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Influence of after-treatment systems on NO_2 emissions in diesel engines

The article discusses the results of bench tests that monitor the increase of NO_2 emissions in the heavy duty vehicles engines' exhausts as a result of the use of particulate matter filters. The use of passive particulate matter filters inevitably leads to an increase in NO_2 emissions from the engine. The particularly intensive increase in the emissions occurs when SCR reactors are shut off, which is still a common practice among drivers. NO_2 concentrations in exhaust gases of DPF-equipped engines reach concentration dangerous for human health and life. The causes of the NO_2 formation in the vehicles' exhaust systems, the harmfulness of this chemical, and the results of NO_2 measurements in different tests, are discussed. In addition, the effect of the presence of this compound on the accuracy of opacity measurement is discussed.

Key words: *emissions measurements, after-treatment system, particulate filters*

1. Introduction

The systematic decrease in pollutants emissions limits in Heavy Duty vehicles engines has led to significant expansion of the exhaust after-treatment systems in these type of engines. A number of systems designed to reduce the selected exhausts component may be included in the exhaust system of an engine compliant with the Euro VI limit. The most popular are the Diesel Oxidation Catalyst (DOC), which reduces CO and THC concentrations in the exhaust gases, Selective Catalyst Reactors (SCRs) that reduce NO_x emissions in the exhaust gas by the chemical reaction that occurs on the catalytic converter between NO_x and the urea solution fed from the outside to the converter. SCRs type reactors are equipped with Ammonia Slip Catalyst (ASC), which is a system for reducing excess ammonia produced in SCR.

Another exhaust after-treatment system is the Diesel Particulate Filters (DPF) that reduce the particulate number emissions and the mass of solid particles contained in the exhaust gases. Heavy Duty vehicles usually are equipped with kind of them as so-called, passive filters. Passive particulate filters are coated with a catalyst layer to facilitate the oxidation of the soot particles contained in the exhaust gases. Typically, in such processes, the reaction (1) between the soot particles and the NO_2 contained in the exhaust gases, is used:

$$C + 2NO_2 \rightarrow CO_2 + 2NO \quad (1)$$

For this reason, the proper amount of NO_2 is needed for the proper functioning of the DPF filter. Nitrogen oxides (NO_x) contained in the raw exhaust gases coming from outlet port of cylinder head consist mainly of nitrogen oxide (NO). This is an unstable compound formed at high temperatures during the combustion process in the cylinder. At ambient temperature NO is gradually converted to NO_2, which is a form of nitrogen oxides that is more natural to lower temperatures. The exhausts, having left the engine outlet port are immediately cooled which favours conversion of NO into NO_2, especially in the presence of ozone. We may notice that in the engine without exhaust after-treatment system, the predominant majority of the emitted nitrogen oxides leaves the engine exhaust pipe as NO and the share of NO_2 in the NO_x emitted is only a few percent.

For engines equipped with DPF, the systems need more NO_2 for their operation. This makes it easier by the catalyst layer on PDF core converting part of NO formed during fuel combustion in the cylinder into NO_2. The share of NO_2's created that way in the NO_x amounts to tens of percent. For this reason, NO_x leaving the DPF-equipped engine's exhaust system, owing to the high NO_2 content, may be completely unlike the NO_x composition measured before DPF. On the other hand, in the shorter scale of time and in the NO_x concentrations measured in street conditions, a DPF-equipped engine and one not equipped with this system will emit nitrogen oxides with completely different toxic properties. When comparing NO and NO_2, the properties of the latter one should be considered more toxic. Especially unpleasant are its irritating properties and the ability to create aerosols with droplets of condensed moisture in the cooled exhaust gases. So far, because of low NO_2 content in NO_x, no significance attention has been paid to the toxic properties of this gas, considering the NO toxic properties as representative for NO_x.

2. NO_2 properties

NO contained in the exhaust gases is generated in the combustion chamber of the engine, where the high temperature during fuel combustion and the oxygen excess contribute to its formation. As a result of the decrease of the temperature of the exhaust gases in the expansion stroke, there occur conditions for oxidation of the part of NO contained in the exhaust gas, to the NO_2 form according to the reaction (2). However, this reaction is slow enough, compared to the duration of the expansion and exhaust stroke, that only a small fraction of NO may be oxidized at this time.

$$2\,NO + O_2 \rightarrow 2\,NO_2 \quad (2)$$

At ambient temperature NO_2 it is a brown, strongly toxic gas with a sharp odour reminiscent of chlorine gas.

