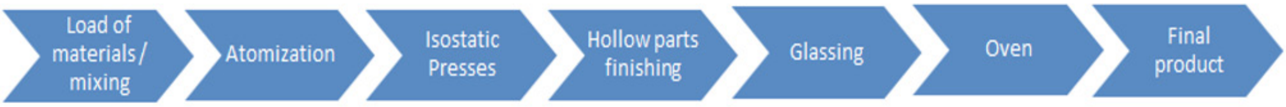
This work took place during 2019. Measurements with the duration of one hour were considered to be significant of the productive processes in the 3 ceramic plants – sanitary, refractory bricks and ornamental crockery (red paste). Shorter (Zero) measurements were taken in order to understand whether the amount of particulate matter resulting from the production process was actually high compared to the outside.

Schemes of the manufacturing process of the 3 production units are the follows:

- Sanitary ware production unit:




- Porcelain crockery production unit:




- Decorative tableware production unit (red clay):


The study consisted of 8 phases:
- knowledge of manufacturing processes and processed materials;
- the survey of activities, jobs and working conditions of the environments under study and the previous selection of sampling points in the 3 factories including an outdoor point (white);
- occupational exposure measurements at selected sampling points;
- temperature and humidity measurements in areas where occupational exposure measurements have been taken;
- data processing and analysis using Excel;
- the capture of particles in copper grids to send to the laboratory;
- nanoparticle analysis by High Resolution Transmission Electron Microscopy – TEM;
- the application of the risk assessment matrix - Control Banding Tool.

Data collection was performed with calibrated equipment, placed at a height corresponding to the workers' breathing zone (1.5 m), from a workplace evaluation perspective and the following equipment was used:

- Nanoparticle Surface Area Monitor (NSAM), for the determination of surface areas deposited in the human lung expressed as square micrometers per cubic centimeter of air ($\mu m^2/cm^3$), corresponding to the tracheobronchial (TB) or alveolar (A) regions of the lung. The operation of the equipment is based on the diffusion of electrostatic charges deposited on the electrostatically charged particle aerosol, followed by detection by an electrometer. The sample is collected by a pump after passing through a cyclone that holds particles larger than 1 µm. After this, the sample flow is divided into two: one at a flow rate of 1 l/min passes through a carbon filter, a HEPA filter and an ionizer that induces positive ion charges and ultimately goes into a chamber of mixing.

The other flow at a flow rate of 1 l/min then proceeds to the mixing chamber where it mixes with the ionized flux, where excess ions are removed by an ion trapping system. The voltage of the ion trapping system can be changed to choose between tracheobronchial and alveolar mode. For nanoparticle exposure assessment, the equipment is operated in "A" mode, corresponding to the deposition of particles in the alveolar region of the lung of a reference worker according to International Commission of Radiological Protection (ICRP) and American Conference models. of Governmental Industrial Hygienists (ACGIH).

- NanoScan SMPS Scanning Mobility Particle Sizer Spectrometer for determination of nanoparticle particle size distribution. This equipment makes it possible to measure the distribution by ultra-fine particle size between 10 and 420 nm, measurement made by separating the particles based on their electrical mobility. The particle detection mode of a selected size is accomplished using optical detection technology which allows the particles to be enlarged by condensing them on an isopropanol medium. Particle separation is performed by a Differential Mobility Size Analyzer (DMA). DMA selects particles by distributing their electric charge, passing them through an electric field where particles of different sizes are separated, and determining the diameter of electrical mobility of the particles. Particle counting is done by a condensed particle counter (CPC) which counts the particles that have been increased through condensation by passing them through a laser beam. The light diffraction of the particles is then detected by a photodetector.

- Nanometer Aerosol Sampler (NAS), for collecting nanoparticles in metal grids, this equipment draws the nanoparticles through an airflow to a grid (copper) attached to an electrostatic precipitator.

- BABUC A, for direct measurement of temperature, relative humidity and air velocity using natural vented wet temperature probes, natural vented dry temperature probes, forced vent psychrometric probe and hot wire anemometric probe.

- High Resolution Transmission Electron Microscope (TEM), equipped with EDS probe, to perform the magnification and characterization of nanoparticles, this equipment emits an electron beam over the selected nanoparticle sample. The absorption of electrons by the material present in the samples allows to know their chemical composition, crystal orientation and electronic structure, besides the images based on the absorption of the material.

In terms of risk assessment, a qualitative risk assessment matrix was used, the Control Banding Tool in the work zones that presented the highest risk to workers in the 3 plants. The choice focused on the load of material / mixing zone for the 3 companies because they had the highest measured nanoparticle values and for the glassing zone (for the companies performing this task) given the constitution of the materials concerned, essentially silica powders.

## 3. Results

Graphs were made to understand the amount of nanoparticles released their particle size and their lung accumulation in the load of materials / mixing zone and in the glassing zone. Some examples of the graphs made for the porcelain crockery factory in the load of materials / mixing zone as presented on figures 1 to 3.

