ASSESSMENT OF EXPOSURE TO NANO-OBJECTS AND THEIR AGGLOMERATES AND AGGREGATES (NOAA) DURING NANO-POWDERS HANDLING

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Risk bands as a result of hazard bands and exposure bands

ISO/TS 12901-2:2014

		Exposure band (EB)			
Hazard band (HB)		**EB 1**	**EB 2**	**EB 3**	**EB 4**
	A	Low	Low	Low	Medium
	B	Low	Low	Medium	High
	C	Low	Medium	Medium	High
	D	Medium	Medium	High	High
	E	Medium	High	High	High

A-E (hazard bands) inhalation hazard groups according International Labour Organization Control Banding Toolkit http://www.ilo.org/legacy/english/protection/safework/ctrl_banding/index.htm

EB1- EB-4 (exposure bands) on the basis of a comprehensive evaluation of all available data of the exposure scenario under concern, e.g. physical form of NOAA, amount of NOAA, dust generation potential of processes and actual exposure measurement data.

The key issue in controlling occupational risk is assessment of exposure to NOAA, which occurs at the workplace during manufacture or use of nanomaterials.

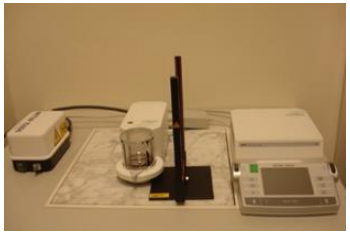
The aim of investigations

Investigations were focused on measurements of NOAA parameters which can be used for determination of workers individual exposure to NOAA:

- ✓ number concentrations and average size of particles in real time (nanospecifice),
- ✓ mass concentrations of particles with gravimetric method (exposure index for dusts),
- ✓ shape and chemical composition of particles with electron microscope with EDS detector (confirmation / exclusion of the presence of NOAA).

Methods and devices used for determination of particles parameters

measurements were done about 30 cm from the source of particles

Measurements of: ✓ number concentrations (10-700nm) and average size of particles (10-300nm) ✓ in real time	Taking samples and determination: ✓ mass concentrations of particles ✓ with gravimetric method	Taking samples for analyse of: ✓ shape and chemical composition of particles ✓ with electron microscope with EDS detector
➢ Miniature Diffusion Size Classifier, Matter Aaerosol DiscMinis	➢ FSP10 cyclone (GSA) with cellulose nitrate membrane filter 37 mm (8 µm) and pump SG10-2 (GSA) (10dm^3/min) ➢ METTLER TOLEDO type UMX2 scales	✓ Mini-Particle Sampler - MPS (Ecomesure) with TEM Cu Quantifoil 1.2/1.3, 400 mesh grid and pump GilAirPLUS (0.3 and 1dm^3/min) ✓ Ultra High Resolution FE-SEM ✓ EDS-Bruker Quantacs 400
	 	 

Processes with nanomaterials

Day	Processes	Processes duration	Fume cupboard
1	Processes P1, P3, P5 (filling the form) and P2, P4, P6 (transfer back to the plastic bag) with silica aerogels (50cm^3): modified of polyester resin, commercially available (SJ1800Series), modified of phenol formaldehyde resin "1„.	3-4 min	Switched-off
2	Processes P7, P9, P11 (filling the form) and P8, P10, P12 (transfer back to the plastic bag) with silica aerogels (50cm^3): no modified „0", modified of divinylbenzene, modified of phenol formaldehyde resin „2„.	2-3 min	
3	Processes P13 (filling the form) and P14 (transfer back to the plastic bag) with silica aerogel (50cm^3) no modified „2". Processes P15, P17 (filling the form) and P16, P18 (transfer back to the plastic bag) with silica modified of silver (50cm^3) traditionally dried and ground or spray dried.	2-3 min	
4	Processes P19, P20 – filling the nanopowder ZrO_2+8%CaO (2g) to the open rotating drum, carrying out the process in a hermetically sealed drum, dumping nanopowder from an open drum and removing the residue with a brush. During process P20 rotating drum was open longer time than during process P19.	7-24 min	Switched-on
5	Process P21 (2g), processes P22, P23, P24, P25, P26 (6g) – filling the nanopowder ZrO_2+8%Y_2O_3 (2g) to the open rotating drum, carrying out the process in a hermetically sealed drum, dumping nanopowder from an open drum and removing the residue with a brush.	20-34 min	

