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MOCVD IRON OXIDE NANOPARTICLE GENERATION NOT ONLY FOR FOLLOW-UP INALATION EXPOSURE EXPERIMENTS

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INTRODUCTION

Iron oxide nanoparticles (NPs) are industrially produced and commercially available and they are also frequently emitted into the environment by iron making plants. In the human body, iron is maintained at homeostatic fairly low level. However, freshly generated iron oxide NPs cause febrile and inflammatory response known as metal fume fever, but the potential in vivo consequences of inhalation of iron oxide NPs from the atmosphere has not yet been investigated. An overview of recent studies evaluating iron oxide NPs cytotoxicity, genotoxicity, developmental toxicity and neurotoxicity was presented by Valdiglesias *et al.* (2015). Toxicity of iron oxide NPs has been studied both in vitro and in vivo. Exposure chamber for the whole body inhalation experiments with small laboratory animals was constructed at the Institute of Analytical Chemistry of the CAS (Večeřa *et al.*, 2011) and some methods of NPs generation for these experiments were already tested in our laboratory (Moravec *et al.*, 2015; Moravec *et al.*, 2016). In this study we tested a method of long lasting generation of iron oxide NPs by pyrolysis and oxidation of ironIII acetylacetonate (FeAA3).

EXPERIMENTAL SETUP

NPs generation was studied in an externally heated work tube with i. d. 25 mm and the length of heated zone 1 m. Total length of the work tube made from impervious aluminous porcelain was 1.5 m. Experimental setup was described in more detail at Moravec *et al.* (2015). A stream of nitrogen carrier gas, saturated by precursor vapours in a saturator (Q_S), was fed into the reactor, where it was mixed with a stream of either nitrogen (pyrolysis) or a mixture of nitrogen and air (oxidation), see Figure 1. A stream of particle laden gas (Q_R) was diluted at the outer part of the work tube by a diluting stream (Q_{Dil}) of nitrogen (pyrolysis) or air (oxidation). The particle production was studied in dependence on precursor vapour pressure (P_{FeAA3}), reactor (T_R) and saturator temperature (T_S) and on flow rates Q_R, Q_S and Q_{Dil}. Precursor vapour pressure was controlled by saturator temperature and/or saturator flow rate and its values in the reactor were calculated on the basis of the data of Göetze *et al.* (1970) from the equation:

$$P_{FeAA3}(Pa) = 133.32 \times 10^{\left(12.98 - \frac{5943.4}{T_S(K)}\right)} \times \frac{Q_S}{Q_R}. \quad (1)$$

NPs production was monitored using SMPS (TSI model 3936L75). Samples for NPs characterization were deposited onto TEM grids, using a nanometer aerosol sampler (TSI model 3089) and on cellulose, quartz, and Sterlitech Ag filters. The particle characteristics were studied using HRTEM (*JEOL 3010*), energy dispersive spectroscopy (EDS; *INCA/Oxford* connected to *JEOL 3010*), selected area electron diffraction (SAED; *JEOL 3010*), inductively coupled plasma – optical emission spectrometry (ICP-OES; *Agilent 4200 MP-AES*), elemental and organic carbon analysis (EC/OC; Model 4, Sunset Laboratory) and X-ray diffraction (XRD; *Bruker D8 Discover diffractometer*).

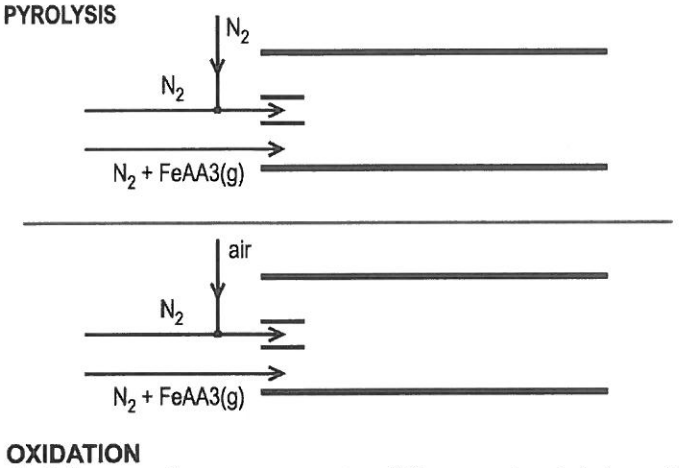

Fig. 1: Scheme of arrangements of the reactor inlet section.