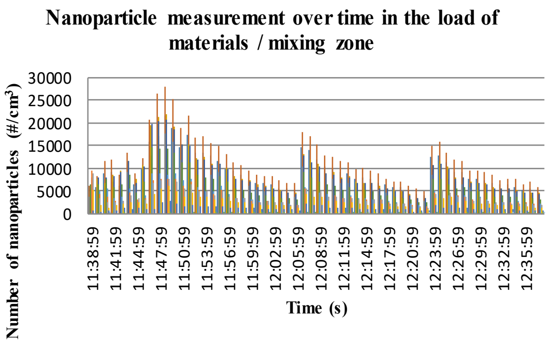



**Figure 1:** Measurements of nanoparticles in the mixing zone at the porcelain crockery production unit.

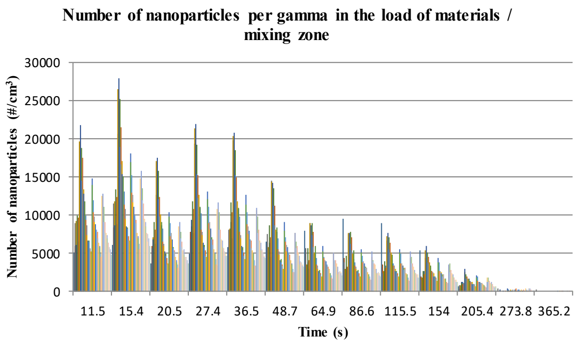



**Figure 2:** Number of nanoparticles per gamma in the mix charge at the porcelain crockery production unit.

It was noticed that the observed peaks are due to the 3 passes of the forklift (resuspension of nanoparticles) and the remaining oscillations are due to the atomized material that is transported in the transporter belt and enters the Big Bags.

The amount of nanoparticles released in this zone is small, with air nanoparticles predominating at 15.4 nm.

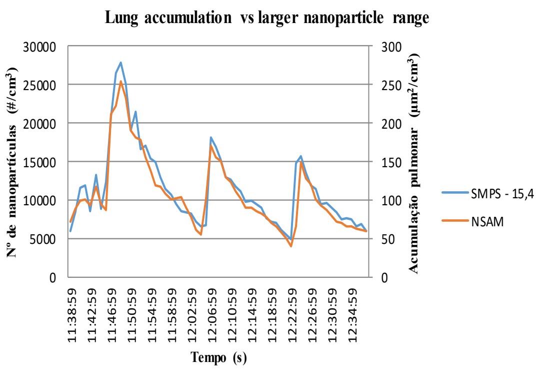



**Figure 3:** Pulmonary accumulation measured in the load of materials / mixing zone at the porcelain dishware manufacturing plant in the largest range of nanoparticles.

From the pulmonary accumulation it is clear that the amount of nanoparticles that accumulate in the lung in the mixing zone is high and corresponds to small nanoparticles 15.4 nm, with strong penetration capacity and pulmonary accumulation.

With this set of graphs, obtained for each measuring point (workstation), in each factory unit, it is possible to determine the amount of nanoparticles released in the tasks performed at each workstation, and the pulmonary input associated with each workstation, which is the size of the nanoparticles in question, both at peak and hourly exposure of the measurement.

After analyzing data from the measurement sites it was found that it was at the workstation load of materials / mixing zone that there was the greatest release of nanoparticles in all the manufacturing plants where measurements were taken, regardless of the products manufactured, as it can be noticed in **Table 1**.

**Table 1:** Graphical results of the workplace nanoparticle evaluation in the load of materials / mixing zone at the 3 production units.

| Measurements | Highest peak value (# / cm3) and respective nanoparticle range (nm) | Highest value of accumulated nanoparticles (# / cm3) and respective range (nm) |
|---|---|---|
| Sanitary ware production unit | 32790.6 – 15.4 | 927803.7 – 15.4 |
| Porcelain crockery production unit | 27888.9 – 15.4 | 696793.9 – 15.4 |
| Ornamental tableware production unit (red paste) | 93283.7 – 11.5 | 1088907.0 – 15.4 |

**Table 2** presents the results of the measurements made in the glassing in order to understand the amount of nanoparticles released in this work, taking into account the dangerous composition of the materials used, essentially silica powders.

**Table 2:** Graphical results of the evaluation of nanoparticles in the glassing in the 3 production units.

| Measurements | Highest peak value (# / cm3) and respective nanoparticle range (nm) | Highest value of accumulated nanoparticles (# / cm3) and respective range (nm) |
|---|---|---|
| Sanitary ware production unit | 2411.8 – 15,4 | 118495.6 – 15,4 |
| Porcelain crockery production unit | 1464.4 – 15,4 | 47152.1 – 15,4 |
| Ornamental tableware production unit (red paste) | 13409.8 – 11,5 | 351132.4 – 15,4 |

After making the measurements inside the production units it was necessary to perform measurements outside (Zero) to gauge what was actually released by comparing values, as can be seen in **Figures 4** and **5**.

