Nanoparticle concentration in engine emissions

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Abstract. Nanoparticles arising during the operation of the internal combustion engine are dangerous for human health, as they easily penetrate the body through the respiratory tract. Nanoaerosol in car exhaust gases is a complex mixture of different components, often having a polydisperse size distribution of particles, most of which are from 5 to 100 nm. In Europe, since 2008, the Regulation establishes limits of the mass concentration and the counting concentration of nanoparticles in engine emissions (European Commission, Commission Regulation No. 692/2008), however, there is no such Regulation in Russian Federation, which in turn leads to the deterioration of the environmental situation and people health.

1. Introduction

In Russia, all existing regulatory documentation in the field of control of particulate matter in atmospheric air is based on mass concentration measurements. However, in the case of automobile exhausts, most of the particles are in the nanoscale range.

The main problems of the existing approach are related to:

— Rationing of maximum permissible concentrations of solid particles in atmospheric air by measuring their mass concentration leads to the fact that at very small mass concentrations, the number concentration of particles can be extremely high, since more than 90 % of the solid particles in the exhaust are in the nanometer size range.

— Particulate matter is the greatest threat to humans. In the process of breathing, they freely penetrate into the lungs, subsequently causing bronchitis and cancer, and especially small particles act as condensation nuclei and can penetrate into the blood.

— At the moment, particle number concentration in automobile exhausts is not controlled.

2. Nanoaerosol in car exhaust gases

Car exhausts in most cases contain solid particles based on carbon materials, ash and volatile components. The schematic ratio of the components in the exhaust is shown in figure 1. When enriching the combustible mixture, solid carbon particles are formed [1]. A small fraction of the oil
and fuel are not oxidized and remain as volatile compounds. The main difference between the exhaust gases of diesel and gasoline engines is that in the case of the latter, the proportion of metallic inorganic particles is much higher due to the spark when igniting the mixture.

One of the most important points is that when sampling and measuring the size and concentration of particles in the exhaust gases, the cooling of the sample is an integral part of the sampling. During cooling, there is transition of volatile materials from the gas phase, which is accompanied by the processes of nucleation, condensation and adsorption on solid particles. This process leads to distortion of the real particle size distribution.

![Figure 1. Schematic ratio of the components in the exhaust](image1)

Figure 1. Schematic ratio of the components in the exhaust

Typical engine exhaust size distribution both mass and number weightings are shown in figure 2 [2].

![Figure 2. Typical engine exhaust size distribution both mass and number weightings](image2)

Figure 2. Typical engine exhaust size distribution both mass and number weightings
The largest share of particles in total number concentration are particles with sizes less than 100 nm, while the largest share in the total mass is made by particles of large sizes. When measuring only the mass concentration, the share of nanoparticles is insignificant, and their harm may not be reflected because of the extremely small masses (table 1). However, huge number concentrations and good penetrating ability make them extremely dangerous for human health.

Table 1. Dependence of particles number concentration of the same density and optical properties in 1 mcg / m$^3$ on their diameter

| Mass concentration, μg/m$^3$ | Particle diameter | Number concentration, m$^{-3}$ |
|------------------------------|-------------------|-------------------------------|
| 1                            | 1 nm              | 1,91E+15                      |
| 1                            | 10 nm             | 1,91E+12                      |
| 1                            | 100 nm            | 1,91E+09                      |
| 1                            | 1 μm              | 1,91E+06                      |
| 1                            | 10 μm             | 1,91E+03                      |

3. Measurements of nanoparticle size distribution and number concentration

The measurement method is based on the size separation of aerosol particles as they pass through an electric field, where charged aerosol particles change their trajectory depending on their size, aerosol flow rate, electric field strength and the geometry of the classifier [3].

The relationship between differential electrical mobility and particle size for spherical particles is described by the equation (1):

$$Z = \frac{NeSc}{3\pi\mu d}$$

Where:

$N = \text{number of elementary charges per particle;}$
$e = \text{elementary charge;}$
$\mu = \text{gas dynamic viscosity;}$
$Sc = \text{slip correction factor;}$
$d = \text{particle diameter.}$

The slip correction is based on the frictional force (Stokes’ law) acting on a spherical particle of very small size moving with a low Reynolds number in a gas medium. The correction is approximated by the equation (2):

$$Sc = 1 + Kn\left[A + Bexp\left(-\frac{C}{Kn}\right)\right]$$

Where:

$A$, $B$, $C$ = constants.
Where:
\(A, B, C\) = empirical constants;
\(K_n\) = Knudsen number.

