

Introduction

The greatest development of nanotechnology has been reported during the last 15 years and its positive contribution to society is undisputable. As „nanoparticles“, particles which are smaller than 100 nanometers are identified. Beside of engineered (intentionally produced) nanoparticles, it is necessary to take into consideration the fact that nanoparticles are also a part of many natural processes and they have been present in environment for a long time. Particles with microscopic dimensions originate during vegetation fires, erosion of earth, eruptions of volcanoes and other natural phenomena. In addition to intentionally produced and naturally originated nanoparticles, we can define the third area of the creation of nanoparticles which is the undesired creation of ultra-fine particles from anthropogenic activities (combustion, braking processes, friction, abrasion and degradation of painting and other materials, etc.). One potentially important source of nanoparticles are combustion processes using solid fuels, mainly combustion of coal in thermal power plants and at a local level the combustion of solid fuels in local heating facilities. The latter mechanism is supported by the existing economic situation, because people have started to return to solid fuels with increased ash material content. From the viewpoint of the environment, the combustion of coal is a significant source of pollution and the history of industrial development is connected with the contamination of environment caused by the coal combustion. Originally, the emission measurement and the monitoring of air pollution were limited to the sulphur dioxide and solid particulate matter, followed later by the measurement of nitrogen oxides and hydrocarbons, and recently by series of research studies which have dealt with emissions of other pollutants as persistent organic pollutants (e.g. PAHs, PCDD/Fs) and toxic heavy metals. An interesting category is the group of solid particles where we measure their total content in emissions we measure their total content, but in imissions, only fine fractions of particulate matter (indicated as PM10 a PM2.5) are monitored.

Experimental methods

The measurement of nanoparticles emissions from the combustion process does not represent an easy task because it is a procedure with high demands on instrumentation, and because the overall approach and performing of measurements requires both an general overview and a sense for detail. For small combustion sources these conditions are twice as valid, because complications related to the measurement of nanoparticles are combined with difficulties of the measurement of small boilers. This is caused by the character of such small particles, which involves the tendency of their mutual interaction and which comprises behavior which differs from common particulate matter. Another complication is high nanoparticles concentrations in combustion gases from the boiler in relation to the concentration which can be directly measured and the consequent necessity to use series dilution of emissions. Difficulties arise also from the complex composition of matrix (emissions), including a risk of condensation of the liquid phase and the necessity to recalculate emissions to standardized conditions (oxygen content).

The realized experiments were focused on the measurements of the size distribution of nanoparticles originated during coal briquette burning process in the underfire boiler with the nominal output 16 kW. Brown coal briquettes were used as fuel (Lausitzer Rekord Briketts, V52). During the combustion process, the boiler output varied from 16 to 20 kW, according to a phase of combustion.