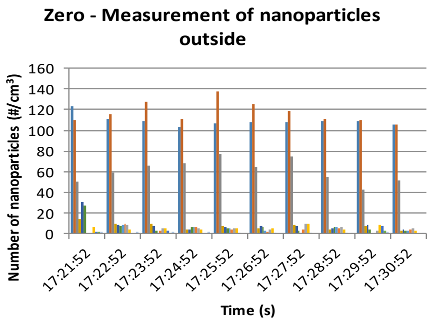



**Figure 4:** Nanoparticle measurements outside in the porcelain crockery production unit – Base line (Zero).

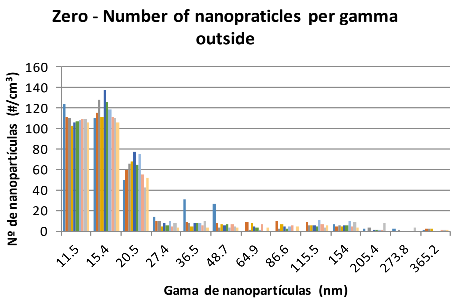



**Figure 5:** Number of nanopraticles per gamma outside in the porcelain crockery production unit – Base line (Zero).

**Table 3:** Comparison of interior and exterior values (Zero) in the 3 production units.

| Measurements | Highest peak value (# / cm3) and respective nanoparticle range (nm) | Highest value of accumulated nanoparticles (# / cm3) and respective range (nm) | Highest peak value (# / cm3) and respective nanoparticle range (nm) in the base line (Zero) | Highest value of accumulated nanoparticles (# / cm3) and respective range (nm) in the base line (Zero) |
|---|---|---|---|---|
| **Load of materials / mixing** | | | | |
| Sanitary ware production unit | 32790.6 – 15.4 | 927803.7 – 15.4 | 80.3 – 15.4 | 4590.5 – 15.4 |
| Porcelain crockery production unit | 27888.9 – 15.4 | 696793.9 – 15.4 | 137.7 – 15.4 | 1172.6 – 15.4 |
| Ornamental tableware production unit (red paste) | 93283.7 – 11.5 | 1088907.0 – 15.4 | 3388.2 – 15.4 | 20113.3 – 15.4 |
| **Glassing** | | | | |
| Sanitary ware production unit | 2411.8 – 15.4 | 118495.6 – 15.4 | 80.3 – 15.4 | 4590.5 – 15.4 |
| Porcelain crockery production unit | 1464.3 – 15.4 | 47152.1 – 15.4 | 137.7 – 15.4 | 1172.6 – 15.4 |
| Ornamental tableware production unit (red paste) | 13409.8 – 11.5 | 351132.4 – 15.4 | 3388.2 – 15.4 | 20113.3 – 15.4 |

**Table 4:** Comparison of interior and exterior values in percentage.

| Measurements | Percentage of peak values released compared to exterior values (Zero) | Percentage of accumulated values released compared to exterior values (Zero) |
|---|---|---|
| **Load of materials / mixing** | | |
| Sanitary ware production unit | 40835.1 | 20211.4 |
| Porcelain crockery production unit | 20253.4 | 59422.9 |
| Ornamental tableware production unit (red paste) | 2753.2 | 5413.9 |
| **Glassing** | | |
| Sanitary ware production unit | 3003.4 | 2581.3 |
| Porcelain crockery production unit | 1063.4 | 4021.2 |
| Ornamental tableware production unit (red paste) | 395.8 | 1745.8 |

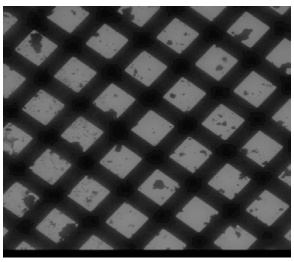
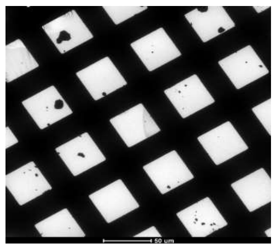
Percentage we can see that there are released nanoparticle values inside 59000% higher than the values measured abroad at load of materials/mixing and 4000% at Glassing.

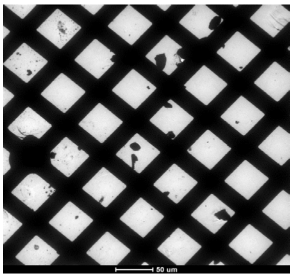
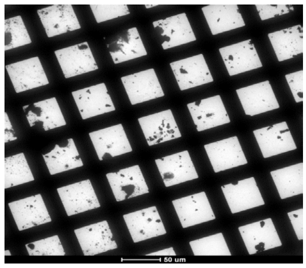
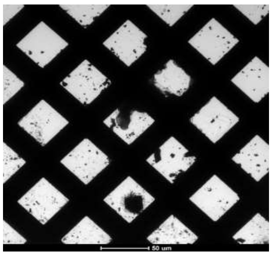
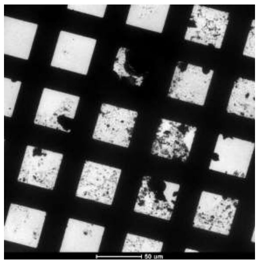
**Table 5** shows the temperature, relative humidity and air velocity values at the measurement locations.