RESULTS AND CONCLUSIONS

Two experimental campaigns in total duration 100 and 80 hours were performed. The NPs production was studied in the range of T_R: 500-800 °C, T_S: 155-160 °C, Q_R: 1200-1500 cm³/min, Q_S: 100-200 cm³/min, Q_{Dil}: 1600-1800 cm³/min, P_{FeAA3}: 1.1-3.5 Pa and c_O: 0 (pyrolysis) or 12-15 vol. % (oxidation). NPs production by pyrolysis and oxidation of FeAA3 is summarized in Table 1.

Tab. 1: NPs production in dependence on T_R. *Different P_{FeAA3} for individual samples.* M_t – total mass concentration, ER – emission rate.

	Pyrolysis		Oxidation			
T_R [°C]	600	700	500	600	700	800
M_t, SMPS [µg/m³]	*480-894*	3785-4739	*1765-2569*	*996-1448*	*584-2056*	1090-1183
M_t, Filters [µg/m³]	*534-668*	1021-1296	*1575-2017*	*2121-2608*	*807-2406*	1719-1744
ER, SMPS [µg/min]	*1.4-2.7*	11.4-14.2	*5.3-7.7*	*3.2-4.6*	*1.9-6.6*	3.5-3.8
ER, Filters [µg/min]	*1.6-2.0*	3.1-3.9	*4.7-6.1*	*6.8-8.3*	*2.6-7.7*	5.5-5.6

Samples of NPs generated by pyrolysis and oxidation of FeAA3 and deposited on cellulose filters are shown in Figure 2. It can be seen that by pyrolysis at T_R 500 °C mostly only evaporation and condensation of precursor occurs. At 600 and 700 °C the decomposition of precursor is much deeper, but samples contain a lot of EC. All samples prepared by oxidation of FeAA3 at T_R 500-800 °C have almost identical colour, content of Fe, very low content of OC and zero content of EC. Nevertheless, they slightly differ in morphology and crystallinity. The NPs characteristics in depence on decomposition process and T_R are summarized in Table 2.

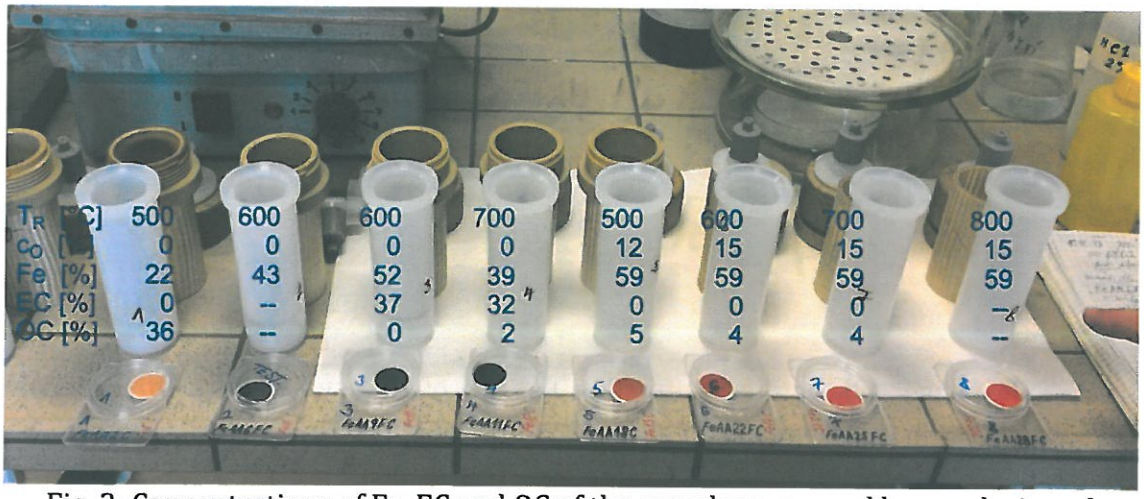

Fig. 2: Concentrations of Fe, EC and OC of the samples prepared by pyrolysis and oxidation of FeAA3 in dependence on T_R.

Tab. 2: NPs characteristics in dependence on decoposition process and T_R. TC – total carbon.