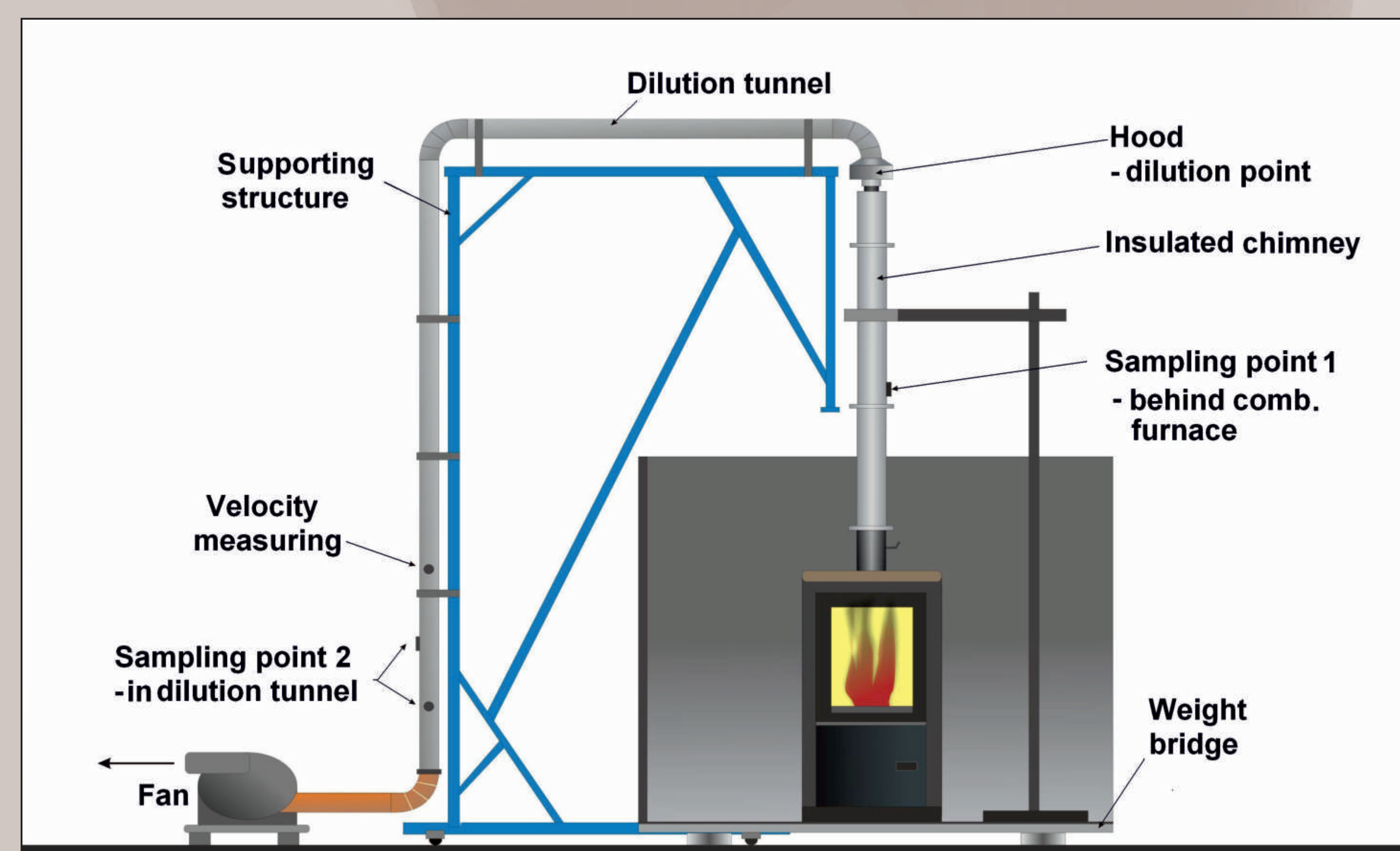


Fig. 1 Experiment scheme for the nanoparticles measurement

The frequency of the fire feeding was 3 hours. The measurement was performed with the reference oxygen content 10 %. Fig. 1 shows the overall arrangement of the experiment. The sampling place was at the end of the dilution tunnel with an internal diameter of 150 mm. Owing to the dilution, in the tunnel is a lower concentration of solid particles and the controlled output of the exhaust ventilator enables the constant gas velocity in the tunnel which was set within the range 5 to 6.5 m/s according to the required under-pressure and dilution. In the sample from the dilution tunnel the concentrations of CO, and CO₂, NO_x, SO₂, and O₂ were measured simultaneously. Because the dilution ratio of combustion gases/air in the dilution tunnel (Sampling point 2) was not sufficient, the combustion gases were further diluted by means of the diluting device (see Fig 2). The resulting dilution factor was adjusted by the flow rate of the filtered diluting air and the flow rate of gas from the dilution tunnel. The total dilution factor is then 2446. A spectrometer FPMS 3091 (TSI) was used for the measurement of nanoparticles size distribution. The characteristic data of particles are given in the form of the mode diameter (MD) as the most frequent size of a particle population and the total number concentration (TNC) as the total amount of particles over the overall measured range. Samples were taken during different combustion phases (after stoke of fuel and devolatilization, overduring the stabilized burning phase and at the end of burning). On the sampling place a cross profile was measured – off-take of a sample of combustion gases on both sides and in the middle of the tunnel. Various materials (silicon, copper) of sampling tubes had been tested previously, as well as the influence of the material of the tube on the concentration and distribution of nanoparticles.