Nitrogen dioxide can irritate the lungs and cause less resistance to respiratory infections such as influenza. Prolonged or frequent exposure to concentrations that are significantly higher than normal in the air can cause an increased incidence of acute respiratory illness in children. It contributes to reducing the immune system and increasing the risk of lung infections, as well as exacerbating asthmatic symptoms and conjunctivitis. Air pollution from vehicle

engines contributes to serious health problems such as chronic respiratory diseases, bronchial asthma, allergies, cancer, and even an increased mortality rate.

Road transport, power industry and local heating systems are the main sources of nitrogen dioxide emissions. In large urban areas, characterized by heavy traffic and the absence of power industry, the predominant importance for NO_2 emissions has vehicle exhaust gases; therefore, the highest pollution most often occurs in the vicinity of busy roads.

Gaseous NO_2 diffuses into the epithelial lining fluid (ELF) of the respiratory epithelium and dissolves, and chemically reacts with antioxidant and lipid molecules in the ELF; NO_2's health effects are caused by the reaction products or their metabolites, which are reactive nitrogen species and reactive oxygen species that can drive bronchoconstriction, inflammation, reduced immune response, and may have effects on the heart.

Acute harm due to NO_2 exposure is only likely to arise in occupational settings. Direct exposure to the skin can cause irritations and burns. Only very high concentrations of the gaseous form cause immediate distress: 10–20 ppm can cause mild irritation of the nose and throat, 25–50 ppm can cause edema leading to bronchitis or pneumonia, and levels above 100 ppm can cause death due to asphyxiation from fluid in the lungs. There are often no symptoms at the time of exposure other than transient cough, fatigue or nausea, but over hours inflammation in the lungs causes edema. Chronic exposure to NO_2 can cause respiratory effects including airway inflammation in healthy people and increased respiratory symptoms in people with asthma.

NO_2 is classified as an extremely hazardous substance in the United States as defined in Section 302 of the U.S. Emergency Planning and Community Right-to-Know Act (42 U.S.C. 11002), and it is subject to strict reporting requirements by facilities which produce, store, or use it in significant quantities[2]. The U.S. EPA has set safety levels for environmental exposure to NO_2 at 0.1 ppm, averaged over one hour, and 0.053 ppm, averaged annually.

However, NO_2 concentrations in exhaust gas of vehicles and near roadways are appreciably higher than the ones measured in considerable distance from the road. In fact, in-vehicle concentrations can be 2–3 times higher than measured at nearby area-wide monitors. Near-roadway (within about 50 m) concentrations of NO_2 have been measured to be approximately 30 to 100% higher than concentrations away from roadways. Individuals who spend time on or near major roadways can experience short-term NO_2 exposures considerably higher than measured by the current network. Approximately 16% of U.S. housing units are located within 91 m of a major highway, railroad, or airport (approximately 48 million people). Studies show a connection between breathing elevated short-term NO_2 concentrations, and increased visits to emergency departments and hospital admissions for respiratory issues, especially asthma.

3. Testing of engines

3.1. NO_2 emissions

In order to determine the NO_2 emissions from the average diesel engine, the engine was tested on engine test bench. Basic technical data of the tested engine are shown in Table 1.

Table 1. Technical data of tested engine

Number of cylinders	6 in-line
Displacement [dm^3]	12,8
Rated power	380 kW
Maximum torque	2300Nm
Fuel injection system	Common Rail
Exhaust after-treatment system	SCR, DOC, DPF, ASC
Fuel type	Diesel oil
Emissions limit	Euro VI
Date of engine manufacture	2014

