OCCUPATIONAL EXPOSURE TO AIRBORNE ULTRAFINE PARTICLES IN VARIOUS INDUSTRIAL WORKPLACES

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Research article

Abstract: Integral part of risk assessment of workplaces includes detailed characterization of airborne aerosols in case of such a considerable risk present in workplace atmosphere. Size, particle size distribution and chemical characterization of ultrafine particles in various industrial workplaces are systematically studied by set of techniques including the wide range size resolving sampling system Nano-ID® Select followed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) exploited for chemical analysis, Scanning Electron Microscopy (SEM), Fast Mobility Particle Sizing (FMPS) and Lung Deposited Surface Area Monitoring (LDSA). Results obtained from expertise on particle fractionated mass and the calculated deposition fraction in various compartments of the respiratory system using the ICRP lung deposition model suggest suitability of size-selective sampling and size-related assessment not only for engineered nanoobjects and their aggregates and agglomerates, but also for inadvertently produced emissions of present-day technologies.

Keywords: Risk assessment, airborne aerosols, nanoparticle, toxicity, size resolved sampling.

Introduction

The inhalation of aerosol particles is known to be a pathway for many substances e.g. heavy metals to reach the internal organs of the body. It is very likely that during routine operations in various industrial situations large amounts of nanoparticles containing heavy metals can be emitted into the atmosphere. The basic definitions, nomenclature and principle of conventions for workplace atmospheres are described in CEN EN 481 (CEN, 1993). Nanoparticles and their toxic impact on the environment and potential health risk is the subject of intense research. The smaller the particulates the deeper they can travel into the lung. Particles smaller than 2.5 micron will even reach the alveoli (Sahu, 2014). Smaller particles are more likely to avoid impaction by following the air mass streamlines through to the alveolar regions, where they can deposit by diffusion processes, in addition, in the nano-range it is important to get information about the size distribution and concentration. As many scientists observed increased specific toxicity of nanoparticles relative to larger particles composed of the same materials, still there is as yet no reliable information on characteristics of nano-scale aerosols containing toxic metals in the workplace atmosphere of industrial workshops. The monitoring techniques utilized for ENMs exposure monitoring can be successfully used for screening of ultrafine fractions of urban aerosols or accidentally produced emissions in working environment. In toxicological studies on nanomaterials, model organisms are typically exposed to single nanoparticle types. However it is unlikely that the workers are exposed to such a uniform particles in any realistic scenario. Further, current workers are already exposed to various mixtures of ultrafine (inadvertently) created (as opposed to engineered) nanoparticles. These particles represent a complex exposure factor, traditionally grouped into fairly gross categories by size of particles. Besides, if chemical makeup

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is considered to be analyzed as the proportion of each size grouping, it is difficult to compare the current levels of ultrafine particle exposure to the new risk being developed through the engineered nanoparticles, because the detailed size distribution information is not available for specific particles on the basis of chemical composition. Reliable size dependent sampling of fine and ultrafine aerosols for observation by scanning electron microscopy and chemical analysis plays the most important role in workplace investigation. Two studies on UFP aerosols published (Bello et al., 2010; Pfeffercorn et al., 2010) studied the occurrence and exposures to nanoparticles and carbon nanofibres during solid core drilling of two types of advanced carbon nanotube composites and airborne nanoscale particles during friction stir welding of aluminium using the same sampling and measurement techniques as used in this paper. Metal oxides aerosols undoubtedly represent a considerable risk factor in many industries, especially if thermally strained, e.g. melted (Donaldson and Poland, 2012) or strained mechanically when e.g. brushed or simply cut. Two types of processes are compared in this paper to focus on production of aerosol emissions of above mentioned operations. First, brushing of carbon composites, second, emissions from welding and flame cutting, processes during which melting and boiling metal droplets or fumes are emitted during joining or flame cutting operations. Airborne particles smaller than 0.1 μm are formed through vapour condensation, while airborne particles larger than 1 micrometer are created through liquid droplet ejection. As particles from 0.5 to 1 μm are a mixture of the two types of particles, these formation paths can strongly influence the particle chemistry with regard to particle size distribution. As the group of professional welders is much bigger than number of persons performing flame cutting and most groups of people exposed to high metal concentrations work in heavy metallurgy, the exposure scenario can be entirely different and the exposure and deposited dose of toxic metals of ultrafine particle fractions underestimated, with respect to findings in biological response of exposed working population (Roels, et al., 1999). Recently published toxicological studies on metals in airborne particles have shown a possible increased toxic effect of metals-containing oxide airborne particles, suggesting that it could be an important occupational and environmental problem. Results indicate that the nanoparticles could gain access to the brain from the airways. A significant increase in reactive oxygen species (ROS) due to metal oxides ultrafine particles exposure published in studies demonstrates necessity for our attention to be addressed to normally occurring element when present in the ultrafine and nano-form. This paper is focused on comparison of different workplace conditions related to different airborne aerosol particles formation, referring to estimation of possible risk related to inhalation of aerosols containing various elements and focused on submicron and nano-size particle emissions, and estimation of the inhaled deposition doses using the ICRP lung deposition model (ICRP, 1994) for selected elements of welding operation.