	Pyrolysis		Oxidation			
T_R [°C]	600	700	500	600	700	800
TC [mass %], EC/OC	37.2	33.7	3.5	3.7	5.4	n.a.
Fe [mass %], ICP-OES	51.9	38.8	58.7	58.7	59.2	59.3
Cryst. Phase, XRD	amorphous	amorphous	**Fe_2O_3**	**Fe_2O_3**	**Fe_2O_3**	**Fe_2O_3**
Cryst. Phase, SAED	n.a.	Fe_2O_3	**Fe_2O_3**	**Fe_2O_3**	**Fe_2O_3**	**Fe_2O_3**

Results have shown that NPs generation by oxidation of FeAA3 at T_R 600 or 700 °C is best suited for long term inhalation exposure experiments. The generation provides NPs production rate sufficiently high (up to 2600 µg/m³, i.e. 8.3 µg/min) and can be further increased by an increase of T_S or/and Q_S, and it is stable at steady state conditions for sufficiently long time. Primary particle size is typically between 10-20 nm, see Figure 3, the content of Fe varies from 58.7 to 59.3 wt. %, which corresponds with 84.0 – 84.7 wt. % of Fe_2O_3. NPs are free of EC and contain only 3.5 – 5.4 wt. % of OC. Both XRD and SAED method identified cubic Fe_2O_3 crystalline phase, Pdf 32-0469. On the other hand, NPs generation by pyrolysis does not seem to be perspective method for exposure experiments due to poorly defined characteristics of NPs. They contain a lot of EC (33.7 – 37.2 wt. %), the content of Fe varies between 22.0 and 51.9 wt. % and

because the NPs are XRD amorphous and almost SAED amorphous, it is very difficult to identify the form of Fe in NPs.

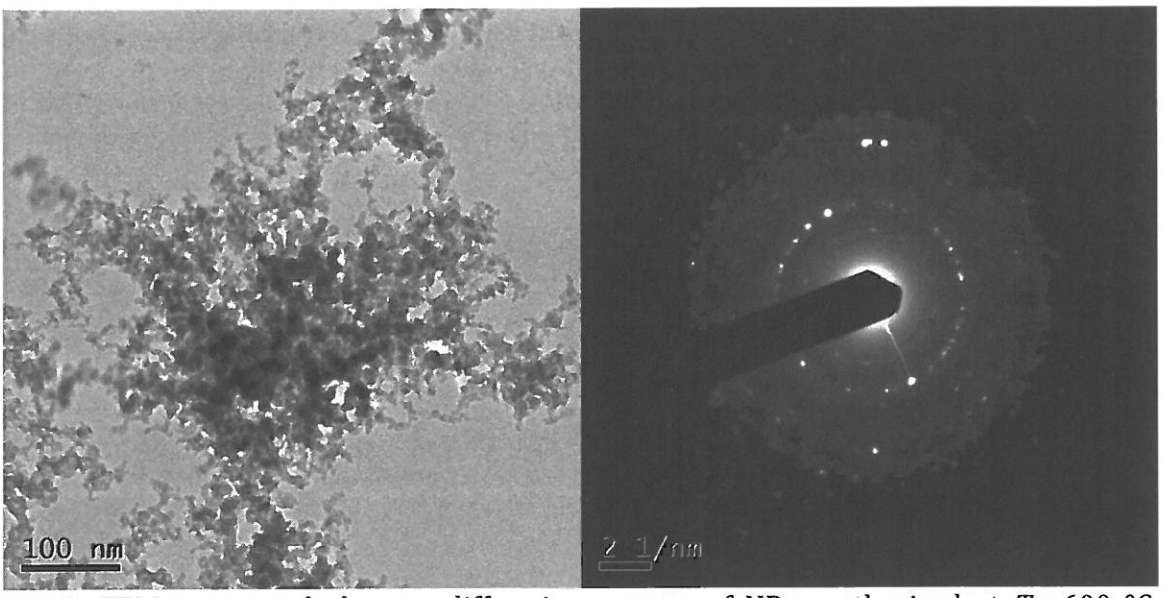

Fig. 3: TEM image and electron diffraction pattern of NPs synthesized at T_R=600 °C, Q_R=1500 cm³/min, Q_{Dil}=1700 cm³/min, P_{FeAA3}=2.4 Pa.

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