**Table 5:** Temperature, relative humidity and air velocity values at the measurement sites.

| Production unit | Measurement location | Average temperature | Average Relative Humidity | Average airspeed |
|---|---|---|---|---|
| Sanitary ware production unit | Load os mate rials / mixing | 18.3 ºC | 82.0 % | 0.02 m/s |
| | Glassing | 23.9 ºC | 74.5 % | 0.14 m/s |
| Porcelain crockery production unit | Load os materials / mixing | 14.8 ºC | 60.1 % | 0.03 m/s |
| | Glassing | 21.4 ºC | 48.2 % | 0.02 m/s |
| Ornamental tableware production unit (red paste) | Load os materials / mixing | 18.6 ºC | 38.8 % | 0.41 m/s |
| | Glassing | 18.7 ºC | 39.4 % | 0.07 m/s |

**Table 6:** Nanoparticle grid images observed at TEM at 50 µm.

| Production unit | Load of matrials / mixing | Glassing |
|---|---|---|
| Sanitary ware production unit | **Figure 6 -** Nanoparticle grid image observed at TEM at 50 µm in the load of materials / mixing  | **Figure 7 -** Nanoparticle grid image observed at TEM at 50 µm in the Glassing  |

| | | |
|---|---|---|
| Porcelain crockery production unit | **Figure 8** - Nanoparticle grid image observed at TEM at 50 μm in the load of materials / mixing  | **Figure 9 -** Nanoparticle grid image observed at TEM at 50 μm in the Glassing  |
| Ornamental tableware production unit (red paste) | **Figure 10** - Nanoparticle grid image observed at TEM at 50 μm in the load of materials / mixing  | **Figure 11 -** Nanoparticle grid image observed at TEM at 50 μm in the Glassing  |

By analyzing the average temperature and relative humidity in the 3 ceramic production units, and the images of nanoparticle capture grids, it can be noticed that where there is greater accumulation of nanoparticles is where the relative humidity is lower. It is noteworthy that the production sites are large industrial buildings without climate control with strong dependence on outside temperatures and humidity, which is a parameter difficult to control.

When this situation was verified, the control banding tool risk assessment matrix was applied to these 2 sites of the factories in question.

**Tables 7, 8** and **9** refer to the application of the control banding tool risk assessment matrix for the 3 ceramic production units.

**Table 7:** Application of the Control Banding Tool in the sanitary ware production unit.

| **Sanitary ware production unit** | | | | | | |
|---|---|---|---|---|---|---|
| **Scenario Description** | **Nanomaterial Name or Description** | **Overall risk level without controls** | **Recommended engineering control based on risk level** | **Recommended Risk Control** | **Existing Risk Control** | **Engineering control improvement?** |
| Load of materials / Mixing to obtain Vitreous China paste | Kaolin Nanoparticles | RL3 | Containment | 3 | 1 | Yes |
| | Feldspar Nanoparticles | RL3 | Containment | 3 | 1 | Yes |
| | Quartz Nanoparticles | RL4 | Seek specialist advice | 4 | 1 | Yes |

| | | | | | | |
|---|---|---|---|---|---|---|
| Load of materials / Mixing to obtain Gresanit paste | Kaolin Nanoparticles | RL3 | Containment | 3 | 1 | Yes |
| | Feldspar Nanoparticles | RL3 | Containment | 3 | 1 | Yes |
| | Quartz Nanoparticles | RL4 | Seek specialist advice | 4 | 1 | Yes |
| | Chamotte Nanoparticles | RL3 | Containment | 3 | 1 | Yes |
| Load of materials / Mixing clay materials | Silicium Dioxide Nanoparticles | RL4 | Seek specialist advice | 4 | 1 | Yes |
| | Alumina Nanoparticles | RL3 | Containment | 3 | 1 | Yes |
| Glassing | Silicium Dioxide Nanoparticles | RL4 | Seek specialist advice | 4 | 2 | Yes |
| | Alumina Nanoparticles | RL3 | Containment | 3 | 2 | Yes |
| | Calcium oxide Nanoparticles | RL3 | Containment | 3 | 2 | Yes |
| | Potassium Oxide Nanoparticles | RL3 | Containment | 3 | 2 | Yes |
| | Sodium Oxide Nanoparticles | RL3 | Containment | 3 | 2 | Yes |

