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Comparison of nitrogen oxide emission with two PEMS measurement methods

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Mobile emission measurement systems (PEMS), according to current legal acts, can measure nitrogen oxide emission intensity using two different methods, one of which uses the chemiluminescence method and the other the ultraviolet light method. Stationary (laboratory) systems, according to the regulation, use only the chemiluminescence method. The following article analyses the results of tests obtained during WLTC tests from laboratory analysers (chemiluminescence method) with the results from two mobile analysers using nitrogen oxide analysers operating on the basis of two different methods. As a result of this analysis, the differences in the results of nitrogen oxide emissions from mobile systems compared to measurements from stationary systems in the WLTC test on a chassis dynamometer were described. The research was performed at the BOSMAL Institute of Automotive Research and Development using a passenger car equipped with a spark-ignition engine. The analysis showed differences in the results of nitrogen oxide emissions between mobile analysers for measuring nitrogen oxide emission intensity using the NDUV method and mobile analysers CLD. Measurements with mobile analysers also differ noticeably from the results obtained from stationary (laboratory) analysers. However, the greatest influence on the difference in the obtained results is the applied measurement method.

Key words: *emission, analyzer, accuracy, PEMS, RDE, WLTC*

1. Introduction

In recent years, environmental protection has become a priority for the whole world, which has also affected means of transport. In order to take care of the environment, the European Union is introducing increasingly stringent exhaust emission standards. Vehicle tests are no longer carried out only on roller stands and engine dynamometers, but since September 2019, a mandatory test is the measurement of exhaust emissions in real driving conditions – RDE performed using mobile PEMS exhaust gas analyzers. Currently, the Euro 6e-bis standard is in force in the EU, which is to be an introduction to the Euro 7 standard. The implementation of the Euro 6 standard and the need to measure emissions of harmful substances in exhaust gases forced manufacturers of measuring equipment to create portable PEMS exhaust gas analyzers. These analyzers should be reliable, and their accuracy and repeatability should be similar to those of stationary analyzers. Over the years, comparisons of these analyzers have been carried out against stationary systems, which confirm their correct operation and correct results [1, 2, 9, 12, 19]. One of the two components covered by RDE limits is nitrogen oxides. They are measured by analyzers using the chemiluminescence method (CLD) and the method using ultraviolet light (NDUV). In stationary systems, in accordance with the regulation, nitrogen oxide emission intensity must be measured using the chemiluminescence method, while mobile analyzers can measure it in two different ways [7]. Analyzers using the NDUV measurement method are cheaper than CLD analyzers and are easier to maintain, which is why many manufacturers use them in mobile systems.

2. Description and construction of stationary measurement systems

BOSMAL's emissions testing laboratories are advanced, ambient (Emission Laboratory No. 1) and climate controlled (Emission Laboratory No. 2) facilities for performing emissions, fuel consumption and performance tests over a range of driving cycles and a broad range of ambient conditions. Exhaust emissions testing itself is carried out with the aid of sampling bags (legislative tests), diluted and raw modal analysis (development tests) for use with CI, SI, and hybrid vehicles.

Table 1. Measurement range and accuracy of nitrogen oxide analyzer systems for stationary systems

System – Lab 1			
Measured range	Bag measurement / continuous measurement		Measurement accuracy
	lowest	highest	
NO_x (CLD)	0–5 ppm	0–1000 ppm	±2% at the measuring point ±1% on the scale

System – Lab 2					
Measured range	Bag measurement		continuous measurement		Measurement accuracy
	lowest	highest	lowest	highest	
NO_x low (CLD)	0–1 ppm	0–50 ppm	0–10 ppm	0–500 ppm	±2% at the measuring point ±5% on the scale
NO_x high (CLD)	0–100 ppm	0–1000 ppm	0–1000 ppm	0–10000 ppm	

These facilities permit the execution of a wide range of legislative and development emissions tests, including:
- CVS bag diluted emissions testing to international standards [6, 8]
- CO_2 emissions and fuel consumption measurement according to EU standards [17, 18]
- gravimetric and numerical quantification of particulate matter emission according to [10, 11]

– measurement of battery current balance according to [8]
– measurement of compounds which are unregulated in the EU, such as N_2O, NH_3, using additional analyzers
– measurement of soot and particulate matter from raw exhaust gases using additional devices
– checks of vehicles according to Conformity of Production (COP) requirements [8, 17]
– maximum power measurement on the wheels of the vehicle [18]
– electric consumption energy and electric vehicles range [6, 8].