Materials and methods

Aerosol size distribution and concentration monitoring

A Fast Mobility Particle Sizer (FMPS, Model 3091, TSI Inc., St. Paul, MN) is used for particle size distribution and total number concentration measurements. Size distributions are measured from 5.6 to 560 nm (16 channels per decade with one-second scan time) (Kaminski, 2013). Measurements are performed at stationary position at working sites and background sites, if reasonable, also in outdoor reference site.

Lung deposited surface area

Aerotrak 9000 (TSI Inc., St. Paul, MN) is used for monitoring of the lung deposited surface area, measuring by means of electrical mobility of particles the total number of particles and calculating the deposition surface of tracheobronchial and alveolar region according to ICRP A and TB deposition functions (ICRP, 1994). Size range of particles being measured from 1 to 1000 nm, measurements are performed at stationary position at working sites and background sites.

Sampling sites

Samplings and measurements are preferably performed in breathing zone of working staff, where no possible, stationary sampling is arranged at reference places estimated as the most suitable sites. Samples are collected by means of a wide-range aerosol sampling system - Nano-ID® Select, (Naneum Ltd., UK), with sessions performed in different locations for working processes and background concentration levels estimation. Sampling times are generally targeted to be as long as possible to achieve sufficient sample quantities for chemical analysis, sometimes limited by the duration of working process. For the evaluation of the health risk related to UFP fraction of aerosol

DOI 10.1515/tvsbses-2015-0001

and nanoparticles, the mass concentrations of toxic elements, e.g. manganese, chromium, nickel or cadmium are measured.

Particle sample collection

The aerosol samples are collected using a wide-range sampler Nano-ID® Select (Gorbunov, 2009) in the size range from 1 nm up to 35 µm or simply using personal sampling heads (e.g. IOM) to a MCE membrane filter. In Nano-ID® Select Sampler, particles are collected simultaneously due to inertial and diffusion deposition and separated into 12 size channels, for further analysis of chemical composition by ICP-MS. Polished glass microscope slides are used as sampling media for stages No. 1 to 7 (0.25 - 35 µm), while nylon nets with mesh openings from 20 to 125 per µm are used for stages 8 to 12 (1 - 250 nm). The samples are collected at a nominal flow rate of the sampler, which is 20 litres per minute for Nano-ID® Select Sampler, 2 litres per minute for IOM (both respirable and inhalable fraction sampling). The sampling flow rates are regularly checked before and after sampling by Drycal DC-Lite flow meter (BIOS, Butler NJ). All samples (slides, nets, filters) are stored in a plastic box or Petri dishes prior to sample preparation and analysis.

Chemical analysis

The samples of all 12 stages collected by the Nano-ID® Select are analysed for metal content by ICP-MS, THERMO XSeriesII, after mineralization in microwave system (Milestone MLS 1200 Mega, Milestone Inc., CT) by concentrated nitric acid and hydrogen peroxide. Blank samples were digested and analysed in the same way as samples from the Nano-ID® Select. The LOD for the elemental analysis ranges from the level of 10 ng/l of sample.