The dependence between the differential electric mobility of the particle and the parameters of the cylindrical classifier is described by the equation (3):
\[
Z = \frac{q_{sh}}{2\pi UL} \ln \left( \frac{r_2}{r_1} \right)
\]  

Where:
\(q_{sh}\) = aerosol flow rate in classifier;
\(r_1\) = outer radius of the inner cylinder of classifier;
\(r_2\) = inner radius of the outer cylinder of classifier;
\(U\) = DC voltage creating an electric field;
\(L\) = effective length between inlet and outlet of aerosol stream in classifier.

According to the described equations can be obtained (4):
\[
\frac{d}{N_e} = \frac{2S_e UL}{3\mu q_{sh} \ln \left( \frac{r_2}{r_1} \right)}
\]

This equation allows to define the size of the particle leaving the electrostatic field of the classifier if the number of elementary charges on the particle is known.

### 4. Regulations for particle number concentration and size measurements in automobile exhaust

Based on the above, it becomes clear that it is imperative to control particulate matter in automobile exhausts. To date, the Russian Federation has a Technical Regulation of the Customs Union "On the safety of wheeled vehicles" TR CU 018/2011, in accordance with which only 2 emission parameters are regulated: level of CO and CH and opacity [4]. These parameters can not fully characterize the harmfulness of automobile exhausts, since they absolutely do not take into account number concentration and size of solid particles.

Commission Regulation No. 6692/2008 was applied in the European Union in 2008 [5], according to which, in addition to gas levels, mass and number concentration of particles in automobile exhausts is monitored (table 2).

Table 2. Euro 5 Emission Limits

| Cat. | Class | Reference mass (RM) (kg) | Mass of carbon monoxide (CO) | Mass of total hydrocarbons (THC) | Mass of nonmethane hydrocarbons (NMHC) | Mass of oxides of nitrogen (NOx) | Combined mass of hydrocarbons and oxides of nitrogen (THC + NOx) | Mass of particulate matter (PM) | Number of particles (P) |
|------|-------|--------------------------|-----------------------------|---------------------------------|--------------------------------------|-------------------------------|-------------------------------------------------|---------------------------|-----------------------|
|      |       |                          | L_1 (mg/km)                 | L_2 (mg/km)                    | L_3 (mg/km)                         | L_4 (mg/km)                  | L_5 + L_6 (mg/km)                     | L_7 (mg/km)               | L_8 (#/km)            |
| M    | All   | 1000                     | 1000                        | 1000                            | 1000                                | 1000                         | 1000                              | 1000                      | 1000                  |
| I    | RM ≤ 1 | 1000                     | 1000                        | 1000                            | 1000                                | 1000                         | 1000                              | 1000                      | 1000                  |
| N    | II    | RM ≤ 1.3                 | 1810                        | 1810                            | 1810                                | 1810                         | 1810                              | 1810                      | 1810                  |
| III  | RM ≤ 1 | 2270                     | 2270                        | 2270                            | 2270                                | 2270                         | 2270                              | 2270                      | 2270                  |
| N    | All   | 2270                     | 2270                        | 2270                            | 2270                                | 2270                         | 2270                              | 2270                      | 2270                  |

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Key: PI = Positive Ignition, CI = Compression Ignition

(1) A revised measurement procedure shall be introduced before the application of the 4.5 mg/km limit value.

(2) A new measurement procedure shall be introduced before the application of the limit value.

(3) Positive ignition particulate mass standards shall apply only to vehicles with direct injection engines.

Taking into account that in the territory of the Russian Federation there is State Primary Standard for the units of disperse parameters of aerosols, suspensions, and powder materials GET 163 which provides metrological assurance for parameters of solid particles in automobile exhausts, it will be appropriate to update the list of parameters regulated in accordance with TR CU 018/2011.

5. References.
[1] Kittelson D B 1998 Engines and nanoparticles: a review. J. Aerosol Sci. 29 (5/6) 575-588
[2] Kittelson D B 2000 Nanoparticle Emissions from Internal Combustion Engines. The Royal Society Discussion Meeting Ultra Fine Particles in the Atmosphere
[3] ГОСТ Р 8.775-2011 "ГСИ. Дисперсный состав газовых сред. Определение размеров наночастиц по методу дифференциальной электрической подвижности аэрозольных частиц"
[4] ТР ТС 018/2011 Технический регламент Таможенного союза "О безопасности колесных транспортных средств"
[5] Commission Regulation (EC) No 692/2008. Official Journal of the European Union