3. Description of measurement methods for NO_x

3.1. Analyzer CLD

The analyzer for measuring the concentration of nitrogen oxide and nitrogen dioxide uses the CLD measurement method. The oxidation of nitrogen oxide with ozone O_3 produces light in the wavelength range of about 600 nm to 3200 nm, with a maximum radiation intensity at about 1200 nm. This is chemiluminescent radiation, which is proportional to the concentration of nitrogen oxide. In the case of excess ozone, it is captured by the detector and converted into an electrical signal. In order to determine the concentration of nitrogen oxides and nitrogen dioxide, the oxides contained in the gas are previously reduced to nitrogen oxide in a convector.

The chemiluminescence measurement is based on the following chemical reactions:

$$NO + O_3 \rightarrow NO_2^* + O_2 \quad (1)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (2)$$

After a partial reaction (1), a certain amount of excited nitrogen dioxide is formed, which changes to the ground state (3) and emits light (electromagnetic radiation):

$$NO_2^* \rightarrow NO_2 + h \cdot \nu \quad (3)$$

where: $h \cdot \nu$ – radiation energy at a specific wavelength:

$$NO_2^* + M \rightarrow NO_2 + M \quad (4)$$

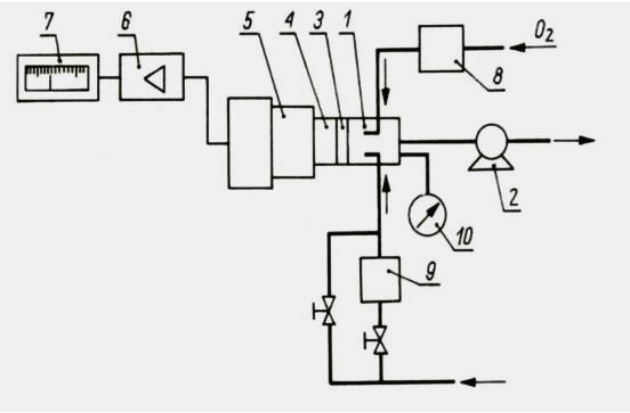

Fig. 1. Analyzer operation diagram CLD [13]: 1 – reactor, 2 – pump, 3 – quartz window, 4 – optical filter, 5 – converter, 6 – amplifier, 7 – meter, 8 – ozone generator, 9 – thermal converter, 10 – manometer

The greater part of the excited nitrogen dioxide releases its energy in the form of kinetic energy to the M molecules according to reaction (4). The ratio of released radiant energy (3) to nonradiative energy (4) depends on the reaction pressure and the type of reaction partners. The lower the reaction pressure, the greater the probability that the excited nitrogen dioxide molecule will release its energy in the form of light (Fig. 1) [3, 5, 14–16].

3.2. Analyzer NDUV

The analyzer for measuring the concentration of nitrogen oxides used in mobile systems is most often an NDUV analyzer (Non-Dispersive Ultraviolet). The UV analyzer is characterized by the following features:

– its measurement capabilities are very sensitive and stable with respect to NO
– the concentrations of nitrogen oxide and nitrogen dioxide are measured directly
– it is characterized by a high level of selectivity in relation to the accompanying components contained in the gas sample (exhaust gas) and has no effect on carbon dioxide and water in particular [4].

The UV analyzer is a multi-component UV photometer with high zero and endpoint stability. Its measurement operation is based on the properties of gases (such as NO and NO_2), which create discrete vibration absorption bands and absorb radiation in the wavelength range from 200 nm to 500 nm. The main element of the analyzer is a UV radiation source, an electrodeless discharge lamp ELD (Electrodeless Discharge Lamp), which, induced by high frequency, emits, among others, radiation specific for nitrogen oxide in an electromagnetic field:

$$N_2 + O_2 \rightarrow NO_2^* \rightarrow NO + h\nu \quad (5)$$

$$2NO \rightarrow N_2 + O_2 \quad (6)$$

This measurement method is therefore a resonance method and is referred to as DUV resonance absorption spectroscopy. Other UV-absorbed gases, such as nitrogen dioxide and sulfur dioxide, are determined by interference filter correlation as a non-dispersive UV method (Fig. 2) [4].