Observation samples on PCLM and SEM/EDX

Particle analysis by scanning electron microscopy/energy dispersive x-ray spectrometry [SEM/EDX] has become the preferred method of analysis over bulk techniques, such as atomic absorption or ICP and is currently the most reliable method (ASTM 1588-08 Standard Guide, Wallace, 2008; Nesbitt et al., 1976). A scanning electron microscope (SEM, FEI QUANTA 450 FEG, FEI Company, WA) equipped with BSE, LF and ET detectors was used for observing the morphology of particles. The SEM and PCLM (phase contrast light microscopy) was used to image the objects of interest and analyse surface topography of particles. For observing electrically non-conductive particles, a low vacuum (80 Pa) is primarily used for better resolution and contrast of images.

Results and discussion

The Fig. 1 shows the particle number concentration (n/l) of selected fractions of the airborne aerosol during composite grinding, with selected period of 10 minutes of measuring the lung deposited surface area (TB region), Fig. 2 Results show that the surface area of UFP fraction exceeds the background parameters only during grinding and the emission production is relatively low.

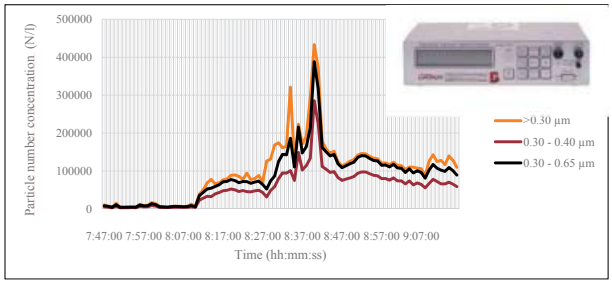


Fig. 1 Particle number concentration (n/l) of selected fractions of the airborne aerosol during composite grinding

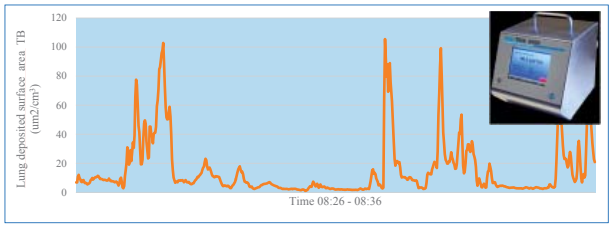
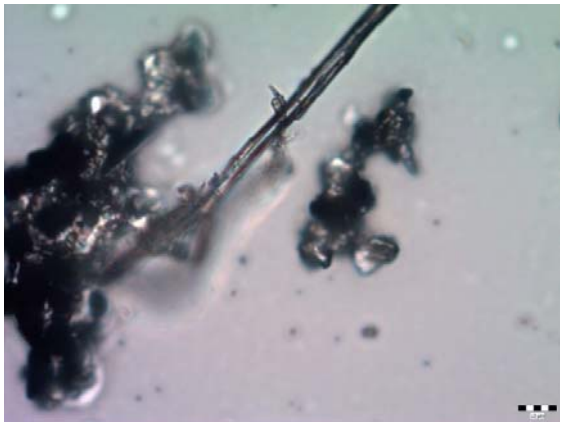


Fig. 2 Lung deposited surface area (TB region), with parameters of average, minimum and maximum surface area values (Tab. 1)

Tab. 1 Lung deposited surface area parameters, TB deposited fraction for glass/carbon composite

Units:	um^2/cc
Average:	14,867
Minimum:	1,057
Maximum:	201,991

The fine particles are often aggregated (glass and carbon particles). They are probably products of mechanical grinding of composite material layers, in a predominant micron or bigger size, as apparent in Fig. 3 and 4 by light microscopy technique, Fig. 5, 6 and 7 by SEM/EDAX technique.