Processes P1-P18 two: DiscMinis, sampling systems FSP10+SG10-2 and systems MPS+GilAirPLUS (measurements inside of fume cupboard)
Processes P19-P26 one: DiscMini, sampling system FSP10+SG10-2 and system MPS+GilAirPLUS (measurements outside of fume cupboard)

The criteria for the evaluation of the exposure levels (EB)

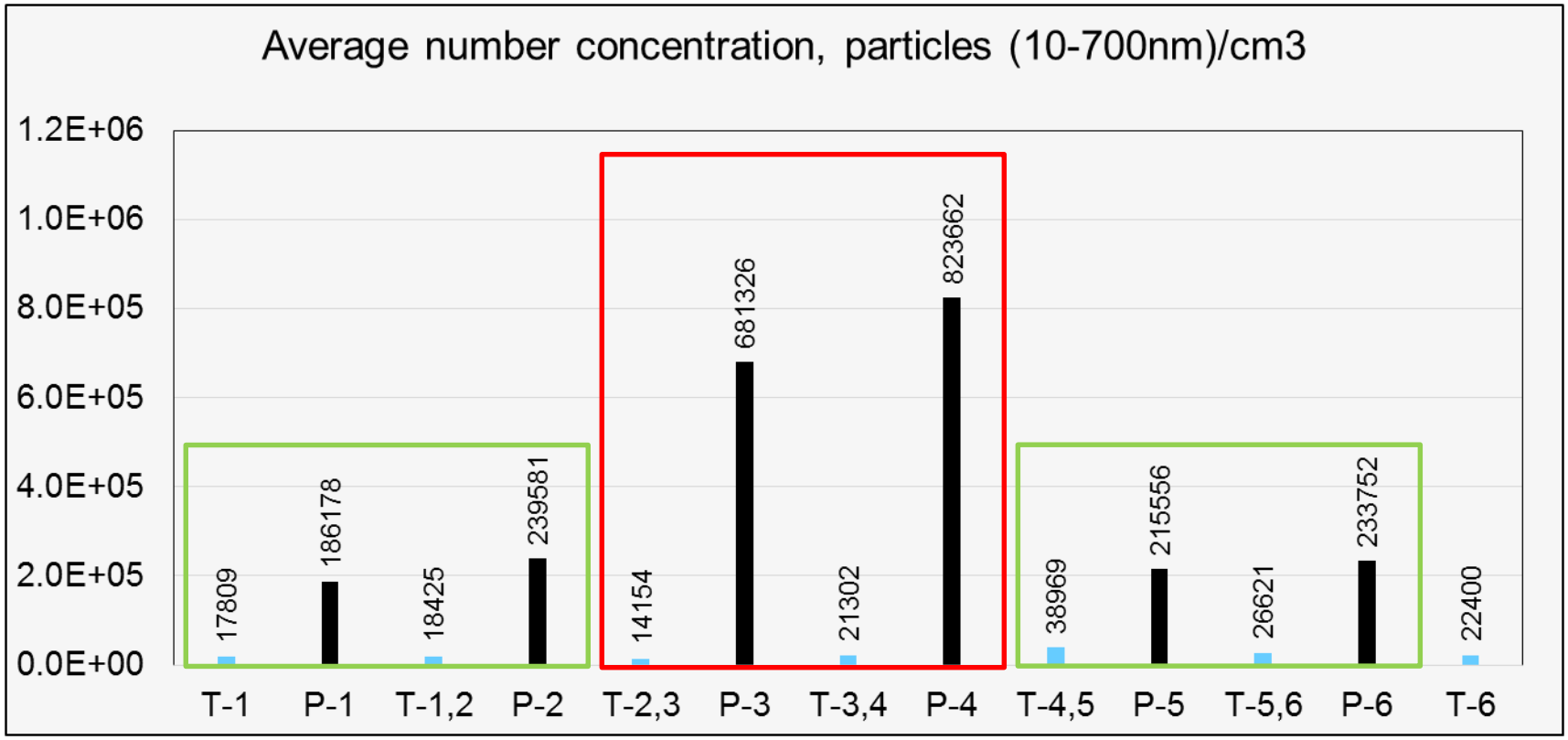
ISO/TS 12901-2:2014

Brouwer D.H, et al: Workplace air measurements and likelihood of exposure to manufactured nano-objects, agglomerates, and aggregates. J Nanopart Res (2013) 15:2090. DOI 10.1007/s11051-013-2090-7