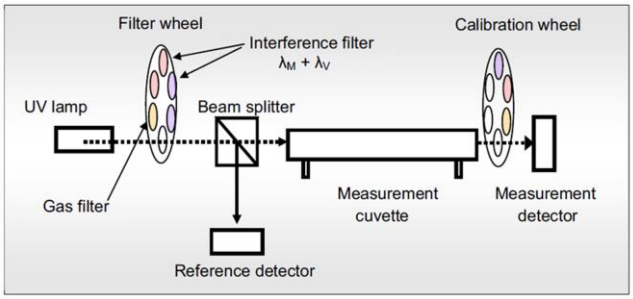

Fig. 2. Analyzer operation diagram NDUV [4]

The radiation emitted by the UV radiation source is modulated by means of a filter wheel and divided into a measuring beam and a reference beam in a semi-transparent divider. During one measurement, a total of four signals were recorded for two positions of the interference filter via the measuring beam and the reference beam, and calculated by forming double quotients. This four-beam method is the basis for the high measurement stability achieved in the measurement of nitrogen oxide concentration. Thanks to this, the analyzer is largely independent of

any contamination in the measuring cuvette or aging of the radiation source (Fig. 3) [4].

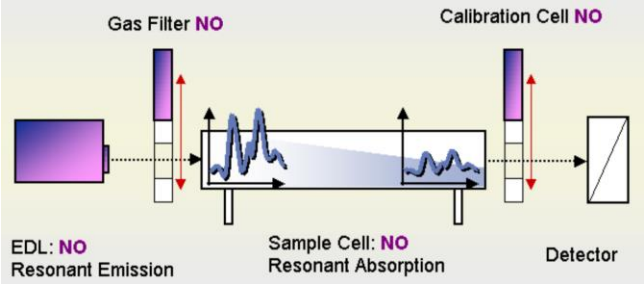

Fig. 3. Absorption measurement NO [19]

The required specific signal is determined in two stages:

– at the beginning, in the measurement phase, the full absorption measurement is recorded
– in the next reference phase, the gas filter filled with nitrogen oxide is set
– in the appropriate position and only those parts of the spectrum that are not absorbed by nitrogen oxide reach the detector through the measuring cuvette [4].

4. Research object

The aim of the research was to measure and analyse the nitrogen oxide emission intensity exhaust emissions results of a passenger car, with measurement carried out over the WLTC test on two stationary laboratories equipped with CLD analysers, with simultaneous measurement from two different PEMS systems, of which the first was equipped with an NDUV analyser and the second with a CLD analyser to measure NO_x. The test objects were PEMS systems, the data for which are shown in Table 2.

Table 2. Parameters of the mobile emissions measurement system

Method and measurement range of mobile analyzers		
Measured component	Continuous measurement of undiluted exhaust gases	Measurement accuracy
System A		
NO_2 (NDUV)	0–2500 ppm	±2% or ≤ 5 ppm
System B		
NO_x (CLD)	0–3000 ppm	±2% in the point ±0.3 on the scale

A brand new passenger car equipped with gasoline direct injection and fulfilling the Euro 6 norm was used for the measurements. Table 3 shows the data on the vehicle.

Table 3. Data of the test vehicle

Parameter	Value
Fuel type	Gasoline
Fuel delivery strategy	GDI
Vehicle mass [kg]	1008
Swept volume [cm^3]	1000
Power [kW]	51
Gearbox	Manual (5-speed)
Mileage [km]	170
Emission standard	Euro 6d

The speed profile of the WLTC test, consisting of four phases: low, middle, high, and extra-high, is the legislative test for EU type approval testing of vehicles with a total weight not exceeding 3.5 t, introduced in September 2018 for all newly manufactured vehicles (Fig. 4; detailed data on test characteristics are presented in Table 4).

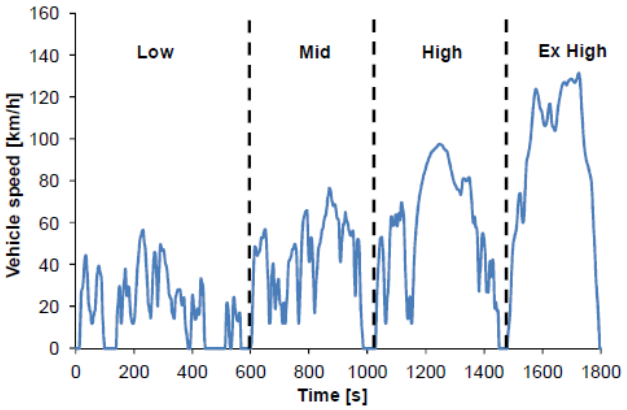

Fig. 4. The speed trace for the WLTC class 3b test cycle

Table 4. WLTC test data

Parameter	Unit	Value
Distance	km	23.266
Duration	s	1800
Number of pull-away events	–	8
Pull-away events per km	km^{-1}	0.34
Length of initial idling (before first pull-away event)	s	11
Total idling time	s	234
Idling time (proportion)	%	13
Maximum speed	km/h	131.3
Mean speed (all phases, including idling)	km/h	46.50
Time at which the mean speed is first exceeded	s	217
Maximum acceleration	m/s^2	1.67
Maximum value of v·a	m^2/s^3	20.57
Proportion of time for which speed > 100 km/h	%	10.11
Engine temperature before test start	°C	23±3