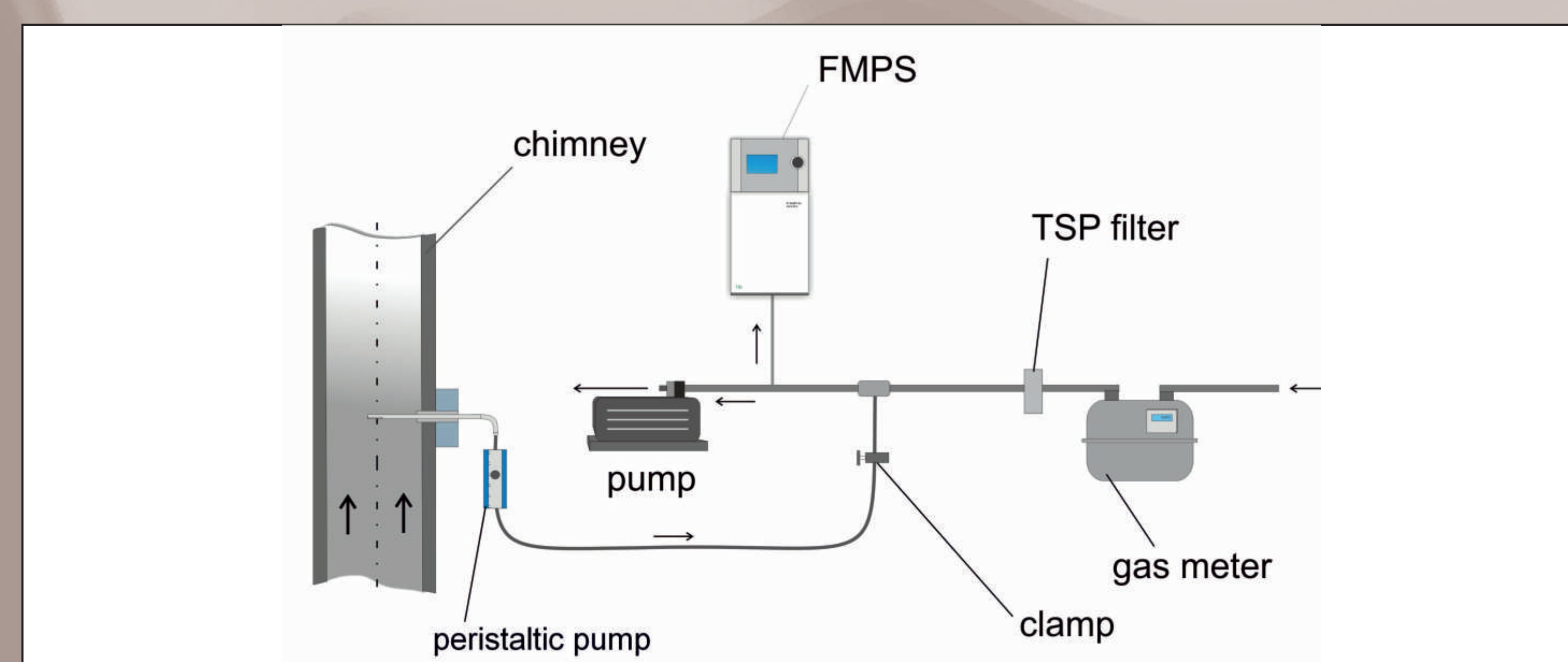


Fig. 2 Dilution equipment

Results

The first set of the measurements was performed immediately after stoke of fuel. It was observed that the concentration of nanoparticles is not constant in the cross profile in the dilution tunnel, and is the highest in the middle of the dilution tunnel. The nanoparticles concentrations were in range 35×10^6 to 63×10^6 particles per cm^3 . This phenomenon is significant for both the phase after stoke of fuel and for the stabilization phase. Immediately after stoke of fuel nanoparticles, the nanoparticles concentration was decreasing, from 56×10^6 to 31×10^6 particles per cm^3 . About 15 minutes after stoke of fuel, the nanoparticles concentration was increasing to 52×10^6 particles per cm^3 . In the particle size distribution graphs we observed two maxims, the first one around 11 nm and the second one around 40 nm (Fig. 3). The next sampling was during the stabilization burning phase. The concentration differences in the cross profile were the same as after stoke of fuel. The nanoparticles concentrations were in range 60×10^6 to 82×10^6 particles per cm^3 . In the particle size distribution graphs were two maxims, again, but with a different shape. The first maximum was in range 12 to 19 nm and the second maximum was in range 30 to 34 nm. In the stabilization phase the influence of the tube material (silicon and copper) to the nanoparticles concentration was compared. Using of silicon tubes caused the decrease of the nanoparticles concentration results, being about 80 % of the original value with the copper tube. The concentration cross profile was different at the end of burning in comparison with the previous phases (Fig. 4). The concentrations were gradually increasing from one side to the other. Another different was a change in the particle distribution graphs. In the histogram, stayed only one maximum around 34 nm remained, around 34 nm and the ultrafine particles (around 10 nm) almost disappeared. With gradual burning out of fuel, the total particle concentration was decreasing, from 24×10^6 to 20×10^6 particles per cm^3 . The maximum peak changed during the burning out phase; the first maximum (smaller particles) nearly disappeared and only small peak corresponding to the smallest particles lasted. The second maximum (from 34 to 52 nm) diminished a little, but it did not change in the shape and position. This implies the hypothesis that smaller nanoparticles originate from the volatile part of fuel, generally hydrocarbon based, and probably is composed by carbon nanoparticles, while bigger particles are linked to char combustion.