Parameter/ method	Exposure levels (EB)			
	1	2	3	4
Number concentration / real time DiscMini measurements	$N_{DiscMini\ P}/N_{DiscMini\ B}$ *Number concentration of particles during the process/ Number concentration of „background„ particles*			
	below 1.1	*between* 1.1 – 1.5	*between* 1.5 – 2	*above* 2
Mass concentration / gravimetric method	$M_C/M_L or M_r$ *Mass concentration of sampling particles/Limit or reference mass concentration*			
	below 0.1	*between* 0.1 – 0.5	*between* 0.5 – 1	*above* 1
Confirmation of the absent/presence of NOAA from applied nanomaterials (shape and chemical composition) / microscopic method with EDS detector	*absent/present*	*absent/present*	*absent/present*	*absent/present*

Example of results received in real time during carried out of processes with silica aerogels

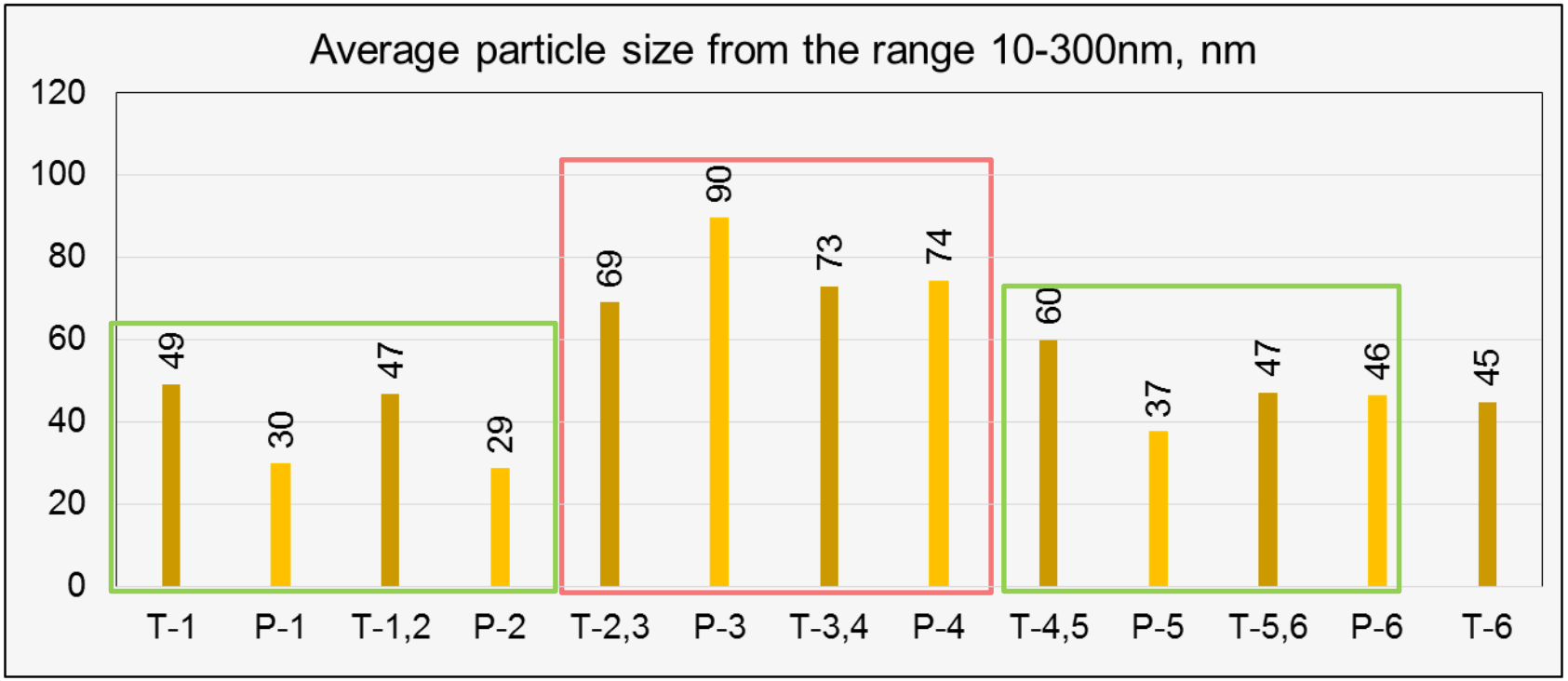
in fume cupboard switched-off (day 1)



Processes P1, P3, P5 (filling the form) and P2, P4, P6 (transfer back to the plastic bag) with silica aerogels (50cm^3): modified of polyester resin, commercially available (SJ1800Series), modified of phenol formaldehyde resin "1„.