5. Research results

Currently, in order to allow a new vehicle type be sold for use on public roads, it is necessary to thoroughly check the exhaust emissions. For this purpose, exhaust gas analyzers – both stationary and mobile – are used. The results presented below show the difference between the results of nitrogen oxide from the stationary and mobile analyzers. Each of the WLTC tests was performed by the same experienced driver, to minimize driver-dependent variables (and their influence on the results) as directly as possible. In addition, the test vehicle performed each test in the same selectable driving mode with the same chassis dynamometer settings. In order to eliminate additional measurement irregularities, prior to each test, the vehicle was stored in a climatic chamber under constant atmospheric conditions. After each test, the vehicle was conditioned for at least 12 hours so that the temperature of operating fluids stabilized in the range of 22–24°C. The results of the three measures of nitrogen oxide emissions were averaged and then analyzed and presented in the graphs below. Tests were con-

ducted with the Start&Stop system turned off, and the results are presented without RCB and S&D corrections.

Below are presented the results of specific distance emissions of nitrogen oxides in laboratory No. 1 and in laboratory No. 2, respectively. The results have been divided into the results from tests at 14 and 23°C and from cold and warm engine start-up.

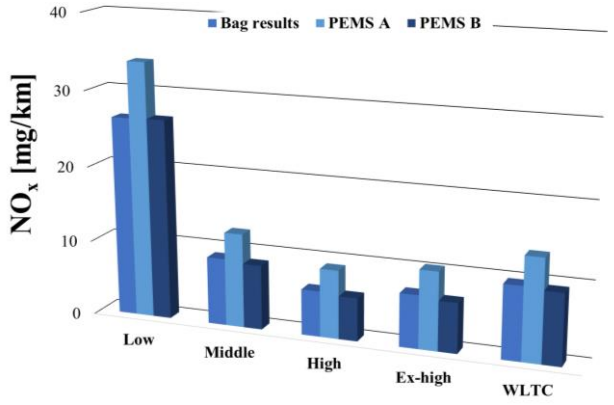

Fig. 5. NO_x specific distance emission in WLTC test in 14°C from cold start engine in laboratory 1

The highest measured specific distance emission level of nitrogen oxides from the WLTC test conducted with a cold engine start at a temperature of 14°C occurred in the low phase and was about 25 mg/km in the case of measurement made using the laboratory system and the PEMS B system (Fig. 5). The specific distance emission level determined using the PEMS A system was about 35 mg/km. The lowest specific distance emission was recorded in the high phase and did not exceed 7 mg/km for the measurement using the laboratory system and PEMS B, while for the measurement using the PEMS A system it was at the level of 9 mg/km. Both in the entire test and in each phase, the results using the PEMS A system differ from those using the other systems (they are higher).

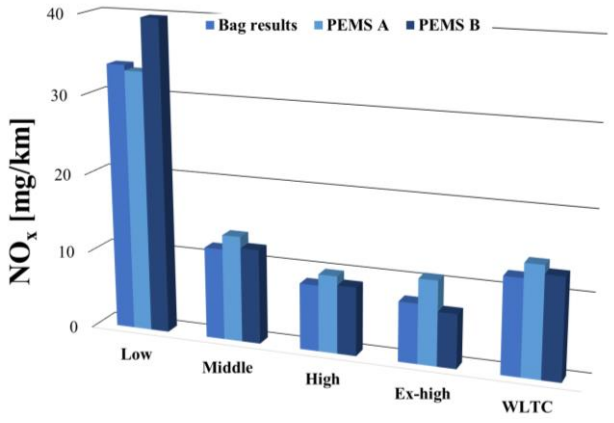

Fig. 6. NO_x specific distance emission in WLTC test in 14°C from hot start engine in laboratory 1

The highest specific distance emission of nitrogen oxides from the WLTC test performed at a temperature of 14°C for a warm engine start was recorded in the first phase, and the lowest in the fourth (Fig. 6). In the first phase, it was found that the PEMS B system determined the specific distance emission value of nitrogen oxides to be about 5 mg/km higher than the other systems, while in the remaining three phases the specific distance emission measurement is higher in the case of the measurement performed using the PEMS A system. In the entire test, the highest determined specific distance emission was recorded by the PEMS A system.