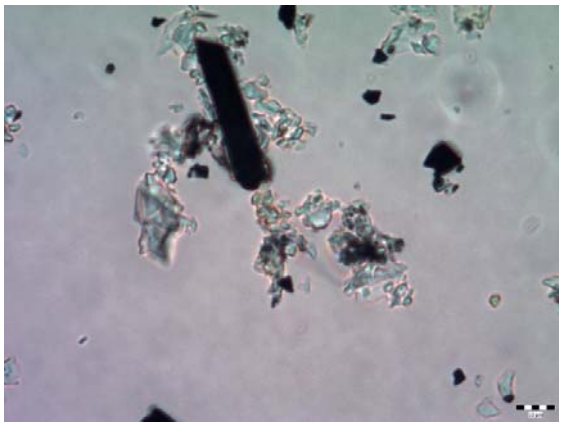
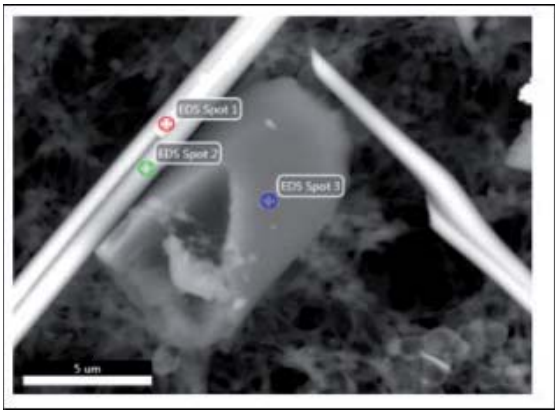
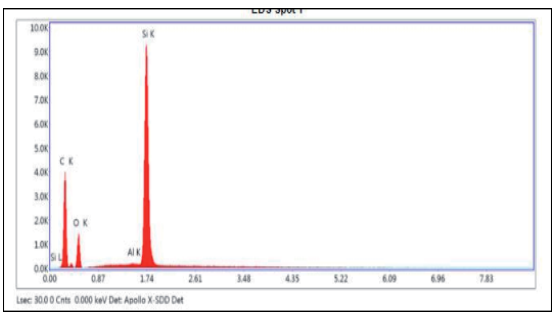


Fig. 3 and 4 Particles observed by light microscopy, magnification 400, particles generated as a products of mechanical grinding of composite material layers, in a predominant micron or bigger size (scale 10 µm)





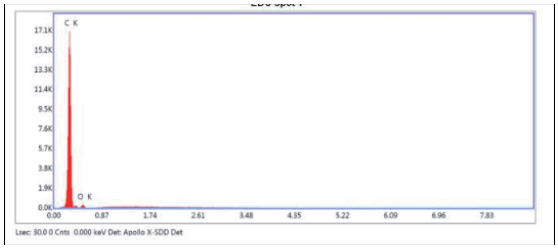
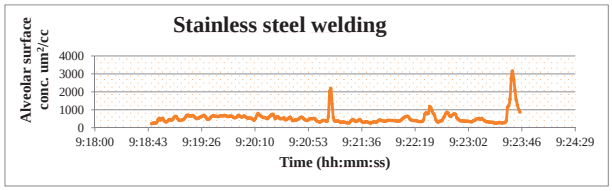


Fig. 5, 6 and 7 Particles observed by SEM in composite emissions, magnification 2100, elemental spectra refer to composite prepregs composition (scale 5 µm)

The chemical composition of particles is not complicated and clear in this case, addressed to glass and carbon ingredients in composite prepregs.

The Fig. 8 and 9 shows selected 5 minute periods of measurement of the lung deposited surface area (alveolar region) for two selected industrial operations (stainless steel welding and black steel welding by electric arc and MIG method). Relatively higher rate of emission production in MIG welding process referring probably to lower melting and boiling temperature of elements of black steel. Surprisingly, the highest surface area values during measurement were obtained during flame cutting process, quickly exceeding the upper limit of detection of the LDSA method. As the material of emissions was not collected for further analysis at this time, it remains unclear if the high surface area of UFP fraction at this process was caused only by solid particles of iron oxide, as the production of organic compounds during flame cutting can play significant role.



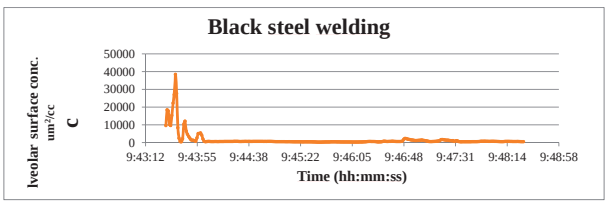


Fig. 8 and 9 Lung deposited surface area (A region), with parameters of average, minimum and maximum surface area values (see Tab. 2 for overall parameters)

Tab. 2 Lung deposited surface area parameters. A deposited fraction surface area for thermally straining processes

LDSA measurement results [µm²/cc]	Mean	Median	GM	SD	MIN	MAX
Outdoor air A	56,33	52,03	55,36	11,20	42,40	110,69
Stainless steel welding A	546,03	471,19	491,26	345,36	225,73	3160,50
Black steel welding A	1539,8	634,47	768,69	3937,89	290,31	38499,86
Flame cutting A	10242,5	1471,8	3031,93	18384,26	405,15	101355,4