**Table 8:** Control Banding Tool application in the porcelain production unit.

| **Porcelain production unit** | | | | | | |
|---|---|---|---|---|---|---|
| **Scenario Description** | **Nanomaterial Name or Description** | **Overall risk level without controls** | **Recommended engineering control based on risk level** | **Recommended Risk Control** | **Existing Risk Control** | **Engineering control improvement?** |
| Load of materials / Mixing materials to obtain atomized paste | Kaolin Nanoparticles | RL3 | Containment | 3 | 2 | Yes |
| | Feldspar Nanoparticles | RL3 | Containment | 3 | 2 | Yes |
| | Quartz Nanoparticles | RL4 | Seek specialist advice | 4 | 2 | Yes |
| | Silicium Dioxide Nanoparticles | RL4 | Seek specialist advice | 4 | 2 | Yes |
| | Alumina Nanoparticles | RL3 | Containment | 3 | 2 | Yes |

| | | | | | | |
|---|---|---|---|---|---|---|
| Glassing | Silicium Dioxide Nanoparticles | RL4 | Seek specialist advice | 4 | 2 | Yes |
| | Alumina Nanoparticles | RL3 | Containment | 3 | 2 | Yes |
| | Calcium oxide Nanoparticles | RL3 | Containment | 3 | 2 | Yes |
| | Potassium Oxide Nanoparticles | RL3 | Containment | 3 | 2 | Yes |
| | Sodium Oxide Nanoparticles | RL3 | Containment | 3 | 2 | Yes |

**Table 9:** Application of the Control Banding Tool in the ornamental tableware production unit (red paste).

| **Ornamental tableware production unit (red paste).** | | | | | | |
|---|---|---|---|---|---|---|
| **Scenario Description** | **Nanomaterial Name or Description** | **Overall risk level without controls** | **Recommended engineering control based on risk level** | **Recommended Risk Control** | **Existing Risk Control** | **Engineering control improvement?** |
| Load of materials / Mixing materials to obtain red paste | Kaolin Nanoparticles | RL3 | Containment | 3 | 1 | Yes |
| | Silicium Dioxide Nanoparticles | RL4 | Seek specialist advice | 4 | 1 | Yes |
| | Alumina Nanoparticles | RL3 | Containment | 3 | 1 | Yes |
| | Calcite Nanoparticles | RL3 | Containment | 3 | 1 | Yes |
| Glassing | Silicium Dioxide Nanoparticles | RL4 | Seek specialist advice | 4 | 2 | Yes |
| | Alumina Nanoparticles | RL3 | Containment | 3 | 2 | Yes |
| | Calcium oxide Nanoparticles | RL3 | Containment | 3 | 2 | Yes |
| | Potassium Oxide Nanoparticles | RL3 | Containment | 3 | 2 | Yes |
| | Sodium Oxide Nanoparticles | RL3 | Containment | 3 | 2 | Yes |

Nanoparticle uptake at NAS and TEM analysis showed several images. The ones presented refer to the glassing area of the sanitary ware production plant.