Example of results received in real time during carried out of processes with silica aerogels

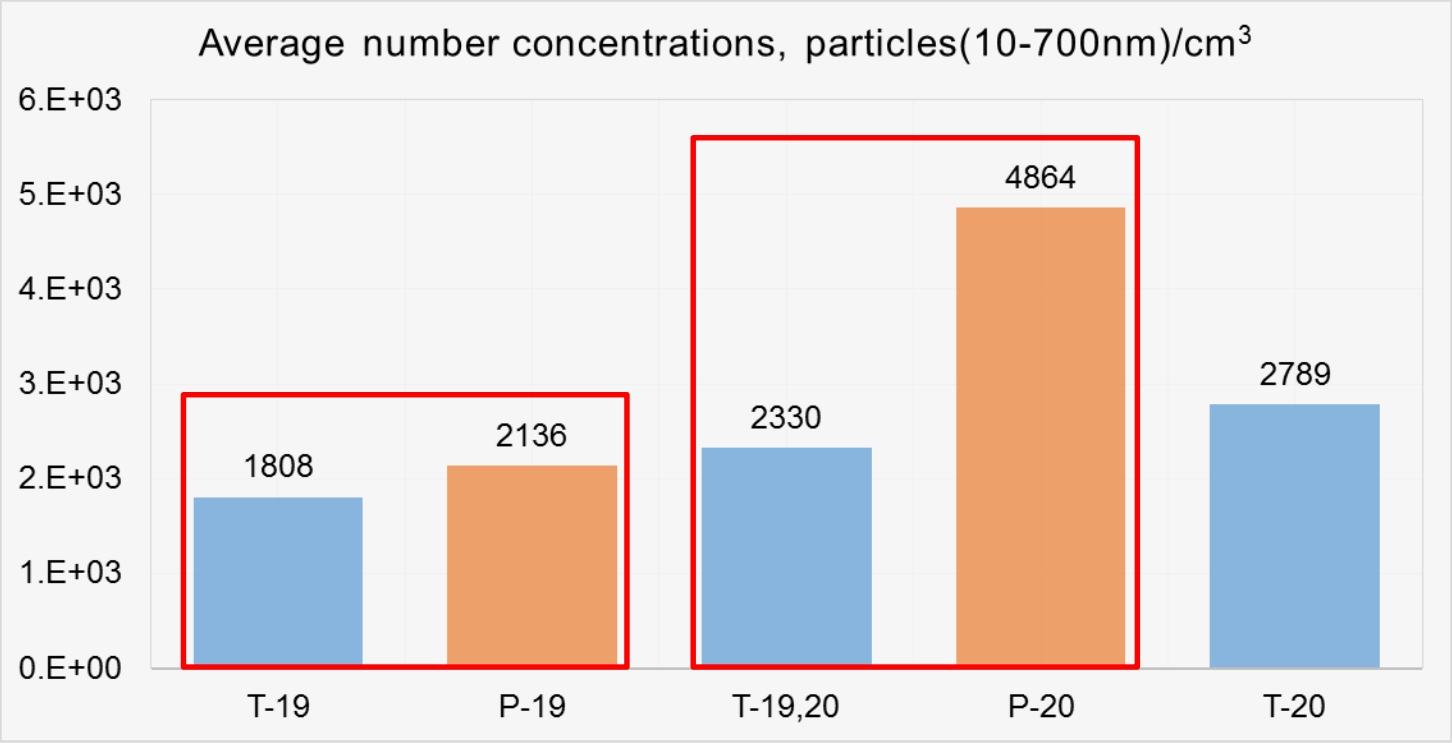
in fume cupboard switched-off (day 1)



Processes P1, P3, P5 (filling the form) and P2, P4, P6 (transfer back to the plastic bag) with silica aerogels (50cm^3): modified of polyester resin, commercially available (SJ1800Series), modified of phenol formaldehyde resin "1„.

Example of results received in real time during carried out of processes with powder of ZrO_2+8%CaO