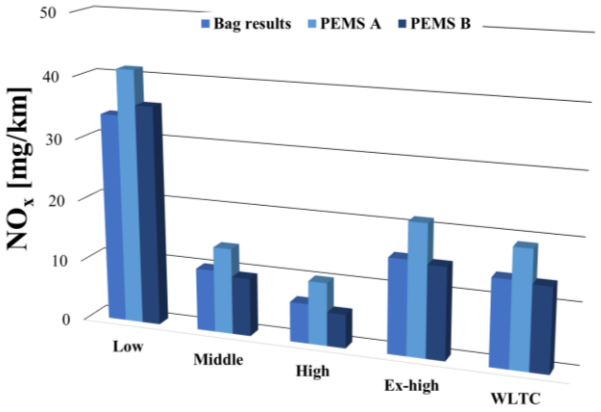

Fig. 7. NO_x specific distance emission in WLTC test in 23°C from cold start engine in laboratory 1

The highest level of specific distance emissions of nitrogen oxides from the WLTC test for a cold engine start at a temperature of 23°C was recorded in the first phase (Fig. 7), while its value for the entire test is about 15 mg/km. Both in the entire test and in its individual phases, the emission measurement results from the PEMS A system differ from those from the rest of the systems and are clearly higher. For the entire test, this difference is about 5 mg/km.

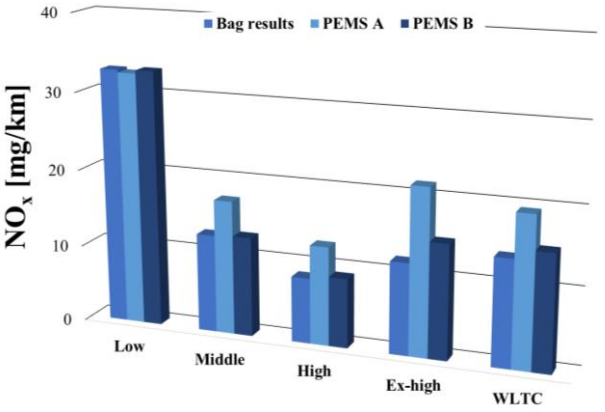

Fig. 8. NO_x specific distance emission in WLTC test in 23°C from the hot start engine in laboratory 1

The highest nitrogen oxide emissions from the WLTC test conducted at a temperature of 23°C with a warm engine start were recorded in the first phase of the test (Fig. 8). In the next three phases, the emission volume is higher for the PEMS A system. In the entire test, the emission measured using the PEMS A system is higher by about 5 mg/km compared to the other systems.

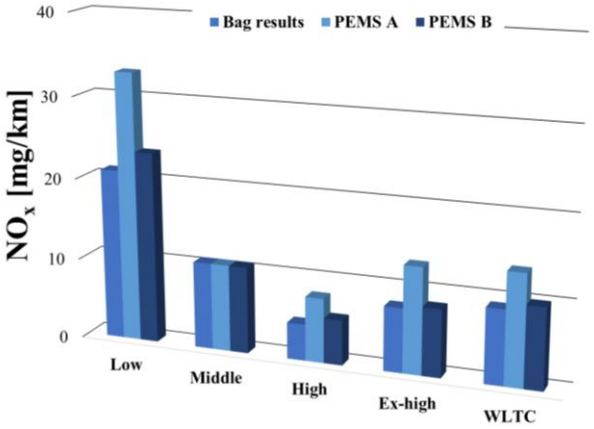

Fig. 9. NO_x specific distance emission in WLTC test in 14°C from cold start engine in laboratory 2

The maximum specific distance emission of nitrogen oxides from the WLTC test conducted at a temperature of 14°C with a cold engine start was measured in the first phase (PEMS A system, Fig. 9). In the second phase, the results obtained from both mobile systems are similar to those obtained using the laboratory system, while in the remaining analyzed phases – the results measured using the PEMS A system are higher than the others. The total measurement results take analogous values in the case of analyses using the laboratory system and PEMS B, while those obtained from the PEMS A system are significantly higher (by about 5 mg/km).