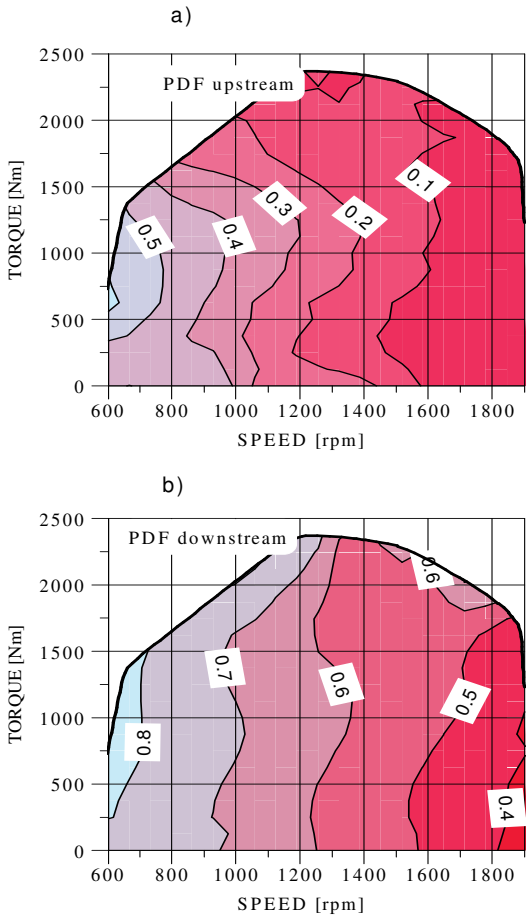

Fig.1. NO_2/NO_x ratio in tested engine

The tests were carried out on a typical test bench equipped and designed for the engine type-approval tests of the pollutants emissions from the engine outlet system. Figure 1 shows the course of the NO_2 concentration share in the NO_x concentration on the general characteristics of an engine operating in the ETC cycle. This graph shows that NO_2/NO_x ratio (NO_2 share in NO_x) increases with decreasing engine speed. This is primarily due to the decrease of the exhaust gas temperature with the reduction of the engine speed and the increasing the time of the exhaust gas flow from the combustion chamber to the point at which the NO_2 concentration was measured. Greater flow times of the expanded and cooled exhaust gas through the engine exhaust system favored a greater conversion of NO to NO_2. The meridian-like character of the isolines shown in Figure 1 indicates that the conversion rate of NO to NO_2 is little dependent on the change in engine load. Apparently, the rise in exhausts temperature caused by the increase of en-

gine loading is compensated by a drop in the air-fuel ratio and lower oxygen content in the exhaust gas. This can be traced on the Figure 2. It is clear from this figure that the main factors influencing the conversion intensity of NO to NO_2 are the temperature of the exhaust gas and the air-fuel ratio.

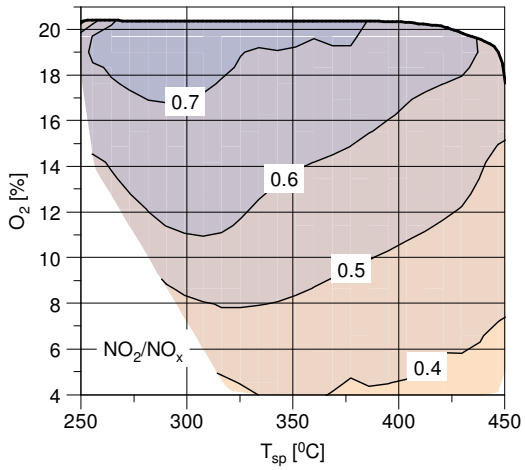

Fig.2. NO_2/NO_x ratio versus exhaust gas temperature (T_{sp}) and O_2 concentration

It is clear from Figs 1 and 2 that the best conditions for the formation of NO_2 in exhaust gases are at high concentrations of O_2 in the exhausts and their low temperature. Such conditions exist when the engine is running on idle. Their opposite state to the idle is where the exhaust gas temperatures reach the highest values and the concentration of oxygen in the exhausts reaches the lowest possible value. Then NO_2/NO_x ratio reaches the lowest values.

The courses shown in Fig. 1 were measured in an engine with a non-functioning SCR system caused by the cutting off the flow of urea solution into the reactor. This was intended to simulate the operating state of the engine, which we deal with when drivers of vehicles, in wrongly perceived savings, decide on such a step. By analysing the NO_2 concentration in the exhaust system of the tested engine, it can be seen that as a result of PDF use, it increased (Fig. 3) from an average of 29 ppm before PDF to 230 ppm after PDF, thus nearly eight times. In section 1 on this article there was written that NO_2 concentration greater than 100 ppm can cause death.

On Figure 1 are shown the results of tests with the SCR reactor inoperative. For comparison, on Figure 4 are shown the results of NO_2 testing in the engine with a functioning SCR reactor. Comparing Figures 1a) and 4, it can be seen that the NO_2 share in NO_x has been noticeably reduced. The nature of the NO_2/NO_x relationship from the engine speed and torque has not changed, but the ratio has decreased by about 30%.