**Table 10:** Nanoparticles captured in the glassing area of the sanitary ware production unit.

**Figure 12** - Nanoparticle grid image observed at TEM at 50 µm

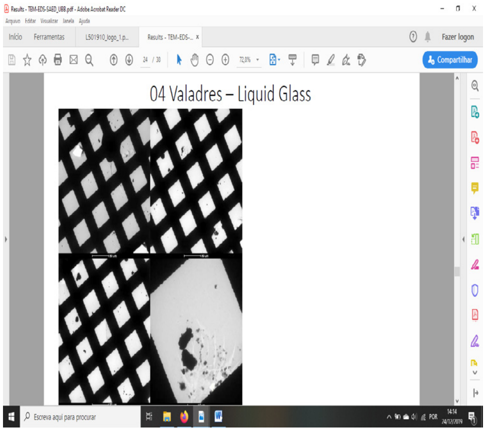



**Figure 13** - Nanoparticle image observed at TEM at 2 µm

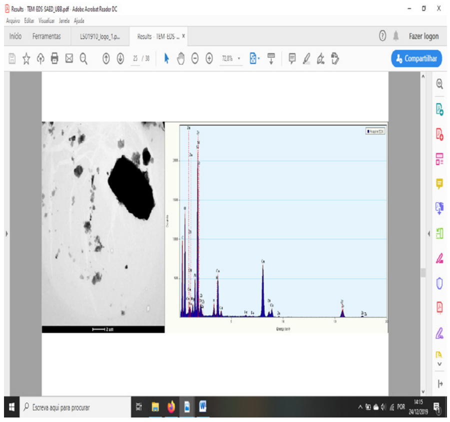


**Figure 14** – Composition of analized glassing nanoparticle

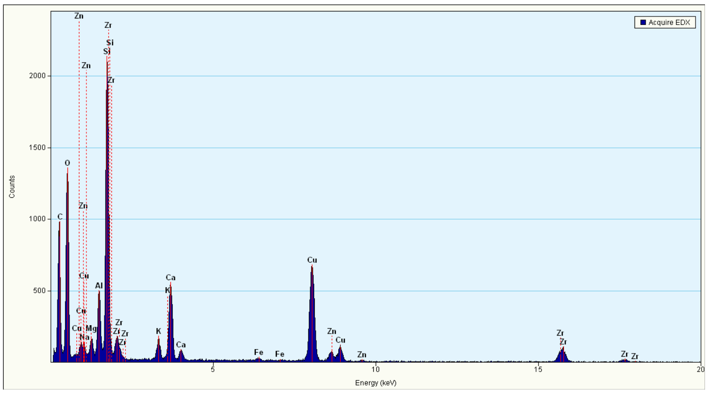



**Figure 15** - Nanoparticle grid image observed at TEM at 50 µm

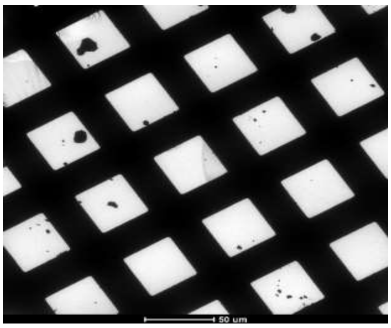



**Figure 16** - Nanoparticle image observed at TEM at 1 µm

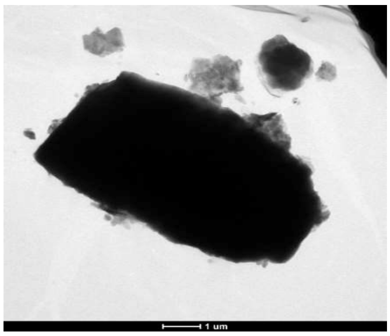
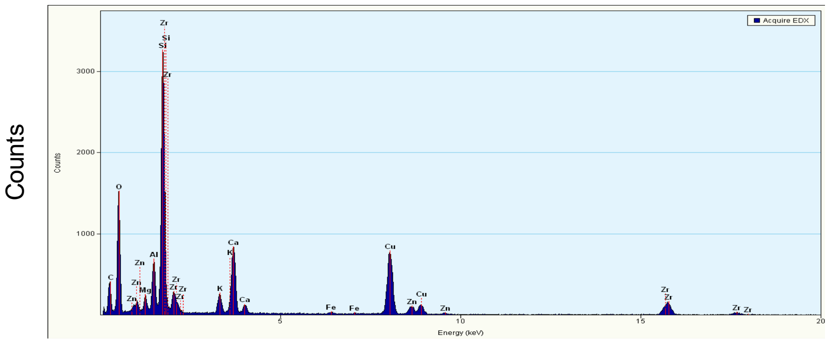


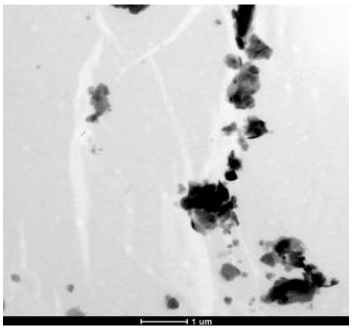

**Figure 17** – Composition of analized glassing nanoparticle




Eneergy (KeV)

**Figure 18** - Nanoparticle image observed at TEM at 1 µm

**Figure 19** - X-ray diffraction image at 5,00/1Gm



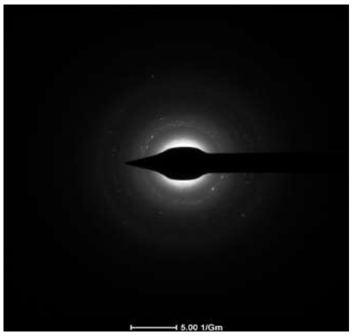
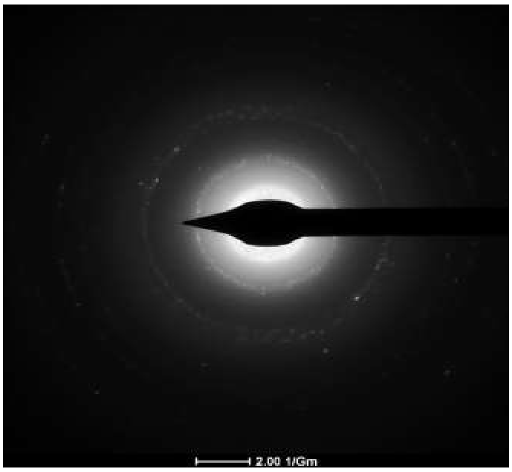




