NON-FUNCTIONALISED AND FUNCTIONALISED SILICA NANOSPHERES

1. Case metadata

▪ *Country/ies of origin:*

Poland

▪ *Year of publication by agency:*

2011

▪ *Sector:*

NACE-Code:

M 72.1 Research and experimental development on natural sciences and engineering

▪ *Keywords:*

40256C Nanoparticles

32801E Silica

56441D Researchers

59951C Laboratory work

12841E Exposure assessment

24361C Good practice

18521C Safety management

2. Organisations involved

- Industrial Chemistry Research Institute (ICRI), Rydygiera 8, 01-793 Warsaw, Poland
- Central Institute for Labour Protection – National Research Institute (CIOP-PIB), Czerniakowska 16, 00-701 Warsaw, Poland

3. Description of the case

3.1. Introduction

In 2009, a study conducted by the Industrial Chemistry Research Institute (ICRI) and the Central Institute for Labour Protection – National Research Institute (CIOP-PIB) attempted to determine the potential exposure of laboratory staff of ICRI to silica nanospheres used for the production of nanocomposites. The investigation conducted by the CIOP-PIB was part of a study done in the NANOSH project [1].

The Industrial Chemistry Research Institute (ICRI) is an R&D centre in Poland in the field of chemistry and industrial chemistry. One of the ICRI's areas of activity includes the development of nanocomposites containing nano-crystals or powders and high-technology oriented organic/inorganic hybrids (nano- and opto- electronics, nano-structured biocompatible materials). The research project, focused on the development of the technologies of non-functionalised and functionalised silica nanospheres, started in 2003. Original technologies of silica nanospheres using the sol-gel process have been developed and are close to commercialization. In addition, research projects focused on application of these nanospheres as fillers for polymer nanocomposites (PVC, PET, PC, PA) started in 2004.

CIOP-PIB is Poland's research institution, comprehensively dealing with issues relating to the improvement of working conditions in accordance with human psychophysical abilities. The main aim of the Institute's research and development work is to build scientific foundations in order to create a system for preventing occupational hazards. Some of the most important topics of CIOP-PIB activities are identification, risk assessment and elimination of harmful aerosols (including nanoparticles) from working and living environments, evaluation the efficiency of Local Exhaust Ventilation (LEV) and general ventilation.

3.2. Aims

The aim of ICRI's activities was to minimise the risk of laboratory staff, arising from exposure to silica nanospheres during the manufacture and application process.

3.3. What was done, and how?

ICRI activities arising from commitment of management to decrease the risk of possible exposure of laboratory staff to silica nanospheres:

- Identification of operations in which laboratory staff can be exposed to nanoparticles during the manufacture and application of silica nanospheres.
- Equipping laboratory rooms with centrally controlled general ventilation systems and manually switching on LEV, used when laboratory staff are working with silica nanospheres.
- Selection of PPE (gloves, half face mask) that must be used by laboratory staff during possible contact with silica nanospheres.

CIOP-PIB and ICRI activities:

Measurements done by CIOP-PIB in ICRI laboratory rooms for the determination of potential exposure during the grinding and packing of silica nanospheres to glass containers (included in the results of NANOSH project).

3.3.1. Identification of potential exposure to silica nanospheres and measures used for laboratory staff protection.

ICRI identified operations in which laboratory staff can be exposed to silica nanospheres during the manufacture and application process. These operations can be defined as follows:

- drying of silica nanospheres (conventional drier or spray drier),
- grinding and packing of silica nanospheres into glass containers,
- manufacture of polymer composites by reactive processing techniques.

Laboratory rooms of ICRI were equipped with the following ventilation systems: LEV – fume hood (Figure 1) and general ventilation (Figure 2).

Figure 1: Ventilation system: LEV

Figure 2: Ventilation system: part of general ventilation

From start of work with silica nanosphers laboratory staff wear personal protection equipment (PPE) including laboratory clothing, half face-masks and gloves (Figure 3).