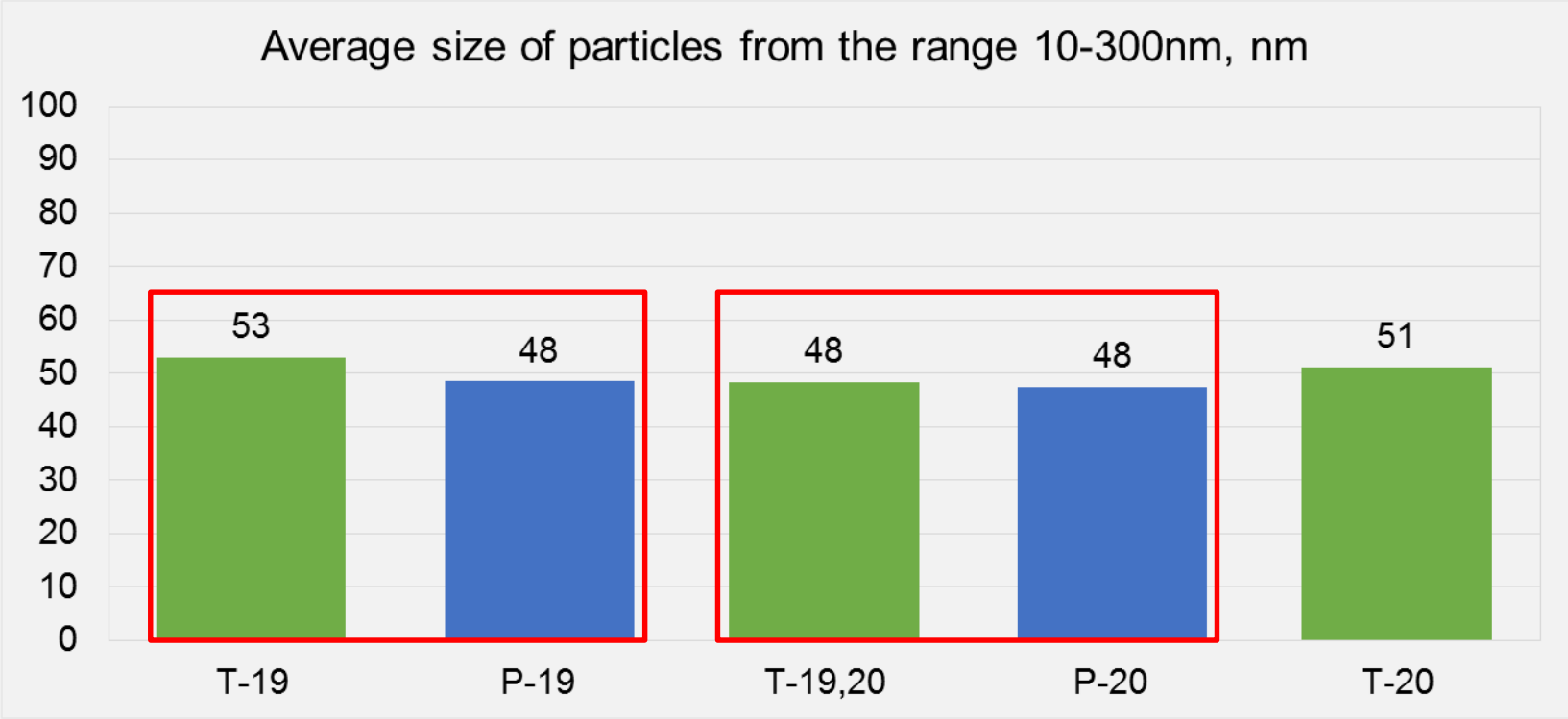
in fume cupboard switched-on (day 4)



Processes P19, P20 – filling the nanopowder ZrO_2+8%CaO (2g) to the open rotating drum carrying out the process in a hermetically sealed drum, dumping nanopowder from an open drum and removing the residue with a brush. During process P20 rotating drum was open longer time than during process P19.

Example of results received in real time during carried out of processes with powder of ZrO_2+8%CaO

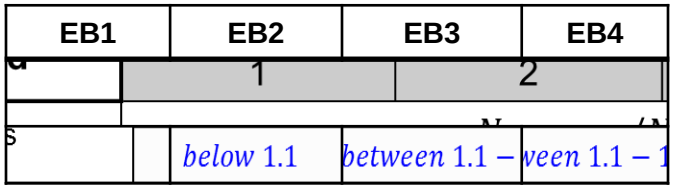
in fume cupboard switched-on (day 4)



Processes P19, P20 – filling the nanopowder ZrO_2+8%CaO (2g) to the open rotating drum carrying out the process in a hermetically sealed drum, dumping nanopowder from an open drum and removing the residue with a brush. During process P20 rotating drum was open longer time than during process P19.