On Figs 5 and 6 are shown the results of NO_2 concentration measurement and the specific emissions of this engine operating as in the conditions shown in Fig. 1b. Comparing Figures 1b and 5, we find that the highest concentrations of NO_2 in the tested engine are near the rated rotational speed, i.e. near the highest occurring exhaust temperatures. The impact of the engine loading on the NO_2 concentration is rather secondary. It appears that despite the significant degree of NO-NO_2 conversion at low engine speeds, the highest NO_2 concentration is obtained at the highest speeds that are precisely where the tested engine has the highest concentrations of NO_x emissions. In terms of the similarity of NO_2 and NO_x, courses, the graphs of these concentrations are quite similar.

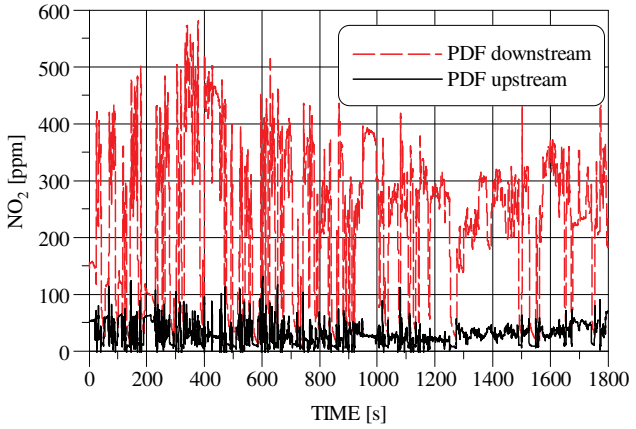

Fig. 3. Concentration of NO_2 in ETC cycle

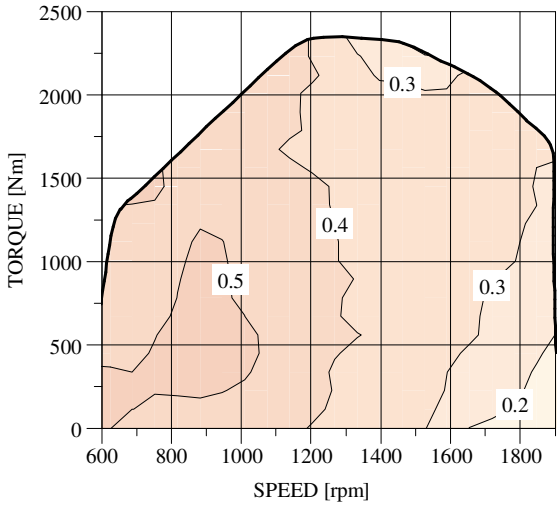

Fig.4. NO_2/NO_x ratio versus speed and torque of the engine equipped with SCR

On Fig. 7 there are compared two speed characteristics of the NO_x and NO_2 concentration measured at a constant engine load. This figure clearly shows how both of these exhaust components depend on engine speed.

On Fig. 6 are drawn NO_2 specific mass emissions. This figure is a reversal of the trend shown on the NO_2/NO_x ratio graph (Fig. 1b). Where the NO_2/NO_x ratio is the highest (high engine loading at low engine speed), the NO_2 specific emissions is the smallest. And vice versa - where the NO_2/NO_x ratio is the smallest (low engine loading at high speed) the NO_2 specific emissions is the highest.

In order to determine the actual emissions of nitrogen oxides, tests were carried out in the cycles foreseen for this purpose in Euro V and Euro VI standards. The results of these tests are summarized in Tables 2–5. By analysing the NO_2/NO_x ratio in each cycle, it can be seen that the ratio is

0.5 to 5.5% for raw (untreated) exhaust gases, from 42 to 52% at the PDF outlet (without SCR) and 30 to 53% in the exhaust gases purified by PDF and SCR. The differences between the NO_2/NO_x ratios measured for each cycle result primarily from different engine operating conditions, producing, inter alia, close to twofold greater work performed by the engine in the ETC cycle compared to the WHTC cycle.

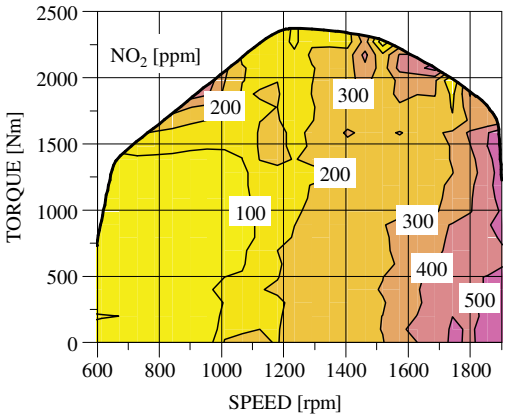

Fig. 5. NO_2 concentration in exhaust gas measured downstream of afertreatment system (without SCR)