Figure 3: Laboratory staff grinding raw product with silica nanospheres

3.3.2. *Investigation of potential exposure to silica nanospheres.*

As result of analysing of the operations in which laboratory staff of ICRI can be exposed to silica nanospheres it recognize that potential exposure mainly can be during the grinding and packing of silica nanospheres into glass containers. Grinding of the raw product is done in order to obtain spherical silica nanoparticles, which are used for nanocomposite production, among other things. Figure 4 illustrates the silica nanospheres as a raw product, while Figure 5 shows it after grinding.

Figure 4: Silica nanospheres: as a raw product

Figure 5: Silica nanospheres: after grinding

Investigations for determination of potential exposure laboratory staff of ICRI to silica nanospheres were conducted by CIOP-PIB [1]. Measurements were done in the areas of possible residence of nanoparticles during manipulations conducted by staff of ICRI.

The aim of this investigations was to obtained:

- number and surface concentrations of nanosize particles emitted during grinding spherical silica nanoparticles in comparison for concentrations of the ultrafine particles presented as a “background” in the room (on the desk) and in the fume hood,
- influence of change of air velocity in the room on the concentrations of nanosize particles in the fume hood during grinding of silica nanospheres,
- possible influence of emission of spherical silica nanoparticles during grinding on the concentrations of the nanosize particles close to the laboratory room: on the corridor.

Number and surface concentrations were measured because these parameters better characterised of nanosized particles than mass concentrations. According to definition of nanoparticles [2] it is also important to know how many of nanosized particles belongs to nanoscale (<100nm) and how many particles are with bigger diameter (>100nm).

The investigations to assess potential exposure to silica nanosphers were done with the use of the following measuring equipment:

- Scanning Mobility Particle Sizer – SMPS (CPC 3022A with long DMA), TSI – number concentration and size distribution of particles of 15–661 nm,
- Ultrafine Particle Counter P-TRAK, TSI model 8525 – number concentration of particles of 20–1000 nm,
- Handheld Particle Counter AERO-TRAK 9000, TSI – surface area of particles of 10–1000 nm: TB fraction.

The location of sampling points for particle parameter determination is presented in Figure 6: sampling points on the desk, Figure 7: sampling points in the fume hood (with open fume sash) and Figure 8: sampling points on the corridor.

Figure 6: Location of sampling points for particle parameter determination on the desk

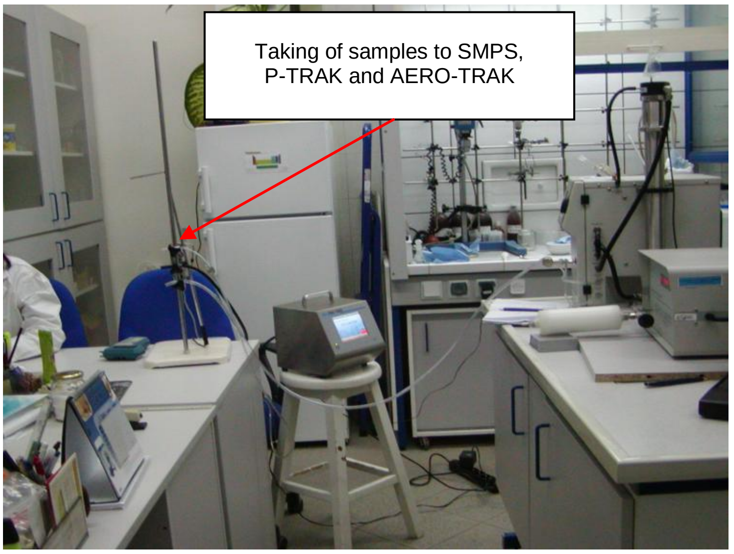


Figure 7: Location of sampling points for particle parameter determination in the fume hood (with open fume sash)