Evaluation of the exposure levels (EB)

average number concentrations determined with DiscMinis



Day	Processes	Fume cupboard	Exposure level (EB)
1	Processes P1, P3, P5, P2, P4, P6 with silica aerogels (50cm^3).	Switched-off	EB4 5.53-48.14
2	Processes P7, P9, P11, P8, P10, P12 with silica aerogels (50cm^3).		EB4 2.92-25.41
3	Processes P13, P14 with silica aerogel (50cm^3). Processes P15, P17, P16, P18 with silica modified of silver (50cm^3).		EB4 3.00-19.40
4	Process P19 with nanopowder ZrO_2+8%CaO (2g)	Switched-on	EB2 1.18
	Process P20 with nanopowder ZrO_2+8%CaO (6g)		EB4 2.09
5	Processes P21, P22, P24, P25, P26 with nanopowder ZrO_2+8%Y_2O_3 (2g or 6g)		EB1 1.02-1.08
	Process P23 with nanopowder ZrO_2+8%Y_2O_3 (6g)		EB2 1.17

Changes of average size of particles

average particle size determined with DiscMinis

Day	Processes	Fume cupboard	Index of average size changes S_c
1	Processes P1, P5, P2, P6 with silica aerogels (50cm^3).	Switched-off	1.02-1.65
	Processes P3, P4 with silica aerogels (50cm^3). commercially available (SJ1800Series)		1.02-1.30
2	Processes P7, P9, P11, P8, P10, P12 with silica aerogels (50cm^3).		1.47-1.94
3	Processes P13, P14 with silica aerogel (50cm^3). Processes P15, P17, P16, P18 with silica modified of silver (50cm^3).		1.03-1.86
4	Process P19, P20 with nanopowder ZrO_2+8%CaO (2g)	Switched-on	1.02-1.09
5	Processes P21, P22, P23, P24, P25, P26 with nanopowder ZrO_2+8%Y_2O_3 (2g or 6g)		1.01-1.05

$$S_c = \frac{S_{DiscMiniB}}{S_{DiscMiniP}}$$

$$S_c = \frac{S_{DiscMiniP}}{S_{DiscMiniB}}$$

In green colour: average particles size decrease

In red colour: average particles size increase

Exposure mass index

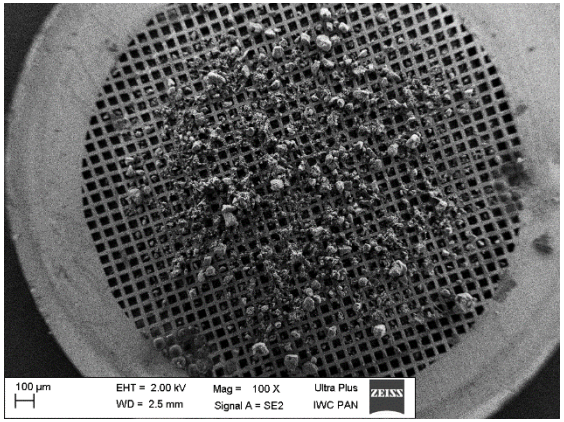
mass concentrations – samples taking with two FSP10 + SG 10-2 systems

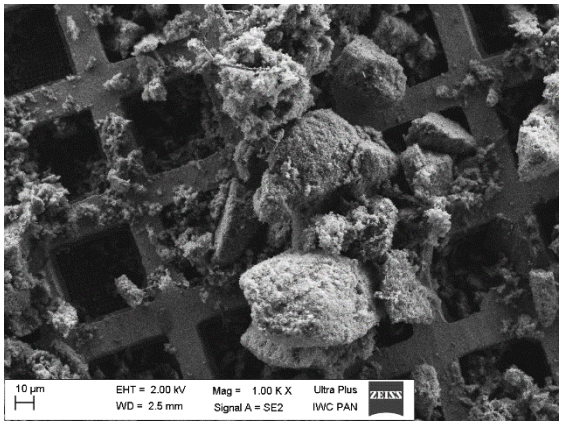
Day	Processes	Fume cupboard	Average exposure mass index mg/m³
1	Processes P1, P3, P5, P2, P4, P6 with silica aerogels (50cm³).	Switched-off	**0.5246** (2) (288min)
2	Processes P7, P9, P11, P8, P10, P12 with silica aerogels (50cm³).		**0.1718** (2) (256min)
3	Processes P13, P14 with silica aerogel (50cm³). Processes P15, P17, P16, P18 with silica modified of silver (50cm³).		**0.2022** (2) (234min)
4	Process P19 with nanopowder ZrO_2+8%CaO (2g) Process P20 with nanopowder ZrO_2+8%CaO (6g)	Switched-on	**0.0175** (1) (360min)
5	Processes P21, P22, P24, P25, P26 with nanopowder ZrO_2+8%Y_2O_3 (2g or 6g) Process P23 with nanopowder ZrO_2+8%Y_2O_3 (6g)		**0.1043** (1) (420min)