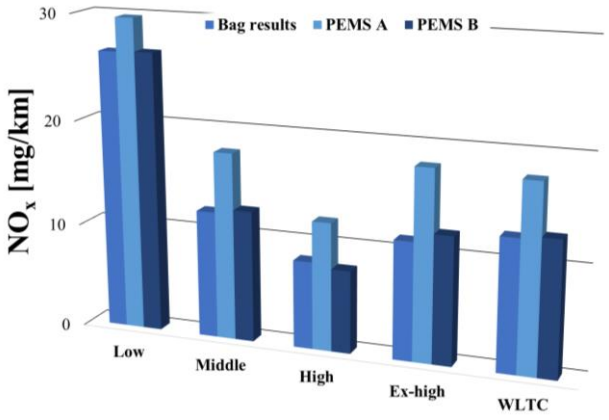

Fig. 10. NO_x specific distance emission in WLTC test at 14°C from the hot start engine in laboratory 2

For the WLTC test, conducted at a temperature of 14°C with a warm engine start, the highest specific distance emission of nitrogen oxides was recorded in the first phase (Fig. 10), and the maximum differences in measurements were characteristic of the PEMS A system (significantly higher specific distance emission levels compared to the other analyzed systems). In the entire test, the emission measured using the PEMS A system was higher by about 5 mg/km compared to the other systems.

The highest specific distance emission of nitrogen oxides from the WLTC test, performed at a temperature of 23°C with a cold engine start, was recorded in the first phase, and the maximum – for the PEMS A system (more by about 6 mg/km than the other systems, Fig. 11). In the subsequent phases, the results obtained using the PEMS A system are also significantly higher compared to the others. In the perspective of the entire test, comparable measurement results were obtained for the laboratory systems and the PEMS B system, while the results obtained as a result of measurements with the PEMS A system were characterized by significantly higher results.

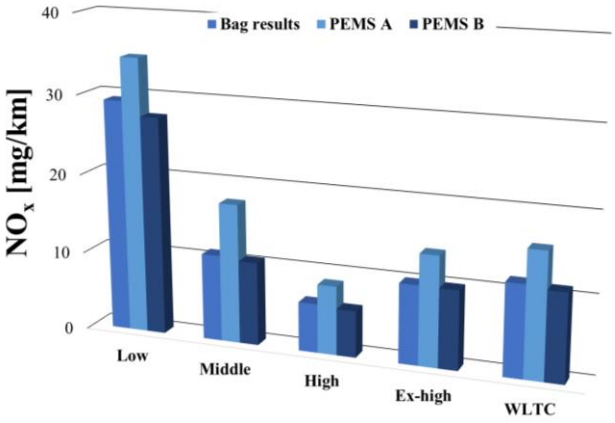

Fig. 11. NO_x specific distance emission in WLTC test in 23°C from cold start engine in laboratory 2

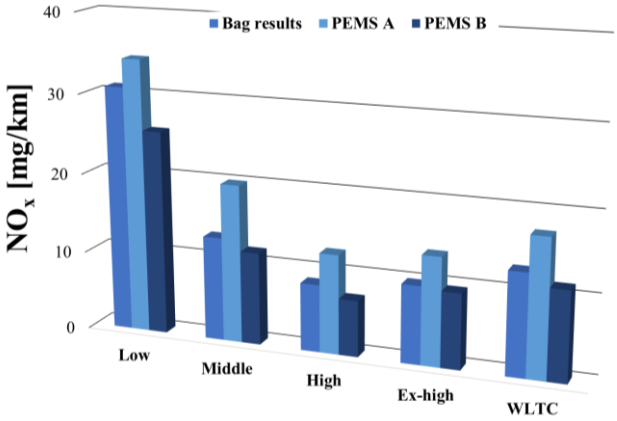

Fig. 12. NO_x specific distance emission in WLTC test in 23°C from hot start engine in laboratory 2

The maximum specific distance emission of nitrogen oxides from the WLTC test, carried out at a temperature of 23°C, with a warm engine start, was recorded in the first phase, and the greatest differences in the measurement were characteristic of the PEMS A system (Fig. 12). The results obtained as a result of its use were higher than the others in all the phases considered, and in the perspective of the entire test – higher in total by about 5 mg/km.

Based on the collected results of specific distance emissions of nitrogen oxides, the obtained results were compared with each other and presented graphically in the charts below, showing relative differences for temperatures of 14 and 23°C from a cold and warm engine start, respectively.