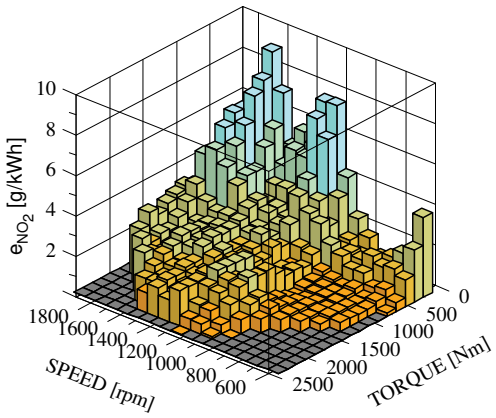

Fig. 6. Specific emission of NO_2 in the engine not equipped with SCR

Table 2. Emissions in ETC cycle [g/kWh]

Pollutant	Without DPF and SCR	With DPF and without SCR	With DPF and SCR
NO_x	5,747	5,089	0,080
NO_2	0,030	2,651	0,024
CO	1,150	0,010	0,011
N_2O	0,085	-	0,070
THC	0,162	0,005	0,015

Table 3. Emissions in ESC cycle [g/kWh]

Pollutant	Without DPF and SCR	With DPF and without SCR	With DPF and SCR
NO_x	5,730	5,548	0,265
NO_2	0,190	2,317	0,096
CO	0,374	0,001	0,014
N_2O		0,007	0,096
THC	0,095	0,001	0,037

Table 4. Emissions in WHSC cycle [g/kWh]

Pollutant	Without DPF and SCR	With DPF and SCR
NO_x	7,326	0,102
NO_2	0,229	0,036
CO	0,538	0,019
N_2O		0,107
THC	0,146	0,002

Table 5. Emissions in WHTC cycle [g/kWh]

Pollutant	Without DPF and SCR	With DPF and SCR
NO_x	6,663	0,051
NO_2	0,367	0,027
CO	2,628	0,013
THC	0,189	0,003

The NO_2 concentration in the exhaust gases of an engine equipped with SCR reached 2 ppm. In the engine without SCR this level exceeded 200 ppm. In both cases, these are multiple times the EPA limit laid down in [2]. For this reason, the NO_2 concentration in the engine exhaust gas system should be considered hazardous to human health and should be monitored by appropriate regulations.

3.2. Effect of NO_2 on the exhausts opacity

NO_2 is a reddish-brown gas whose absorption band of electromagnetic radiation is in the visible region. Its molar light absorption coefficient as a function of wavelength λ [4] ranges from 5.5×10^{-23} m^2/molecule at λ = 400 nm, to 0.5×10^{-23} m^2/molecule at λ = 600 nm. A slight effect of temperature on the absorption coefficient was observed in the range from -30 °C to + 124 °C. In the commercial

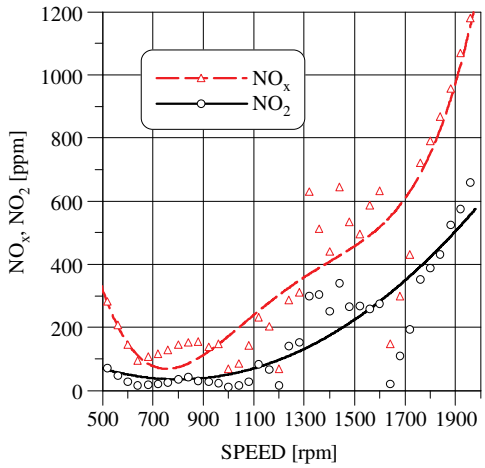

Fig.7. Engine speed characterystic at constant loading T=1000 Nm

opacimeters using tungsten filament lamps and normal UV-absorbing optical glass, we can expect light absorption by NO_2 in the range $(0.5–5) \times 10^{-23}$ m^2/molecule.

Due to the low level of the exhausts opacity in the low-emissions CI engines, the resolution of the conventional opacimeter, the stability of the indications and the noise must be adjusted to allow for measurements in these engines. The catalytic exhausts after-treatment systems such as oxidation reactors (DOCs) or particle filters (DPFs) may cause an increase of NO_x concentration in NO_x. The NO_2

absorbs the green light that is used in traditional opacimeters. The presence of NO_2 in the exhaust gases increases the indications of the current opacimeters from 0.00016 to 0.00024 m^{-1}/ppm NO_2, depending on the width of the band transmitted by the sensor [4].

