Synthesis of Lead and Lead Oxide Nanoparticles for Inhalation Experiments

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SYNTHESIS OF LEAD AND LEAD OXIDE NANOPARTICLES FOR INHALATION EXPERIMENTS

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INTRODUCTION

Nanoparticles (NP's) in the environment may have a significant effect on the living beings. When inhaled these particles enters to the respiratory system and may cause adverse health effects. However, the real data of the impact of NP's inhalation are still rather rare. Recently, an inhalation chamber for study of allocation of nanoparticles in organs of laboratory animals was constructed in the Institute of analytical Chemistry AS CR (Večeřa *et al.*, 2012) and a preliminary study of allocation of MnO_x nanoparticles in organs of laboratory animals in inhalation chamber was presented by Večeřa and Mikuška, 2012. For such experiments a continual generation of nanoparticles in duration of days or even weeks and in sufficiently high number concentration and appropriate particle size distribution is necessary. As far as we know, generation of Pb/PbO_x nanoparticles in the gas phase has not been presented yet. Pb nanoparticles were synthesized using a surfactant-assisted solution dispersion method by Zhao *et al.*, 2004, or by a rapid injection of aqueous solution of lead acetate into an aqueous solution of sodium borohydride (Lee *at al.*, 2009). Synthesis of lead oxide particles by wet-chemistry method was presented by e.g. Karami *et al.*, 2008. In the gas phase the lead bis(2,2,6,6,-tetramethyl-3,5-heptanedionate) (PbTHD2) precursor was used together with other precursors to metal organic chemical vapor deposition (MOCVD) of thin films of lead zirconate titanate ($Pb(ZrTi)O_3$, Jones *et al.*, 1999, Chen *at al.*, 1999), or thin films of $(PbLa)TiO_3$ (Shin et al., 1998). Therefore we decided to use this precursor for generation of nanoparticles of Pb or PbO_x by thermal decomposition and/or oxidation in a hot wall reactor. As an alternative route there was a possibility to generate the lead NP's from metallic Pb by evaporation/condensation (E/C) method.

EXPERIMENTAL

NP's were synthesized in an externally heated tube flow reactor with i. d. 25 mm and length of heated zone 1 m. Three methods of NP's generation were tested: i) thermal decomposition of lead (PbTHD2) in inert atmosphere (pyrolysis), ii) thermal decomposition of PbTHD2 in oxidizing atmosphere (cca 10 vol. % O_2, oxidation), iii) E/C of metallic Pb. Vapour pressure of PbTHD2 (P_{PbTHD2}) was calculated on the basis of experimental data of Krisyuk *et al.*, 1998, vapour pressure of metallic Pb (P_{Pb}) from data presented by Lund. Particle production was studied in dependence on reactor temperature (T_R), precursor concentration (P_{PbTHD2} or P_{Pb}), and reactor flow rate (Q_R). The particle production was monitored by scanning mobility particle sizer (SMPS, TSI model 3936L75) and samples for particle characterization were deposited onto TEM grids using nanometer aerosol sampler (NAS, TSI model 3089) and on PTFE, Zefluor, Quartz and Sterlitech Ag filters. Particle characteristics were studied by transmission/scanning electron

microscopy (TEM, *JEOL 2000FX*/SEM, *TESCAN INDUSEM*), energy dispersive spectroscopy (EDS, *Bruker Quantax*), atomic absorption spectroscopy (AAS, *Avanta Sigma*), elemental and organic carbon analyzer (ECOC, Model 4, Sunset Laboratory), X-ray diffraction (XRD, *Philips X'Pert diffractometer PW3020*) and X-ray photoelectron spectrometry (XPS, *ADES-400, VG Scientific*).

RESULTS

Particle production Generation of particles by thermal decomposition of PbTHD2 is stable at T_R in the range from 500 to 600 °C, see Fig. 1. Above 600 °C the NP's concentration decreases most probably due to deposition on the reactor wall. In oxidizing atmosphere higher precursor concentration (T_S, Q_S) was necessary than in inert one and number concentration of generated particles was still lower, cca on the level $1 \cdot 10^7$ #/cm³. NP's production is in progress at T_R up to 500 °C and increases with reactor flow rate and saturator temperature, see Fig. 2. At T_R higher than 500 °C particle production comes to a standstill. By evaporation/condensation method the particle production runs stably and with sufficiently high number concentration greater than $1.5 \cdot 10^7$ #/cm³ in the whole investigated range of T_R from 830 to 860 °C, which can be seen in Fig 3. NP's production increases with Q_R and temperature of precursor evaporation (T_R).