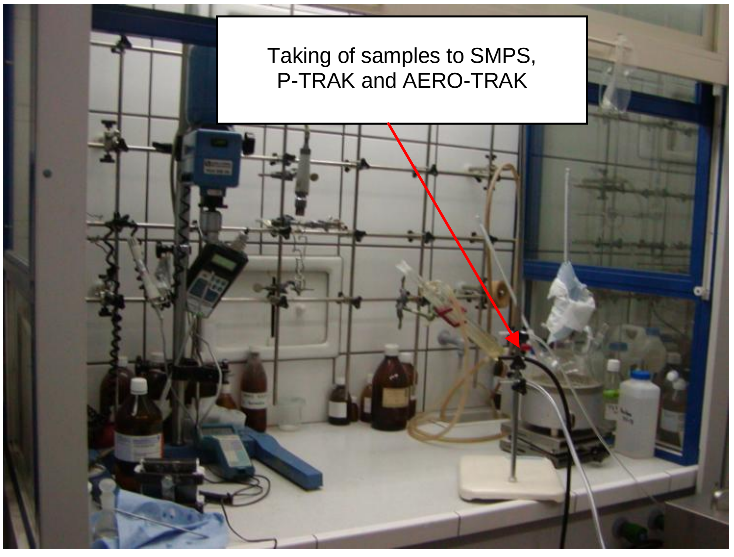
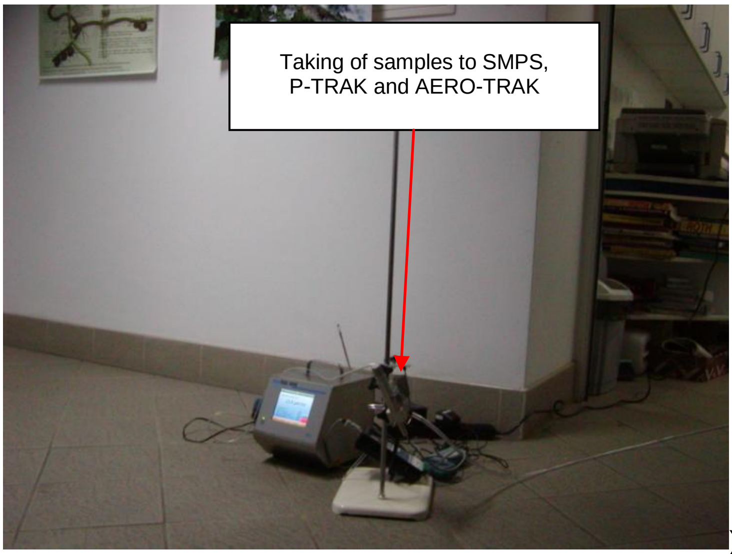


Figure 8: Location of sampling points for particle parameter determination on the corridor



)

Example results of measurements obtained before, during and after the grinding of raw product with spherical silica nanoparticles of 70 nm and 110 nm are illustrated respectively in Figures 9, 10 and 11. Schedule of measurements with clarification of abbreviations (numbers with letters) of the data shown in Figures 9, 10 and 11 are presented in Table 1.

Air parameters at the time of measurements were as follows: air temperature of $22\div25^{0}$C, relative air humidity of $24\div26\%$ and air velocity of 0-1.3 m/s. Air parameters, especially air velocity, can significantly influenced on changes of the nanoparticles concentrations in the air.

Table 1: Schedule of measurements with clarification of abbreviations shown in Figures 9, 10 and 11.

Abbreviations shown on the Figures 9, 10 and 11	Description of measurement points
1a	**On the desk** as 'background' in the laboratory room.
2 a	**In the fume hood** as 'background' (yellow bar).
2 b	**In the fume hood** during grinding of silica nanospheres of 70 nm diameter (first grey bar).
2 c	**In the fume hood** between grinding of silica nanospheres with diameter of 70 nm and 110 nm.
2 d	**In the fume hood** during grinding of silica nanospheres of 110 nm diameter (second grey bar).
2 e	**In the fume hood** after grinding of silica nanospheres of 110 nm diameter.
1 b	**On the desk** in the laboratory room after grinding (green bar).
3	**On the corridor** close to the door of laboratory room (blue bar)
1 c	**On the desk** in the laboratory room after grinding.