The largest difference between the results of specific distance emissions of nitrogen oxides using mobile systems and measurements using measuring bags was noted in the

high phase for the measurement using PEMS A system, compared to the results obtained in laboratory No. 2, and it amounted to 78%, which translated to 3.5 mg/km of absolute difference (Fig. 13). The smallest difference was noted in the middle phase for the measurement using both PEMS A and B systems, compared to the results obtained in laboratory No. 2, and it was below 0.2%. In the perspective of the entire test, the largest difference was noted for PEMS A system in relation to the measurements carried out using laboratory system No. 2, and it amounted to about 50% (4.5 mg/km of absolute value), while the smallest – for PEMS B system in comparison to laboratory system No. 1, and it was at the level of about 3% (0.3 mg/km of absolute value).

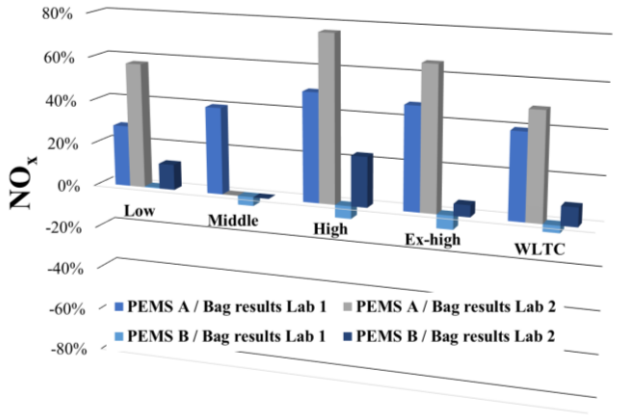

Fig. 13. Relative difference of specific distance emission measurements of nitrogen oxides for WLTC test at 14°C from a cold start engine

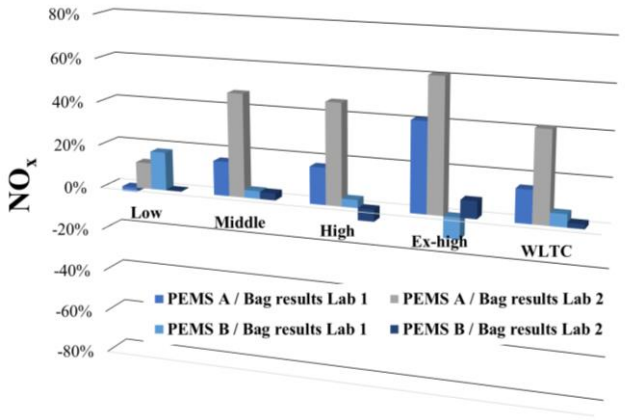

Fig. 14. Relative difference of specific distance emission measurements of nitrogen oxides for WLTC test at 14°C from a hot start engine

The maximum relative difference between specific distance emissions of nitrogen oxides using mobile systems and measurements using measuring bags, for tests conducted at a temperature of 14°C with a warm engine start, was recorded in the extra high phase for measurements using the PEMS A system compared to the results obtained in laboratory No. 2 and amounted to –61%, which translated to 7 mg/km of absolute difference (Fig. 14). The smallest relative difference characterized the low phase and took place with the use of the PEMS B system in relation to the results obtained in laboratory No. 2 and amounted to less than 0.5% (0.1 mg/km of absolute difference). For the entire test, the maximum difference was observed for the PEMS A system compared to the measurements carried out using laboratory system No. 2 and it amounted to approximately 42% (5 mg/km absolute difference), while the smallest – for the PEMS B system compared to laboratory system No. 2 and it took the value of approximately 2% (0.3 mg/km absolute difference).

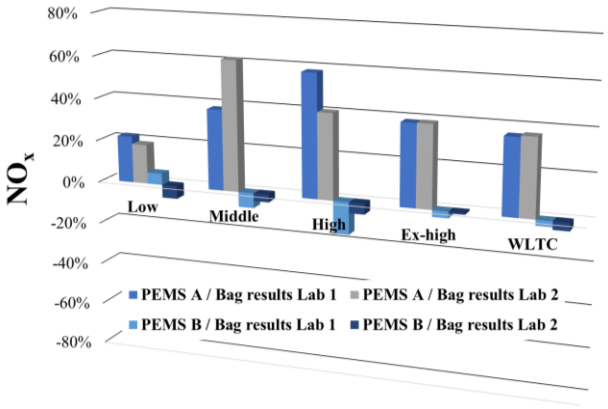

Fig. 15. Relative difference of specific distance emission measurements of nitrogen oxides for WLTC test in 23°C from cold start engine