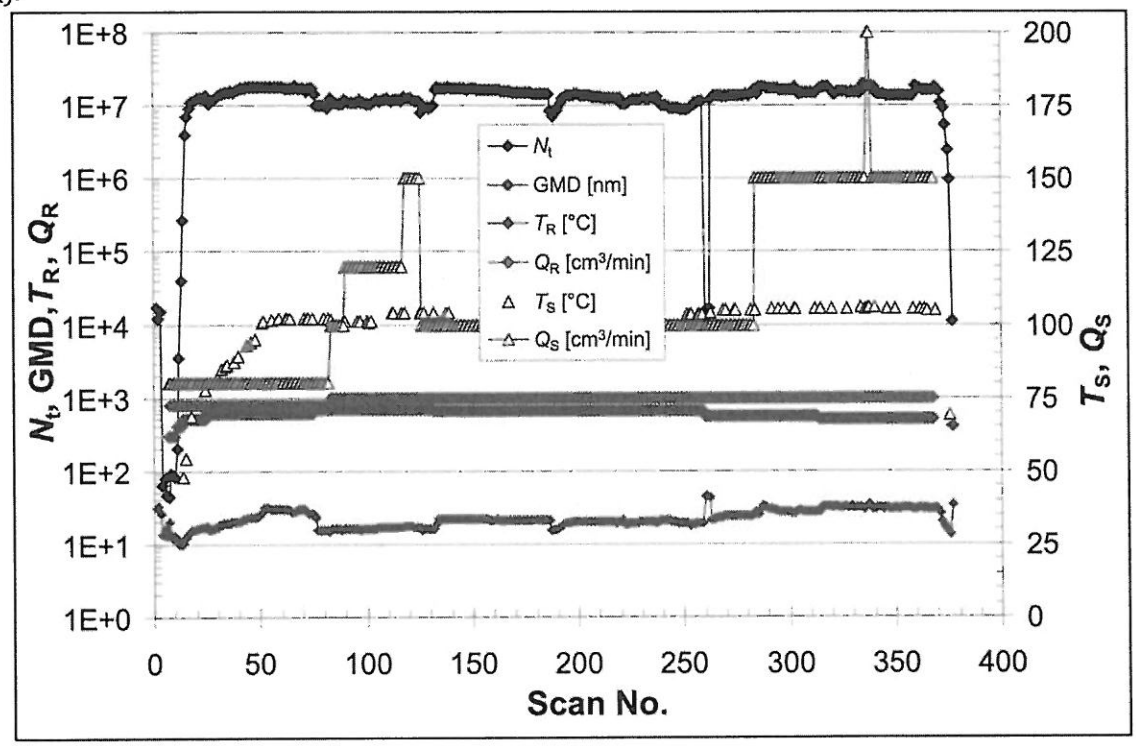

Fig. 1: Time dependence of number concentration (N_t) and geometric mean diameter (GMD) of NP's generated by pyrolysis of PbTHD2 at given experimental conditions, 1 scan = 5 minutes.

Particle characteristics PbTHD2 - Pyrolysis: Particles were typically spherical and agglomerated into clusters and chains with primary particle size between 5 and 10 nm at T_R 500 °C. At T_R 650 °C, NP's were larger and they were more polydisperse with particle size varying between 6 and 17 nm. EDS analysis proved presence of Pb and oxygen in the samples. The content of Pb determined by AAS varied between 46 and 61 mass % and ECOC analysis detected no EC and 22 mass % of OC. XRD pattern was amorphous.

PbTHD2 - Oxidation: Particles were agglomerated into chains and EDS analysis detected besides components from filter (Ag, Cl) also Pb and O. AAS showed 84 mass % of Pb and almost zero content of both EC and OC.