Figure 9: Total number concentrations of particles before, during and after the grinding of raw product with silica nanoparticles (SMPS and P-TRAK results). First grey bar – indicates grinding of nanoparticles of 70 nm diameter, second grey bar – indicates grinding of nanoparticles of 110 nm diameter. Bars of other colours are explained in Table 1

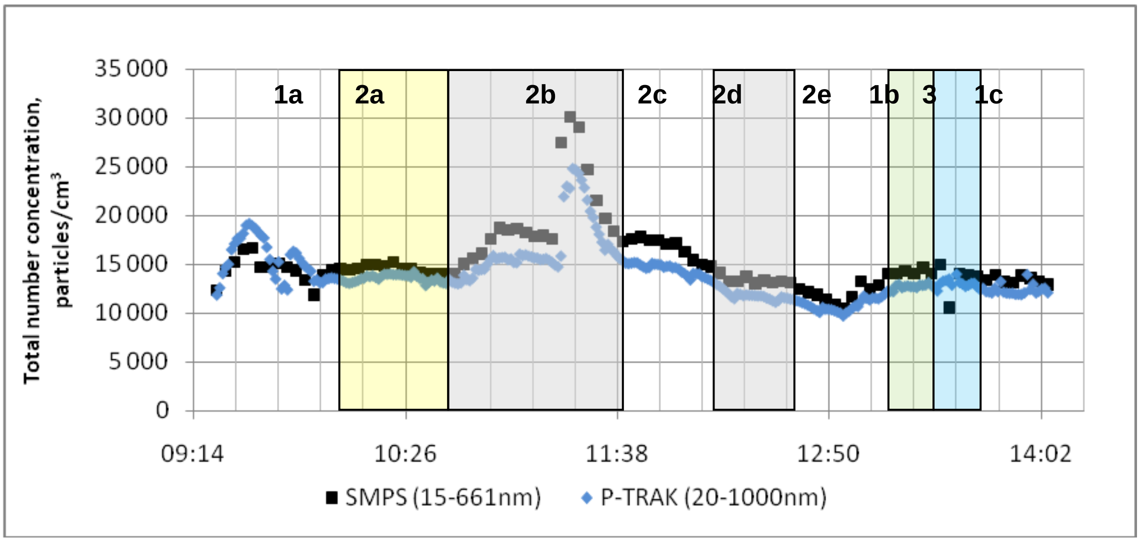


Figure 10: Surface concentrations of particles before, during and after the grinding of raw product with silica nanoparticles (AERO-TRAK results). First grey bar – indicates grinding of nanoparticles of 70 nm diameter, second grey bar – indicates grinding of nanoparticles of 110 nm diameter. Bars of other colours are explained in Table 1

