

Research of the qualitative composition of ice exhaust particulates, produced by the cars with mileage over 100 000 kilometers

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Abstract. This work presents the results of investigation of particulate emissions, produced by the cars with mileage over 100 000 km and actually run under Vladivostok city conditions. The study has been conducted by means of scanning electron microscopy with energy-disperse analysis. It was shown that soot particles, natural (silicate) and metal-containing (Fe, Pb, Cr, Sr) formations predominate among the studied particles.

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Introduction

It is considered that the contribution of vehicle emissions in the environmental pollution of the modern city reaches 75-90% [1; 2]. The atmosphere is being polluted by gaseous and solid components of vehicles emissions; in terms of human health, the most harmful effects are produced by solid and nano microparticles of soot, ozone, carbon monoxide, sulfur oxides, phenols, formaldehyde, metals, and, as it have been shown recently, carbon nanomaterials [3; 4]. Nowadays there are several methods of gaseous substances investigation: gas chromatography, chemoluminescence, infrared dispersion-free analysis and some other methods.

However, a study of "hard" components of emission has relatively short history; it has appeared only in 90th years of the last century in the regulations of some countries. The exhaust particulate matter (PM) has not been evaluated before, and we used the concept of "smoking at the exhaust". The principle of measurement of solid particles in the exhaust gas was laid in the creation of the first opacimeters, operating on the principle of gas filtration.

Present work studies the qualitative composition of the ICE particulate emissions using scanning electron microscopy with elemental analysis.

Investigation methods

To conduct the experiments according to the Sectoral Normal Classification OH 025270-66 [5] and Economic Commission for Europe Classification, we have chosen the most significant in terms of ecology (emissions) and widely represented in the urban environment types of cars. The cars (N = 10, production years from 1993 to 2004) with an

engine capacity from 1.3 to 3.5 liters and mileage over 100 000 km were presented by the authors and their colleagues in a representative sample. Before measurements, the cars actually running in Vladivostok were fueled with gasoline or diesel fuel at a gas station of the same oil company. Motor oils selection is based on the type of fuel and mileage.

The object of investigation is a suspension of exhaust gas (SEG) obtained by the previously described method [6]. Substantial analysis of sediment was performed by the scanning electron microscope Hitachi S-3400N with energy dispersive spectrometry Q150T. A sample spattering for electron microscope was produced by platinum.

Results

Examination by electron microscopy with energy dispersive analysis showed that a vast number of exhaust particulates are carbon black soot, silicates (apparently sucked from the ambient air), and metal compounds.

Soot particles

Soot particles component predominates by weight in the exhaust of both diesel and gasoline engines. There are two forms of soot most often mentioned in the exhaust samples: free lying micro-dispersed mud (Fig. 1) and soot, adsorbed on larger particles (minerals and metal-containing) (Fig. 3).

Soot microparticles (micro-dispersed mud) extracted from the suspension of exhaust gases of 2.0-liter gasoline engine vehicle produced in 1998 year. Lighter particles are aluminosilicate. Scanning electron microscopy in secondary electrons. Measuring section is 50 microns.

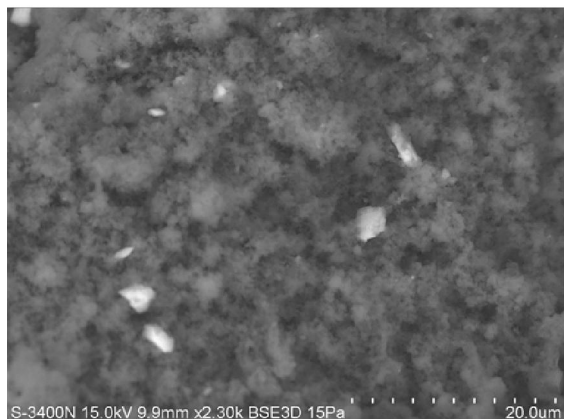
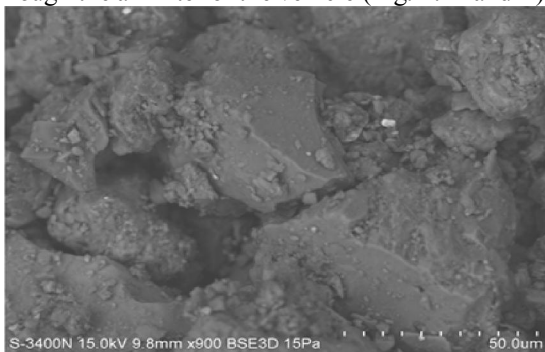


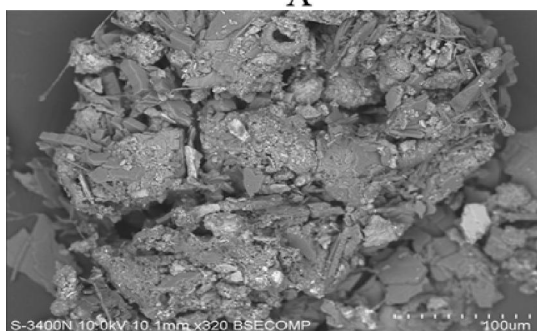
Fig. 1. Soot microparticles (micro-dispersed mud). Magnification ×900.