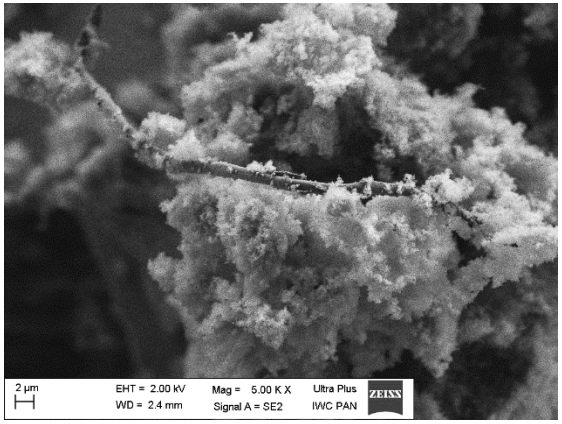
(1) One value
(2) Average from two values

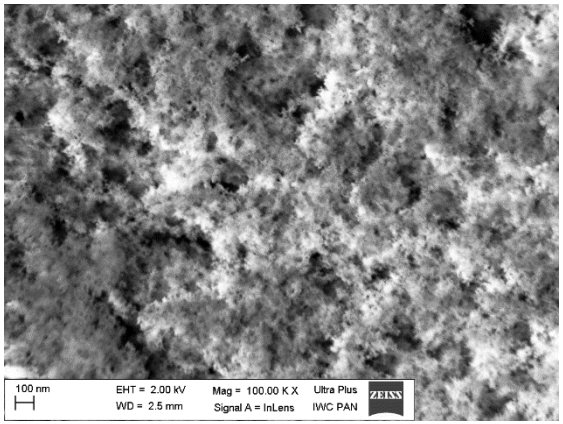
Example of SEM and EDS results

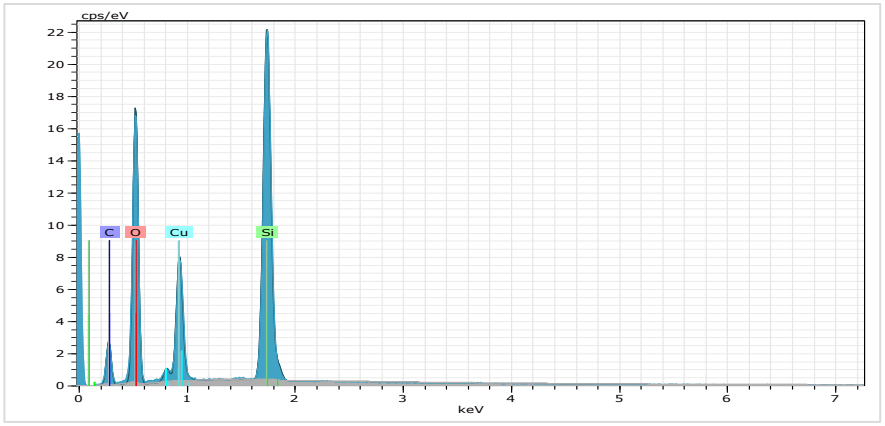
handling of silica aerogel modified of polyester resin (process P1)