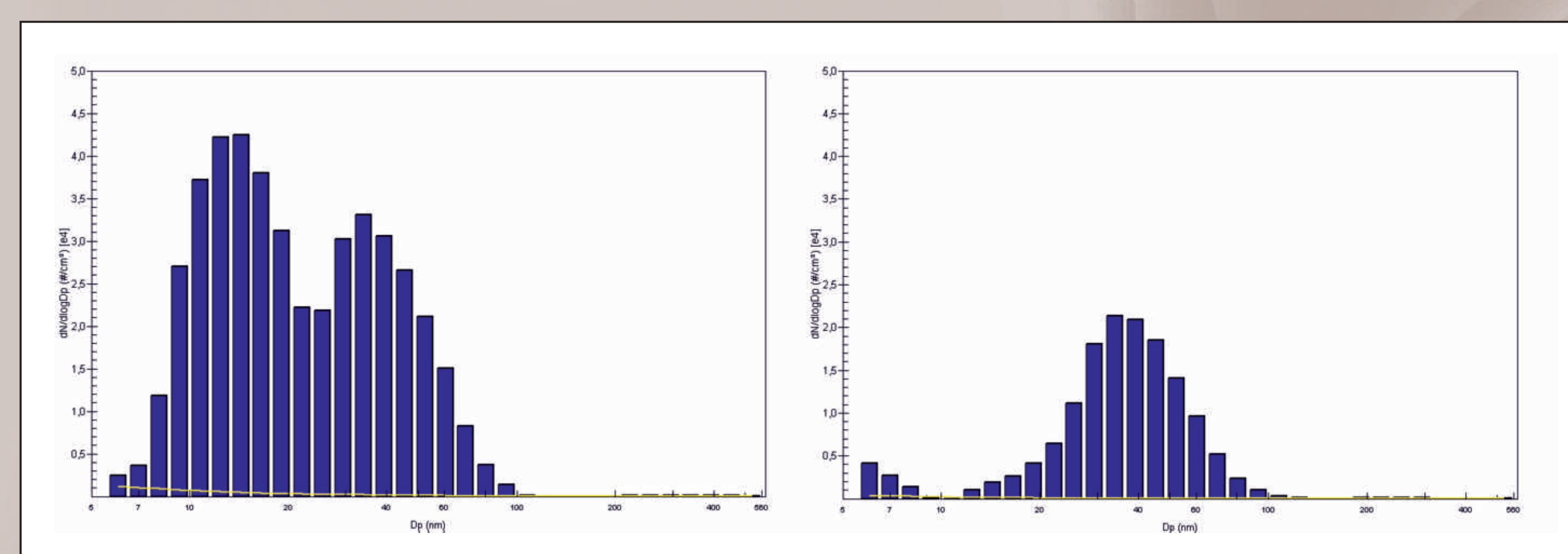


Fig. 3 Histogram of nanoparticles size distribution after stoke of fuel and during the stabilization phase