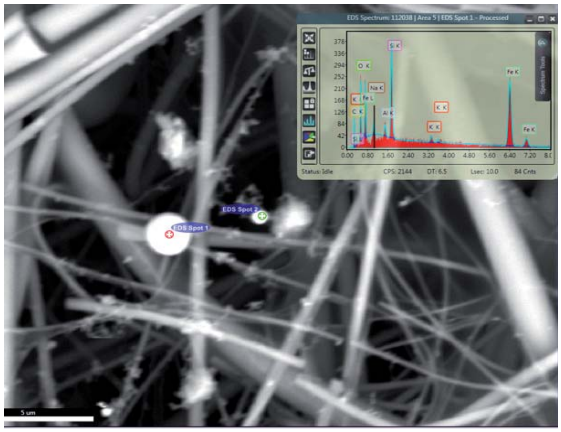
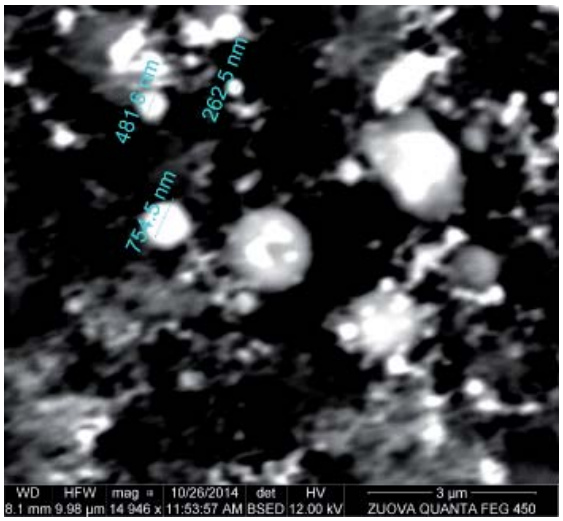
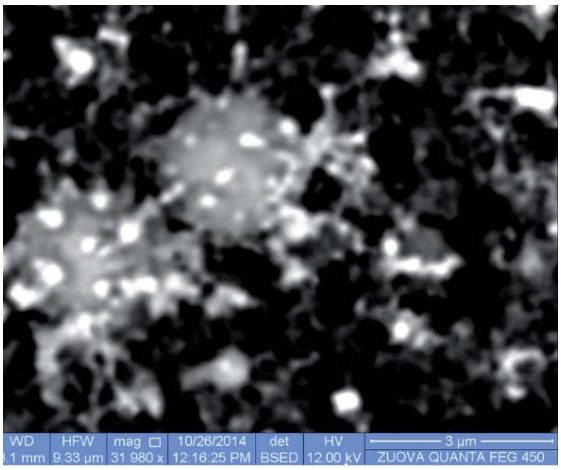


Fig. 10 shows particles of welding fumes, captured on glass fibers of the glass filter, SEM observations of particle individuals with EDX elementary spectrum in PIP





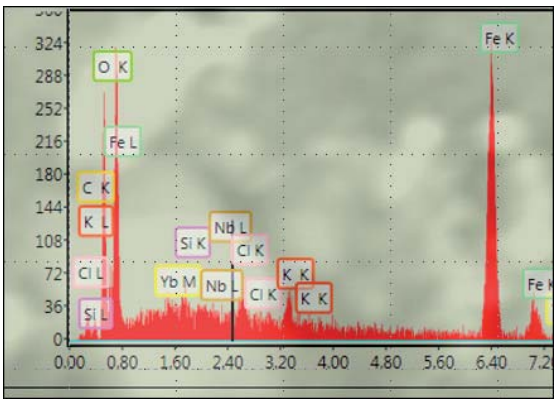


Fig. 11 - 13 shows particles of flame cutting fumes, captured on MCE filter, SEM observations of particle individuals and aggregates. Fig. 11 overall insight to selected field of the filter with geometric diameter of spherical fume particles. Fig. 12 detailed view of smaller particles assembled with a bigger particle. Fig. 13 EDX elementary spectrum in PIP

Estimation of possible risk related to inhalation of aerosols containing toxic elements using the inhaled deposition doses calculated by the ICRP lung deposition model (ICRP, 1994) for selected elements of welding operation.