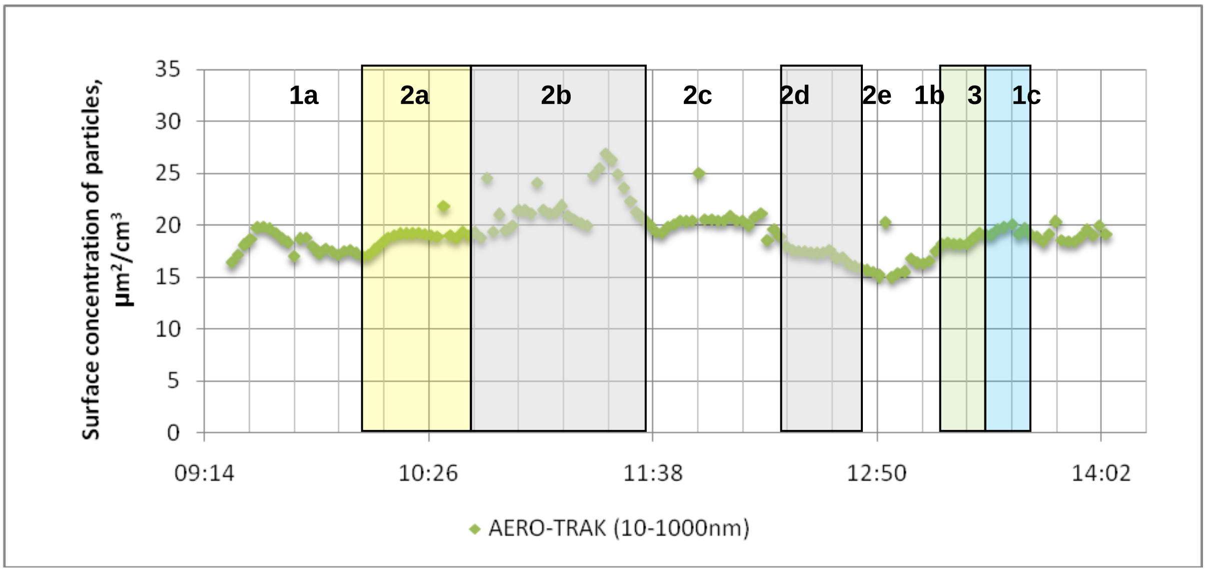
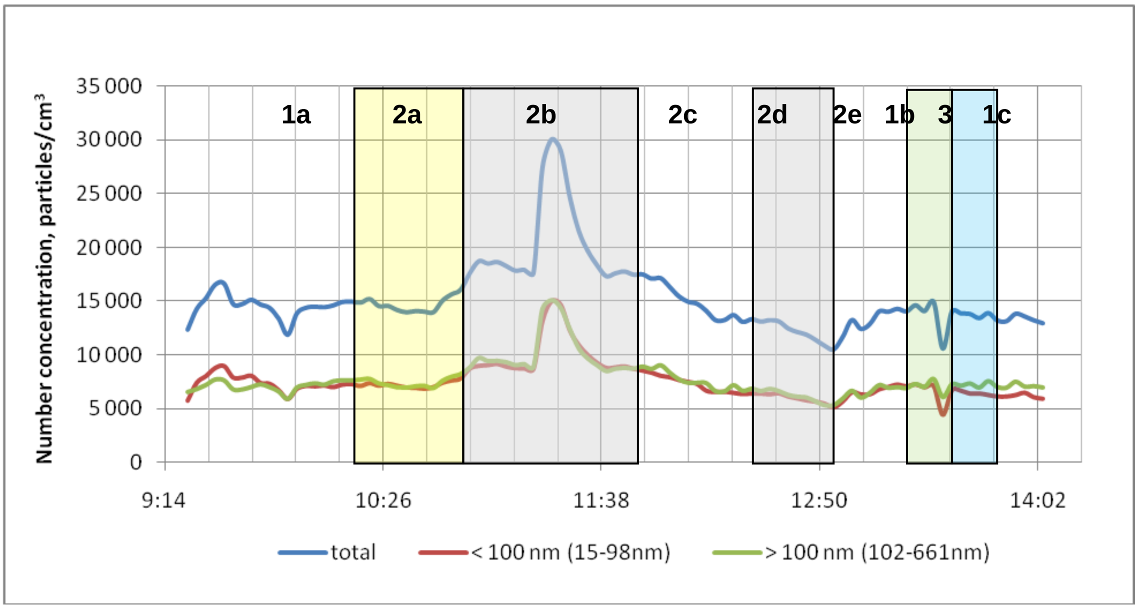


Figure 11: Number concentrations of particles before, during and after the grinding of raw product with silica nanoparticles (SMPS results), as total and for particles in nanoscale (<100nm) and for particles with bigger diameter (>100nm). First grey bar – indicates grinding of nanoparticles of 70 nm diameter, second grey bar – indicates grinding of nanoparticles of 110 nm diameter. Bars of other colours are explained in Table 1