**Figure 20**-X-ray diffraction image at 2,00/1Gm

**Figure 21** - Nanoparticle image observed at TEM at 200 µm



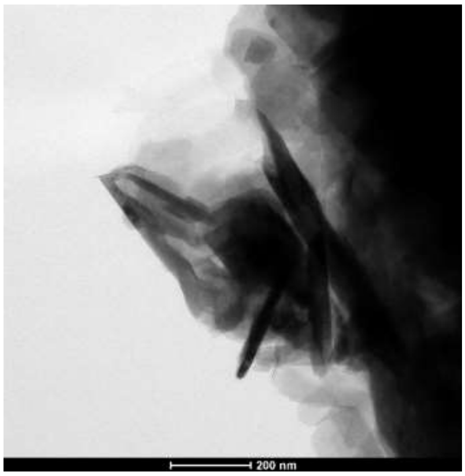




**Figure 22** – Composition of analized glassing nanoparticle

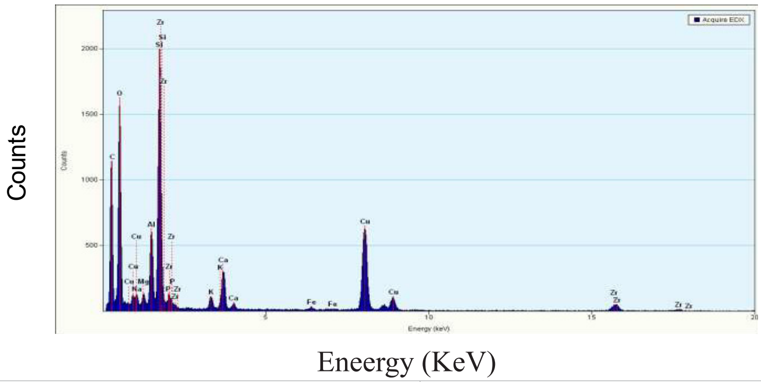
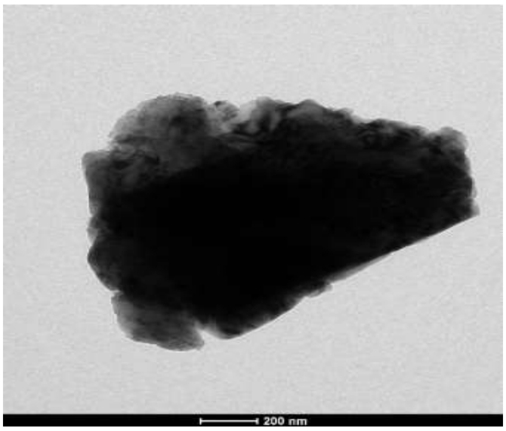



**Figure 23** - Nanoparticle image observed at TEM at 200 µm

**Figure 24** - X-ray diffraction image at 5,00/1Gm



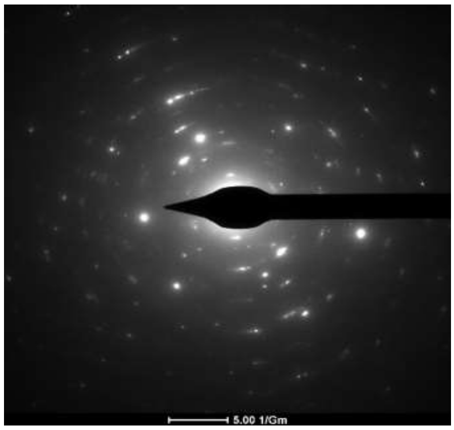
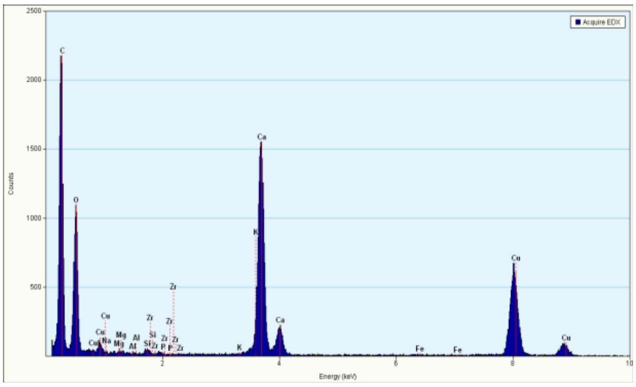




**Figure 25** – Composition of analized glassing nanoparticle



Eneergy (KeV)

## 4. Discussion

As can be seen from the obtained results, there is a high release of nanoparticles at workplaces in the load of materials / mixing zone in all ceramic material production units, regardless of the typology of materials produced.

It can be seen that the exposure values of workplaces in the load of materials / mixing zone assume very significant values, with exposure to very small nanoparticle particle sizes (11.5 nm and 15.4 nm), and their entry into the human organism is possible by several routes, in particular the airway.

In the ornamental tableware production unit, it is found that, in addition to being the unit with a higher nanoparticle value, the highest peak value is of a lower range of nanoparticles in the load of materials / mixing and glassing, maximizing the problem of worker exposure when performing their tasks.

From the graphical appreciation it can be seen that the entry of nanoparticles into the lungs is directly associated with their release, especially those of smaller size due to their very small mass and not being extracted in localized extraction, when existing.

With the realization of the baseline abroad, it became clear that the values released in the ceramic production are very high, hence the Risk Level matrix of the Control Banding Tool is so high and point to containment and demand measures expert advice to limit/minimize worker exposure. It was also apparent from the application of the Control Banding Tool that the amounts of materials used as well as their hazardousness have a strong influence on the increased risk level.

The measures implemented in the ceramics under study are clearly insufficient, as we can see from the results of the risk assessment, all of which need an improvement in risk control to achieve acceptable protection levels.