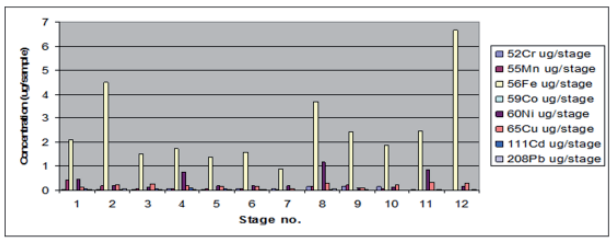


Fig. 14 shows results of chemical characterization of material collected on particular stages of NanoID sampler, selected elements for stainless steel cases welding operation

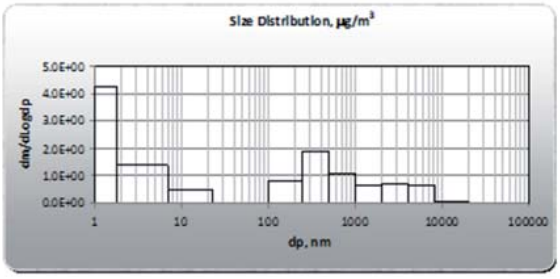
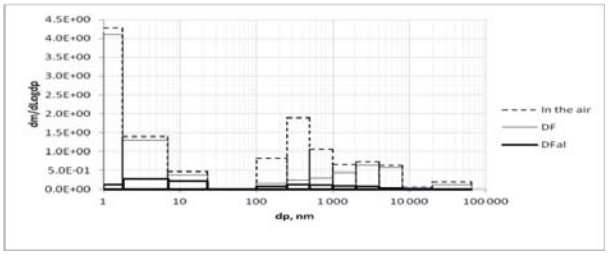


Fig. 15 Nickel mass distribution in the air (stainless steel MIG welding), significant portion of the metal can be detected in the second channel corresponding to deposition in alveolar region of the lungs, the second maximum placed in size range cca 500 nm does not represent such a risk as the probability of deposition in of this size particles is much lower



DF	Dfal	Total in air
µg/m³	µg/m³	µg/m³
2.81E+00	4.54E-01	4.09E+00

Fig. 16 Nickel deposition in the respiratory tract (Total deposition - narrow solid line) and in the alveolar region (bold solid lone), stainless steel welding. The airborne size distribution is shown as a dashed line

The physiological and medical norm for respiratory ventilation at light work rest is 9.6 m³ per shift for a standard man (Guyton, 1984). Given our results, the ICRP deposition curve, and assuming eight hours of exposure, this would correspond to cca 27 µg of nickel deposited in the respiratory track, or 4.3 µg of nickel deposited in the alveolar region. It is important to note that a considerable portion of the nickel in aerosol is concentrated in the nano-region (16 % of the mass of the dose). The biological half-time of nickel in blood can be as much as 20 - 40 days and for inner organs 27 years. (WHO, Air Quality Guidelines for Europe, 2000).

Conclusion

Aerosols formed during various operations have been studied with various techniques including the wide range sampling system Nano-ID® Select and an FMPS. Mass size distributions from the Nano-ID® Selec, number size distributions from the lung deposited surface area from Aerotrak were utilised for health risk evaluation. Comparison with results of standard hygienic risk assessment highlights the need for size resolved sampling and chemical analysis of aerosol particles of separate fractions in health risk evaluation (Jenkins, 2005, Liu, 2011). The deposition fraction in various compartments of the respiratory system calculated using the ICRP lung deposition model enables better management of risks in workplace, as in case of coarse aerosol the results confirm the fact that total airborne mass may overestimate the absorbed dose, but for very fine aerosols, a significance of size-resolved sampling and dose calculation can shed light on biological testing results significantly higher than exposure monitoring data.

Acknowledgments

Project of Czech Ministry of Environment CZ.1.02/5.1.00/10.06301; Project of the Czech Ministry of Education Nanoexpo LD14041; Project SP2015/169 funded by VŠB -Technical University of Ostrava, Faculty of Safety Engineering and Public Health Institute Ostrava.

References

ASTM 1588-08 Standard Guide for Gunshot Residue Analysis by Scanning Electron Microscopy/Energy Dispersive X-ray Spectrometry (SEM/EDS).