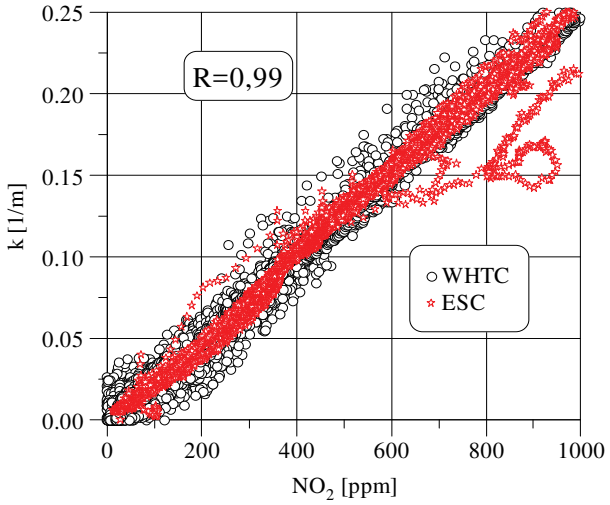

Fig. 8. Opacity versus NO_2 concentration in exhaust gases in ESC and WHTC cycles

In the tested engine, the NO_2 concentration many times exceeded the value of 1000 ppm, hence the values of the light absorption coefficient should be reduced by the corresponding correction. The values of these coefficients are close to the coefficient of the polynomial describing the regression line shown in Fig. 8, which shows the relationship of the light absorption coefficient *k* and the concentration of NO_2 contained in the exhaust gases determined during the ESC cycle. The AVL 439 opacimeter was used in the study. Very high correlation coefficient R = 0.994 between NO_2 concentration and k value was noted. For comparison, in the same test, the correlation coefficient between NO and k was 0.05 and between NO_x and k – 076.

The light absorption coefficient measured by the opacimeter consists of the component associated with the presence of particulate matter in the exhaust gases and the component associated with the presence of NO_2 in the exhausts. Fig. 8 shows the dependence of the exhausts opacity coefficient on the concentration of NO_2 contained in the exhaust gases. The subject tested was an Euro III engine equipped with DPF. The high value of the correlation coefficient obtained indicates that the value of the light absorption coefficient *k* measured by the opacimeter depends primarily on the concentration of NO_2 in the exhausts rather than on the concentration of the light-absorbing particles in the opacimeter. With some approximation it can be assumed that the field shown under the diagram (Figure 8) represents the opacity component associated with the presence of NO_2 in the exhaust gases while the component representing the correct opacity of the exhausts is presented as the width of the graph shown in Fig. 8. From the Fig. 8 it appears that for low concentrations of NO_2 (up to a dozen of ppm) that are encountered in the case of the engines without PDF and SCR–equipped engines, the presence of NO_2 in the exhaust gases does not have practical significance for the measurement of the exhausts opacity. The problem begins with engines equipped with PDF but without SCR. In the tested engine, for the ETC cycle, the average concentration of NO_2 in the test was 230 ppm, which means that for this NO_2 concentration the exhausts opacity was 0.06 1/m (Fig. 8), while the opacity component caused by the presence of NO_2 in the exhaust gases was about 0.04 1/m. This means that the exhausts opacity measurement in these conditions was subject to a 66% error. For this reason the opacimeters indications should be corrected for the presence of NO_2 in the exhaust gases. Looking at Figure 8, we can infer that the opacimeter correction coefficient used in the test should be no more than 0.00024 m^{-1}/ ppm NO_2.

4. Conclusions

1. The use of passive particulate filters in the engine exhaust system results in an increase in NO_2 emissions in exhaust gases
2. NO_2 concentrations in exhaust gases of DPF-equipped engines reach life and human health threatening values reported by EPA. For this reason, this exhaust gas component should become a major concern for ecologists and environmentalists.
3. The presence of NO_2 in the exhaust gases can cause significant measurement errors during measuring exhausts opacity.
4. In order to avoid any possibility of making an error during opacity measurement, it is necessary to use previously developed correction factor.

Nomenclature

CI	compression ignition
DI	direct injection
DOC	diesel oxidation catalyst
ESC	European stacionary cycle
ETC	European transient cycle
PDF	particulate diesel filter
SCR	selective catalyst reactor
WHSC	world harmonized stacionary cycle
WHTC	world harmonized transient cycle

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