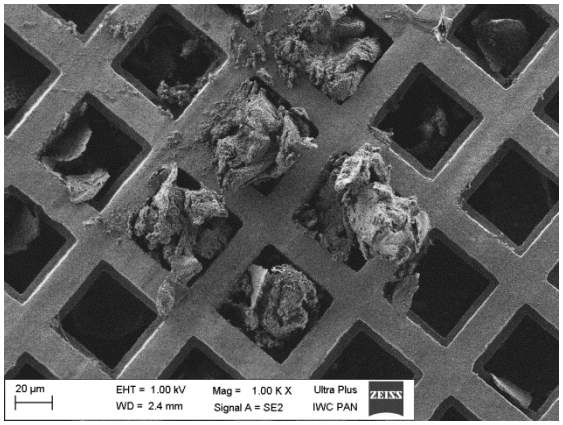


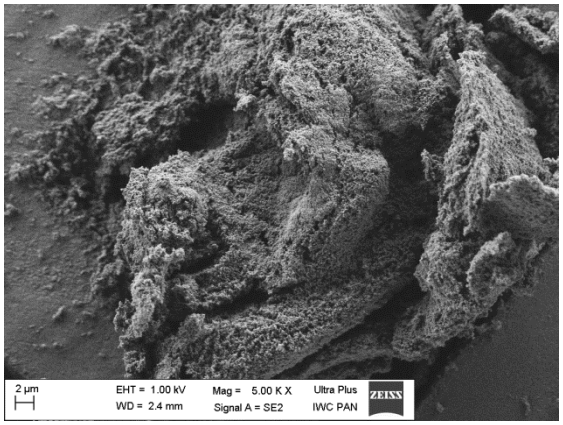


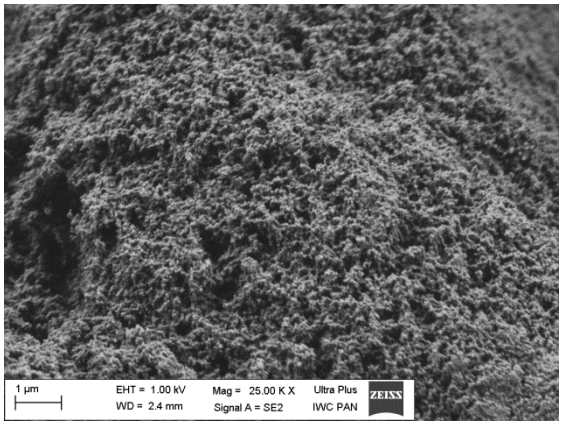
Sampling flowrate1dm^3/min

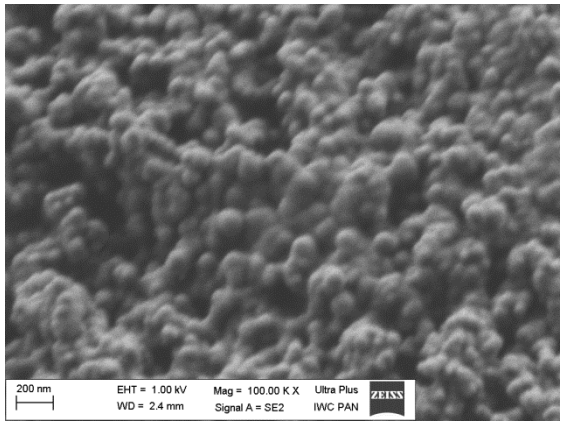
Example of SEM and EDS results

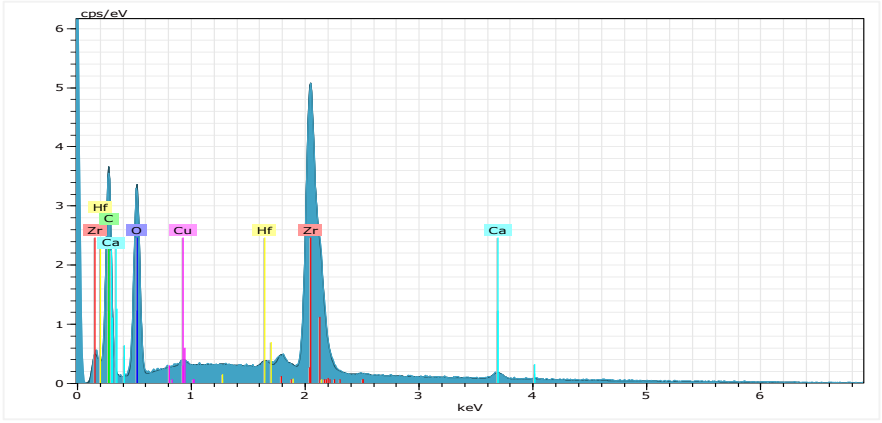
handling of ZrO_2+8%CaO powder (processes P19-P20)











Sampling flowrate1dm^3/min

Conclusions

- Exposure levels (EB), determined as average number concentrations during processes to average number concentrations ”background” particles were in the range 1.02-48.14.
  - for 19 from 26 investigated processes exposure levels were EB4,
  - for 2 processes EB2,
  - and for 5 processes EB1.

- Exposure mass index, determined with gravimetric method, was in the range 0.0175-0.5246 mg/m^3.
  - for processes P1-P18 in the fume cupboard switched-off exposure mass index was in the range 0.1718-0.5246 mg/m^3,
  - for processes P18-P26 in fume cupboard switched-on in the range 0.0175-0.1043mg/m^3.

- Results of analyzing (using microscopic with EDS detector) particles taken from the air during processes with nanomaterials confirmed that in the air were suspended particles of nanopowders used in the processes, and their number was depended on the number of particles emitted in the processes with nanomaterials.

Acknowledgment

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Thank you for your attention

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