BELLO, D., WARDLE, B., ZHANG, J., YAMAMOTO, N., SANTEUFEMIO, C., HALLOCK, M., VIRJI, M. (2010). Characterization of exposures to nanoscale particles and fibres during solid core drilling of hybrid carbon nanotube advanced composites. *Journal of Occuppational Environment Health*, Vol. 16, pp. 434-450.

CEN. EN 481 (1993). Workplace Atmospheres - Size Fraction Definitions for Measurement of Airborne Particles Brussels, Belgium: European Committee for Standardization.

DONALDSON, K., LI, XY, MACNEE, W. (1998). Ultrafine (nanometer) particle-mediated lung injury. *Journal of Aerosol Science*, Vol.. 29, pp. 553-60.

EH40/2005 Workplace exposure limits [online]. ISBN 9780717664467 Available at: http://www.hse.gov.uk/pubns/books/eh40.htm.

GORBUNOV, B., PRIEST, N., MUIR, R., JACKSON, P., GNEWUCH, H. (2009). A Novel Size-Selective Airborne Particle Size Fractionating Instrument for Health Risk Evaluation. *Ann. Occup.Hyg*, Vol.53, pp. 225-237.

GORBUNOV, B, MUIR, R, BELLO, D, GNEWUCH, H, LECLOUX, A, LUIZI, F, DEL TEDESCO, M, GREEN, D. (2010). Exposure - Dose Relationship for Airborne Nanoparticles. *Advances in Environmental Research*. Vol. 4, pp. 213-224. ISBN 978-1-61209-251-5.

HOET, P., BRÜSKE-HOHLFELD, I., SALATA, O. (2004). Nanoparticles - known and unknown health risks. *Journal Nanobiotechnol*. Vol. 2, p. 12.

ICRP (1994). Human respiratory tract model for radiological protection. ICRP Publication 66. Ann ICRP, Vol. 24.

JENKINS, N.T., EAGAR, W. (2005). Chemical Analysis of Welding Fume Particles, Welding Research, SUPPLEMENT TO THE WELDING JOURNAL, JUNE 2005.

KAMINSKI, H, KUHLBUSCH, T, RATH, S, GÖTZ, U, SPRENGER, M, WELS, D, POLLOCZEK, J, BACHMANN, V, DZIUROWITZ, N, KIESLING, H-J, SCHWIEGELSHOHN, A., MONZ, C., DAHMANN, D, ASBACH, C. (2013) Comparability of mobility particle sizers and diffusion chargers. *Journal of Aerosol Science*. Vol. 57, pp. 156-178.

LIU S. I., HAMMOND, SK, RAPPAPORT, SM (2011). Statistical modelling to determine sources of variability in exposures to welding fumes. *Ann Occup Hyg*. Vol. 55, No. 3, pp. 305-18. DOI: 10.1093/annhyg/meq088.

PFEFFERKORN, F., BELLO, D., HADDAD, G., PARK, J., POWELL, M., MCCARTHY, J., BUNKER, K., FEHRENBACHER, A, JEON, Z., VIRJI, M., GRUETZMACHER, G., HOOVER, M. (2010). Characterization of exposures to airborne nanoscale particles during friction stir welding of aluminium. *Ann Occup Hyg*, Vol. 5, pp. 486-503.

ROELS, H., HOET, P., LISON, D. (1999). Usefulness of biomarkers of exposure to inorganic mercury, lead, or cadmium in controlling occupational and environmental risks of nephrotoxicity. *Ren Fail*; Vol. 21, pp. 251-62.

SAHU, D., KANNAN, G., VIJAYARAGHAVAN, R. (2014). Carbon black particle exhibits size dependent toxicity in human monocytes. *Journal Inflamm*. DOI: 10.1155/2014/827019.

WHO (2000) [online]. Air Quality Guidelines for Europe, 2nd edition, World Health Organization Regional Office for Europe, Copenhagen, WHO Regional Publications, European Series, No. 91, Second Edition, CD-ROM version. Available at: http://www.euro.who.int/en/health-topics/environment-and-health/air-quality/publications/pre2009/who-air-quality-guidelines-for-europe,-2nd-edition,-2000-cd-rom-version. Last accessed Apr 2014.