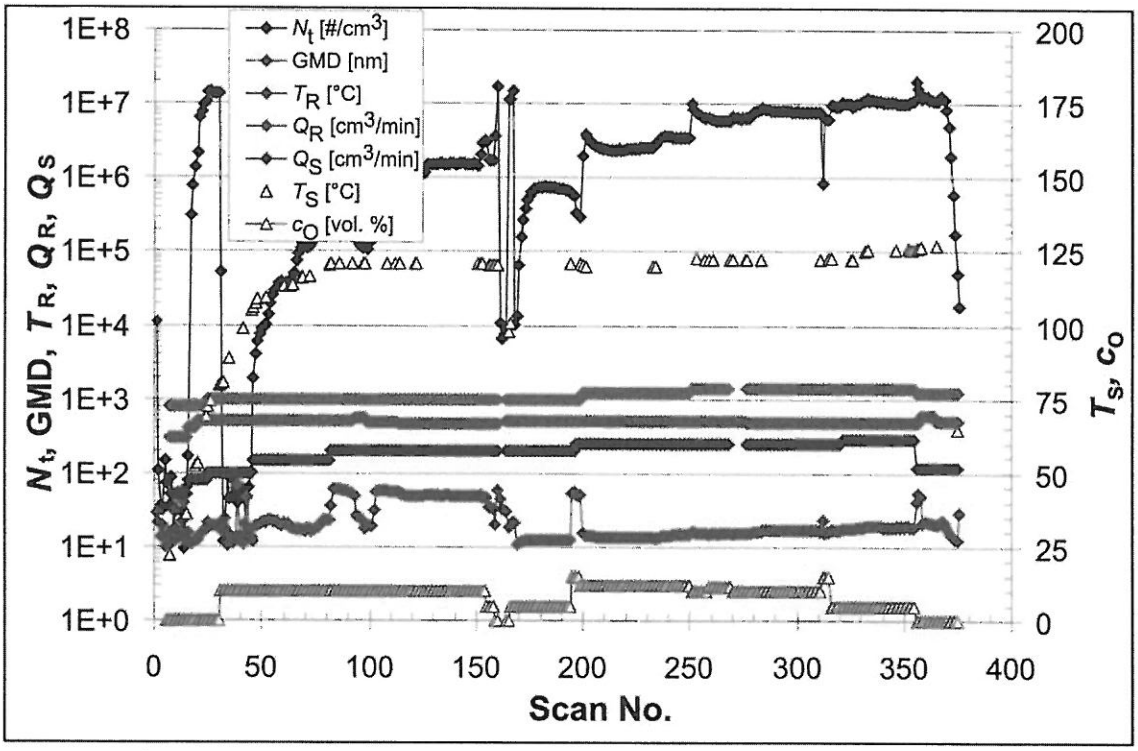

Fig. 2: Time dependence of N_t and GMD of NP's generated by oxidation of PbTHD2 at given experimental conditions, 1 scan = 5 minutes.