Fig. 4 Histogram of nanoparticles distribution at the end of burning

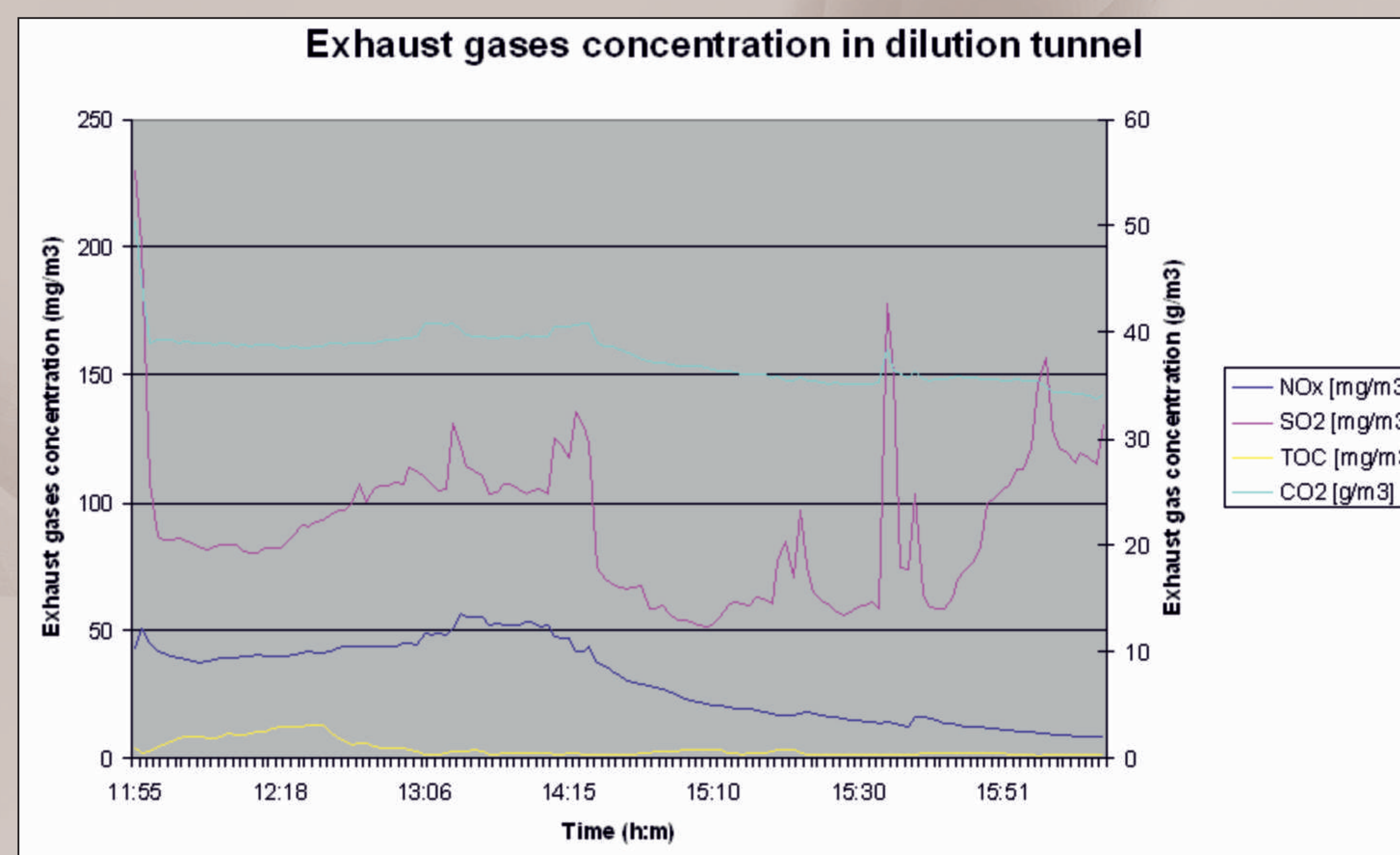


Fig. 5 Exhaust gases concentration in dilution tunnel

Sampling point	Total concentration (dN/dlog Dp) [#/cm ³]			
	pre-burning		post-burning	
	copper tube	silicon tube	copper tube	silicon tube
SP1	62×10^6	65×10^6	60×10^6	25×10^6
SP2	63×10^6	82×10^6	66×10^6	25×10^6
SP3	35×10^6	53×10^6	40×10^6	15×10^6

Tab. 1 Total particle concentration
 In the sampling point, were measured the cross profile was measured in 3 points (SP1, SP2, SP3) for each burning phase.

Sampling point	Pre-burning phase			
	CO	NO _x	SO ₂	CO ₂
	[mg/m ³]	[mg/m ³]	[mg/m ³]	[g/m ³]
SP1	0.22	0.09	0.51	0.11
SP2	0.06	0.11	0.44	0.10
SP3	0.12	0.10	0.24	0.09

Sampling point	Stabilized phase			
	CO	NO _x	SO ₂	CO ₂
	[mg/m ³]	[mg/m ³]	[mg/m ³]	[g/m ³]
SP1	0.11	0.11	0.24	0.09
SP2	0.12	0.11	0.23	0.09
SP3	0.12	0.11	0.23	0.09

Sampling point	Post-burning phase			
	CO	NO _x	SO ₂	CO ₂
	[mg/m ³]	[mg/m ³]	[mg/m ³]	[g/m ³]
SP1	0.12	0.08	0.16	0.08
SP2	0.14	0.08	0.15	0.08
SP3	0.14	0.07	0.15	0.08

Tab. 2 Exhaust gases concentrations in the sampling points for the burning phase

Discussion and Conclusion

The experiments have shown, that during the combustion of coal briquettes in the underfire boiler, were produced nanoparticles in range from 6 to 100 nm were produced. The highest nanoparticles concentration was achieved during the stabilized burning phase, where the most frequent particles were the ultrafine nanoparticles in the range from 12 to 19 nm. The lowest total particle concentration was measured immediately after stoke of fuel, approximately about 20 % less. In this phase the ultrafine particles (9 to 16 nm) were the most frequent. A noticeable change was observed at the end of burning. The total particle concentration decreased almost to a half and ultrafine particles represented in the earlier phases almost disappeared. Only one maximum (around 34 nm) stayed remained in histogram. During the fuel burn out phase of fuel, the particle concentration decreased and the maximum was found at higher values (45 and 52 nm). Beside of the main measurement, the influence of sampling tubes material was recognized; using of silicon rubber tubes caused decreasing of particle concentration approximately about 20 %.

Acknowledgements

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