Mineral particles

Mineral (silicate and aluminosilicate) particles enter the exhaust gas from air penetrating through the air filter of the vehicle (Fig. 2: A and B).



A



B

Fig. 2. Aluminosilicate particles from exhaust gas suspension of the 2.0-liter gasoline engine vehicle produced in 1998 year

(A). Magnification ×900. B) Aluminosilicate particles from exhaust gas suspension of the 3.1-liter diesel engine vehicle produced in 1993 year. Magnification ×320.

Scanning electron microscopy in secondary electrons. Measuring section is 50 microns for A) and 100 microns for B).

Scanning electron microscopy in the secondary electrons, the measuring section of 10 microns is shown on Fig. 3.

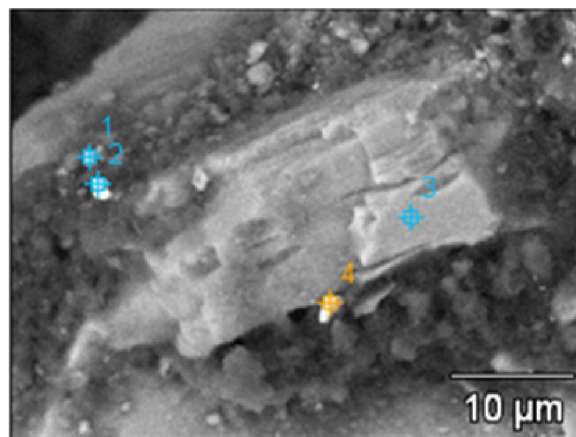


Fig. 3. Large aluminosilicate particle from the exhaust gas suspension of the 3.1-liter diesel engine vehicle produced in 1993 year.

Element	Spectrum 1	Spectrum 2	Spectrum 3	Spectrum 4
	Atomic %	Atomic %	Atomic %	Atomic %
C	50.01	37.17	40.81	51.62
O	42.37	45.84	40.26	32.39
Na			0.93	0.74
Mg	0.25	0.55	2.55	0.72
Al	0.47	0.59	2.26	0.99
Si		1.32	8.13	3.36
S	3.14			0.40
K	0.14		0.13	
Ca	0.25	0.16	1.91	0.50
Fe	0.39	14.37		9.19
Ba				0.10
Ti			0.30	
Sr	2.97		2.71	
Totals	100.00	100.00	100.00	100.00

As the Fig. 3 illustrates, mineral particles take on themselves both soot and metal particles, including toxic ones (Sr).

Sometimes one can find rather exotic materials among the components, such as diatomic shells (see fig. 4).

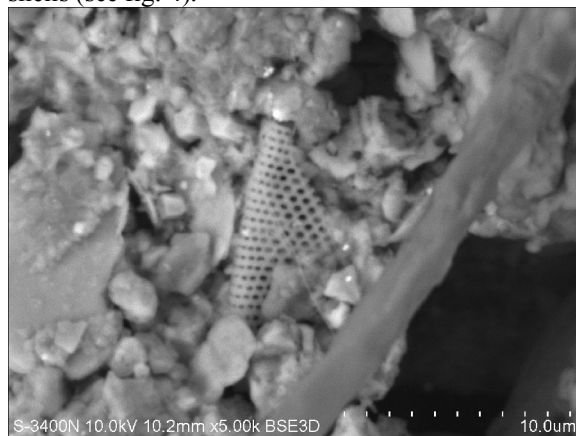
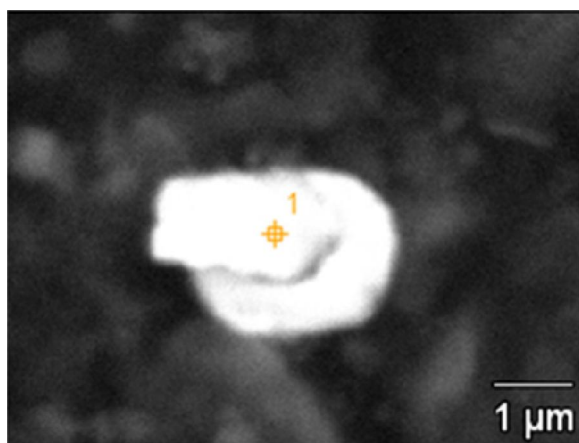


Fig. 4. Diatomic algae shell

"Grate" in the middle of the exhaust gas suspension of 3.1-liter diesel engine vehicle produced in 1993 year. Scanning electron microscopy in secondary electrons. Measuring section is 10 microns. Magnification $\times 5000$.