The materials that were identified by the TEM analysis were as follows:

**Table 11:** Materials present in the sampled nanoparticles and their crystallinity.

| Production unit | Zone | Most present materials | Molecular structure |
|---|---|---|---|
| Sanitary ware production unit | Load of materials / Mixing | Na, C, Cu, O, Na, Ca, F, S, K, Cl, Si, Al, P, Fe, Cl | Amorphous |
| | Glassing | Zr, Si, Zn, Cu, Al, Na, Mg, K, Ca, Fe, C, CO, O, P, | Essentially amorphous with some sparkles of crystallinity |
| Porcelain crockery production unit | Load of materials / Mixing | Fe, S, Cu, Cl, Al, C, O, Si, Ni, Na, K, Mg, Ca | Crystalline |
| | Glassing | Al, Si, Cu, Na, Cl, S, P, Zn, Mg, Ca, Fe, Ni, Cu, C, O, K, Cl | Essentially amorphous with some sparkles of crystallinity |
| Ornamental tableware production unit (red paste) | Load of materials / Mixing | Si, Cu, O, C, Cl, Na, Al, K, Mg, Fe, S, Ca | Crystalline |
| | Glassing | Al, Si, Na, C, O, Cl, K, Ca, Cu, Fe, Ti, P, Sc | Crystalline |

It is noted that, at present, occupational exposure limit values for nanomaterials are very scarce and specific and no concise assessment can be made on whether or not limit values are exceeded, as is the case for respirable and/or inhalable particles because all materials present in the ceramic production units are missing from **Table 9**.

**Table 12:** Occupational Exposure Limits (OEL) for specific nanomaterials adopted by different agencies.

| **Occupational exposure limit (OEL) adopted by different agencies** | | | |
|---|---|---|---|
| **Material** | **SER**[a] | **ECHA**[b] | **NIOSH**[c] |
| Nano-$TiO_2$ | - | - | 0.3 mg/cm$^3$ |
| Nano-fibers | 0.01 fibers/cm$^3$ | - | 0.001 mg/cm$^3$ |
| Nan-$SiO_2$ (fumes) | - | 0.3 mg/cm$^3$ | - |
| Biopresistent nanomaterial (density > 6x10$^3$ Kg/cm$^3$) | 2x10$^4$/cm$^3$ | - | - |
| Biopresistent nanomaterial (density < 6x10$^3$ Kg/cm3) | 4x10$^4$/cm$^3$ | - | - |

a – Social and Economic Council (Netherlands);

b – European Chemical Agency (EU);

c – National Institute for Occupation Safety and Health (USA).

If these reference values are exceeded, preventive and corrective measures are recommended to reduce exposure levels.

## 5. Conclusions

From the results analysis we can conclude that ceramic plants generally process very thin materials that lead to a large release of very small nanoparticles (predominantly 11.5 nm and 15.4 nm nanoparticles) with strong penetration capacity alveolar and consequently strong possibility of passing into the bloodstream, accumulating in the body. Most of the particles found are within the nanoscale range of 1-100 nm.

Exposure of workers to high nanoparticle peaks is found to be a significant problem as all peaks are small nanoparticles. The size of nanoparticles is also manifestly small in daily exposure at the workplace, as can be seen from their accumulated value.

Comparison of NAS crop and TEM photographs leads to the conclusion that relative humidity may cause nanoparticles to agglomerate, causing them to increase in size and precipitate so that they are not captured in the grids in higher humidity environments.

By applying the Control Banding Tool risk assessment tool we can verify that the 3 ceramic production units in question are not prepared to deal with this problem, since the results of the existing risk assessment are high (risk level 3 and 4), which requires containment measures and seeking specialist advice.

Analyzing the existing removal/protection equipment we find that there are many who are ideal in protecting workers to nanoparticles and a significant improvement in all situations is necessary.

The sanitary ware production plant is the one that presents the worst results in relation to the materials used in the production (quantity and hazardousness) versus existing removal/ protection equipment, although it is not the one with the highest nanoparticle release values.

Regarding the materials present in the constitution of the nanoparticles analyzed by TEM, we can see that they are mainly derived from the materials used in the production, since most of the materials that appear in the results have a direct relationship with the materials that give them source. As for the nanoparticle molecules structure we can see that the different concentrations of the present materials influence the molecular structure to be crystalline or amorphous, since the materials present in the analyzed nanoparticles are very similar, changing only the nanoparticle to nanoparticle concentrations.

There are several problems associated with the production process in these companies such as the existence of forklift trucks moving inside. Their movement causes a resuspension of the nanoparticles and an increase in their stay in the air. It would be important to know their terminal velocity, which, technically, is not yet possible due to the lack of knowledge about their mass and surface area, hence the relevance of this typology of studies to understand what is the real need for increased time automated localized extractions, as well as to redefine their extraction flow rates due to their small mass, thus making their extraction difficult. Another problem was the cleaning of the clothes by the operators with compressed air, which results in very significant nanoparticle release peaks.

Finally, it can be argued that occupational exposure to nanoparticles is both a new and increasing risk, which can be considered as an emerging risk. Therefore, there is a great need to define risk assessment methodologies adapted to these situations and thus contribute to increase knowledge about the health effects of workers exposed to nanoparticles in the ceramic industry, as a basis for creating normative / guidelines containing limit values exposure, with the ultimate aim of reducing the risk to human health.

Given the almost inexistence of nanoparticle exposure limit values in Legislation, standardization and entities such as NIOSH or ACGIH for the materials studied, it is difficult to make any comparison. Given the lack of information, a search of scientific articles made in the area was performed, but no experimental methods of comparison were found.

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