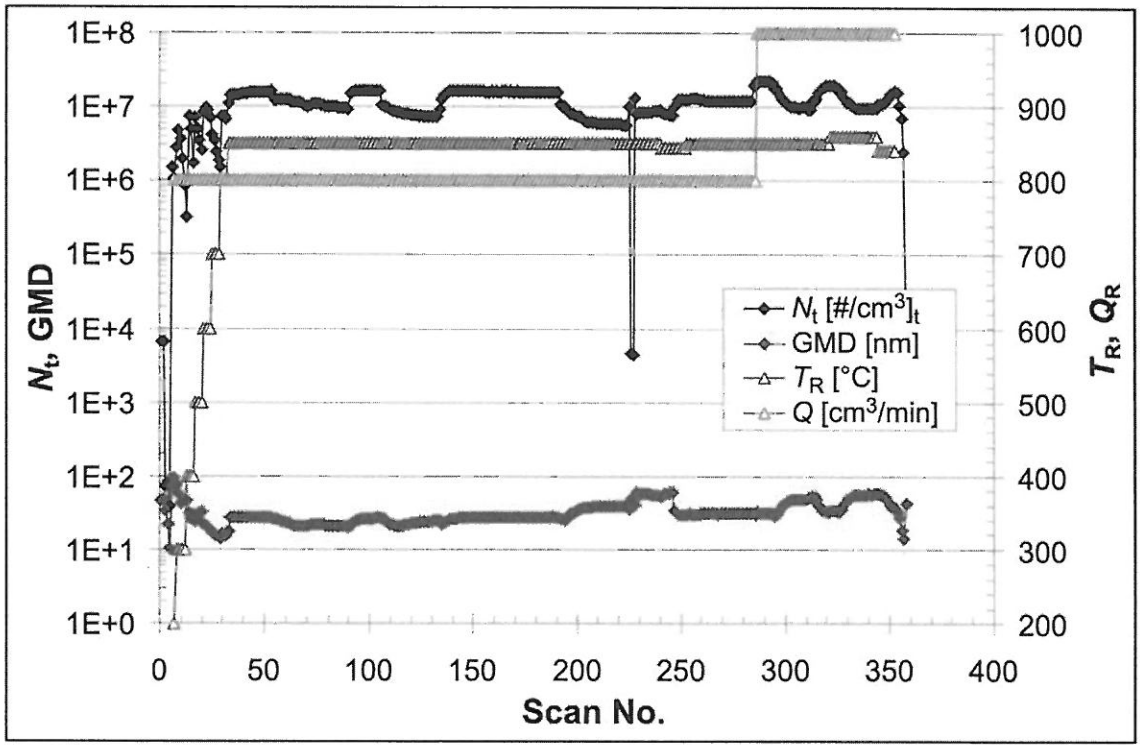

Fig. 3: Time dependence of N_t and GMD of particles generated by evaporation/condensation of Pb at given T_R, and Q_R, 1 scan = 5 minutes.

Pb – E/C: Particles were agglomerated into clusters and chains, too. The content of Pb was slightly above 80 mass % (AAS). XRD analysis (performed with the time-lag of about three weeks) showed rhomboedric diffraction pattern of hydrocerussite ($Pb_3(CO_3)_2(OH)_2$, (PDF 0131), which indicates that lead NP's are not long-term stable in the atmosphere and react with oxygen, CO_2 and air humidity. XPS analysis showed that lead in the surface layer of NP's is present in bonds Pb-O.

CONCLUSIONS

From the three tested methods of NP's generation the evaporation/condensation of metallic Pb seems to be the most suitable for long lasting inhalation experiments due to its simplicity, unambiguous mechanism of NP's formation and well defined composition. Nevertheless, NP's can change their composition, at least on the surface layer, during the time-lag between their formation and inhalation. Thermal decomposition of PbTHD2 can produce sufficiently high concentration of NP's but there is some uncertainty about their composition due to presence of OC in NP's. Oxidation of PbTHD2 produces carbon free NP's, but the number concentration of NP's is somewhat low.

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LITERATURE

Chen I.-S., Roeder J.F., Glassman T.E., Baum T.H., Liquid delivery MOCVD of Niobium-Doped $Pb(ZrTi)O_3$ Using a Novel Niobium Precursor, *Chem. Mater.*, 11, 209-212, (1999).

Jones A.C., Leedham T.J., Writh P.J., Williams D.J., Crosbie MJ., Davies H.O., Fleeting K.A.,O'Brien P., Metalorganic Chemical Vapour Deposition of Zirconia and Lead Zirconate Titanate Using a Novel Zirconium Precursor, *J. Eur. Ceram. Soc.*, 19, 1431-1434, (1999).

Karami H., Karimi M.A., Haghdar S., Sadeghi A., Mir-Ghasemi R., Mahdi-Khami S., Synthesis of lead oxide nanoparticles by sonochemical method ad its application as cathode and anode of lead-acid batteries, *Mater. Chem. Phys.* 108, 337-344, (2008).

Krisyuk V.V., Turgambaeva A.E., Igumenov I.K., Volatile Lead β-Diketonates as CVD Precursors, *Chem. Vapor Dep.* 4, 43-46, (1998).

Lee G., Choi S.-I., Lee Y.H., Park J.T., One-pot Syntheses of Metallic Nanoparticles of Tin and Lead, *Bull. Korean Chem. Soc.* 30, 1135-1138, (2009).

Lund M.W., Vapor Pressure of the Chemical Elements, PowerStream Technology http://www.powerstream.com/vapor-pressure.htm.

Snin J.C., Hong S.-K., Lee J.M., Cho H.J., Kim K.S., Hwang C.S., Kim H.J., Preparation and Characterization of (Pb, La)TiO_3 Thin Films by Solid Source Mixture Metal Organic Chemical Vapor Deposition, *J. Korean Phys. Soc.*, 32, S1529-S1531, (1998).

Večeřa, Z., Mikuška P., Moravec P., Nanočástice a jejich zdravotní rizika, *Sborník konf. 35. pracovní dny České a slovenské společnosti pro mutagenezi zevním prostředím, Brno, 9.-11. 5. 2012: 33-35.*

Večeřa, Z., Mikuška, P., První zkušenosti s inhalací nanočástic malými zvířaty, *Proc. 13th An. Conf. of the Czech Aerosol Soc., October 2012, Třeboň,* (2012).

Zhao Y., Zhang Z., Dang H., Fabrication and tribological properties of Pb nanoparticles, *J. Nanoparticle Res.* 6, 47-51, (2004).