Metal compounds particles

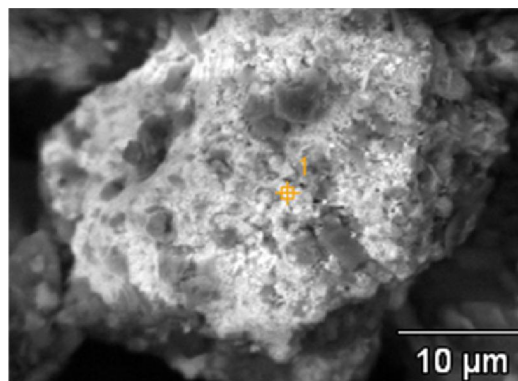
Based on their sizes metal-containing particles can be divided into two large groups: micro group (under 100 microns) and macro group (from 100 microns to 2000 microns). Microparticles are the products of combustion of fuel and motor oil (Fe (see Fig. 5), Pb (see Fig. 6.), Cr, Zn, Sr), while macro-particulates are the elements of the exhaust system (mainly Fe-containing).



	Spectrum 1
Element	Atomic %
C	38.67
O	3.75
Na	0.53
Al	1.42
Si	0.70
Ca	0.39
Fe	54.55
Totals	100.00

Fig. 5. Fuel and motor oil combustion products (Fe)

Fe-containing microparticle from the exhaust gas suspension of 3.1-litres diesel vehicle produced in 1998 year. Scanning electron microscopy in secondary electrons. Measuring section is 1 micron.



	Spectrum 1
Element	Atomic %
C	28.01
O	21.56
Mg	0.55
Al	3.03
Si	3.25
P	3.74
Cl	15.27
Ca	2.19
Fe	0.87
Pb	21.53
Totals	100.00

Fig. 6. Fuel and motor oil combustion products (Pb)

Pb-containing microparticle from the exhaust gas suspension of 2.0-liters gasoline vehicle produced in 1999 year. Scanning electron microscopy in secondary electrons. Measuring section is 10 micron.

Studying of the exhaust gas suspension by the electron microscope helps us to find metal particulates (according to the results of energy dispersive analysis), mostly it is Fe (Fig. 7).

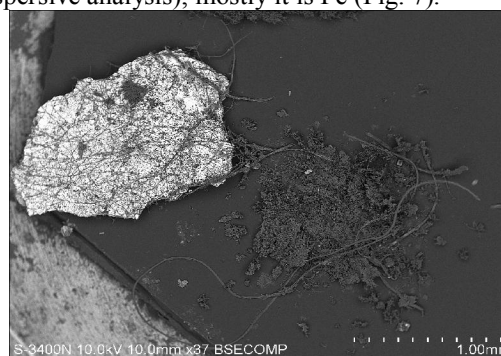


Fig. 7. Fuel and motor oil combustion products (Fe)

Fe-containing macro-particle (light color from the left side) from the exhaust gas suspension of 2.0-liters gasoline vehicle produced in 1998 year. Scanning electron microscopy in secondary electrons. Measuring section is 1000 micron. Magnification $\times 37$.

Conclusion

Soot emissions prevailing on mass fraction are especially noteworthy among the exhaust particulate matter. As we see, car soot emitted into the environment with transport exhaust gases, has difficult component system containing not only carbon but also a large number of metals, including toxic (Cr, Sr). No wonder that previously it has been already shown that soot particles are capable to increase the risk of cancer and result in premature mortality, causing the complications of respiratory and cardiovascular diseases [7; 8].

The other toxic exhaust components are metal particles [9; 10]. Researches count metal particles and their compounds as the most toxic elements. Thus, medicine faced a new nosological entity – metallic alergyosis [11; 12]. We shall note the unprecedented growth of allergic and bronchopulmonary diseases in cities that cannot but correlate with the general atmospheric pollution, caused by cars in most cases. Mineral particles per se are the components of the natural background and do not have any health hazards. However, it is worth noting that while they "fly" through the engine, they adsorb on their surface a large number of toxic components (soot and metals).

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