As follow from results show on Figures 9-11, during measurements described in Table 1:

– Before grinding, number concentrations of “background” in the laboratory room (Figure 9:1a) were higher than that determined as “background’ in fume hood (Figure 9: 2a). It indicate that some particles from the size range 15-1000nm are captured by fume hood. Surface concentrations for both “backgrounds” were quite close (Figure 10: 1a, 2a), however longer time surface concentrations were higher as a “background” in the fume hood. It means that in the fume hood were particles with the sizes giving higher surface concentrations results.

– Number concentrations of “background” can be significant (almost half – Figures 9 and 10: 1a, 2a) in comparison for the highest concentrations (number up to 30,000 particles/cm^3, and surface up to 27 µm^2/cm^3) obtained during grinding raw product with silica nanosphers of 70nm diameter in the fume hood (Figures 9 and 10: 2b – first grey bar). It means that always before measurements pointed to determination of potential exposure to nanoparticles, “background” concentrations must be determined. Data show also that increase of the concentrations can be not only on the beginning of the grinding, and concentrations can varied during the time of operation. Air velocity determined in the centre of laboratory room was during this measurements not higher than 0.1m/s.

– When grinding the raw product with spherical silica nanoparticles of 110 nm (Figures 9 and 10: 2d – second grey bar), noticeable peaks of concentrations were not observed - concentrations decreased and were lower than the “background” before grinding (Figures 9 and 10: 2a). During this time in the laboratory, as a result of the operation of general ventilation, a perceptible draught was observed (air velocity in the centre of room increased to 1.3 m/s), which could explain this phenomena.

– After both grindings, number and surface concentrations of particles on the desk (Figure 9 and 10: 1b, 1c) were similar or lower than that determined as 'background' before grinding (Figure 9 and 10: 1a) and were comparable with concentrations obtained in the corridor (Figure 9 and 10: 3).

– The total number concentrations obtained with SMPS (for particles from the range 15-661nm) were almost identically divided into concentrations of particles from nanoscale (<100 nm) and particles with bigger diameter (>100 nm) – Figure 11. Information about particles with bigger diameter, than particles from nanoscale, is also important, because most nanoparticles very easy formulated agglomerates or aggregates, what can be also in this situation.

3.4. What was achieved?

- The providing protections measures of laboratory staff against silica nanosphers, both collection protection (ventilation systems: general and LEV) and suitable personal protection equipment (PPE).
- The determination of potential exposure of laboratory staff to silica nanospheres. Because standardised methods of assessment and occupational exposure limits are not available, received data are giving useful information about possible exposure of laboratory staff to silica nanospheres.

3.5. Success factors

- The determination of the potential exposure of laboratory staff to silica nanospheres.
- The commitment of management to decrease the risk of possible exposure of laboratory staff to silica nanospheres.
- The useful cooperation between CIOP and ICRI in order to investigation of potential exposure of ICRI laboratory staff to silica nanospheres.
- Further research on silica nanospheres is continuing in order to elaborate the method of modification of these nanoparticels by the immobilisation of silver or copper nanoparticles on the surface of silica nanospheres. During this research, laboratory staff are using protective measures described in this case study.

3.6. Further information

Contact person: Dr Maria Zielecka

E-mail: maria.zielecka@ichp.pl

Internet: http://www.ichp.pl

3.7. Transferability

Knowledge about:

- necessity, during investigation of potential exposure to nano-objects, taking into consideration data concerning “background” arising from always presenting in the air ultrafine particles,
- possibility of the big influence of air parameters, especially air velocity, on the concentrations of nanosized particles presented in the air.

4. References, resources:

1. http://www.ttl.fi/partner/nanosh/Sivut/default.aspx
2. ISO/TS 27687:2008. Nanotechnologies -Terminology and definitions for nano-objects - Nanoparticle, nanofibre and nanoplate.