The maximum relative difference between specific distance emissions of nitrogen oxides using mobile systems and measurements using measuring bags, for tests conducted at a temperature of 23°C with a cold engine start, was observed in the middle phase using the PEMS A system, in relation to the results obtained in laboratory No. 2, and it amounted to 61%, which translated to less than 7 mg/km of absolute difference (Fig. 15). The smallest relative difference was characteristic of the extra high phase using the PEMS B system, in comparison to the results obtained in laboratory No. 2, and it amounted to about –1% (0.1 mg/km of absolute difference). For the entire test, the largest difference was observed for the PEMS A system, in relation to the measurements performed using laboratory system No. 2, and it amounted to approximately 37% (4 mg/km of absolute value), while the smallest – for the PEMS B system in comparison to laboratory system No. 1, and it was at the level of approximately –3%, 0.4 mg/km of absolute value.

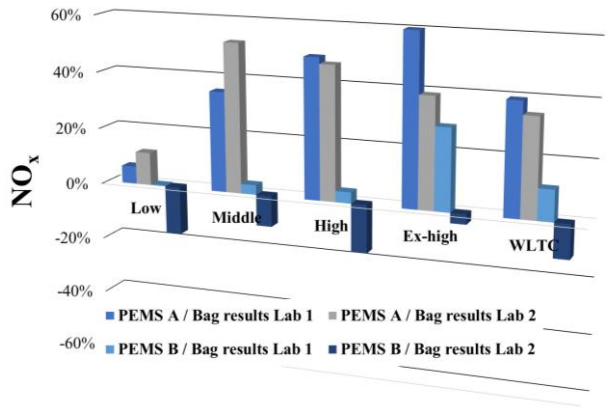

Fig. 16. Relative difference of specific distance emission measurements of nitrogen oxides for WLTC test in 23°C from hot start engine

For specific distance emissions of nitrogen oxides using mobile systems and measuring bags, for tests conducted at a temperature of 23°C with warm engine start-up, the largest relative difference between measurements was noted in the extra high phase for the PEMS A system compared to the results obtained in laboratory No. 1 and amounted to 66%, which translated to 9 mg/km of absolute difference (Fig. 16). The smallest difference was noted in the low phase for the PEMS B system compared to the results obtained in laboratory No. 1 and amounted to about 0.5% (0.1 mg/km of absolute difference). In the perspective of the entire test, the largest difference was noted for the PEMS A system in relation to laboratory system No. 1 and amounted to about 40% (5.5 mg/km of absolute value), while the smallest – for the PEMS B system in relation to laboratory system No. 1 and it was at the level of about 11% (1.5 mg/km of absolute value).

6. Conclusion

Based on the obtained results, it can be stated that mobile analyzers using the NDUV measurement method for measuring nitrogen oxide emissions are characterized by lower measurement accuracy, and the results differ by several dozen percent compared to the others.

A detailed comparison of the results for distance emissions of nitrogen oxides is provided below:

- For tests conducted at 14°C from a cold engine start, the largest relative difference is at the level of about 49% for the specific distance emission value of nitrogen oxides for the mobile PEMS A system compared to Laboratory 2, while the smallest is –3% for the mobile PEMS B system compared to the laboratory system 1, which translated into a relative value of 4.5 mg/km and –0.3 mg/km, respectively.
- At a temperature of 14°C from a warm engine start, where the specific distance emission of nitrogen oxides was at a similar level to the emission of nitrogen oxides from a cold engine start, the largest difference was also recorded for the measurement with the PEMS A system compared to the measurement from the Stationary Laboratory No. 2 I, it amounted to 41%, which gave about 5 mg/km of absolute difference. On the other hand, the smallest relative difference was recorded for the measurement results from the mobile PEMS B system compared to the measurement from the Stationary Laboratory No. 2 I, which amounted to 2%, giving 0.2 mg/km of absolute difference.
- In tests at an ambient temperature of 23°C, the largest differences at cold engine start were recorded for the mobile PEMS A system compared to the measurement from the laboratory system 2 and amounted to 32%, while the smallest relative difference was –2.6% for the measurement from the mobile PEMS B system compared to the measurement from laboratory No. 1. The absolute values were approximately 4 and –0.3 mg/km, respectively.
- Tests with warm engine start at a temperature of 23°C showed that the largest difference in measurements is for the measurement from the mobile PEMS A system compared to the measurement from the stationary laboratory No. 1, and is 39%, which gives approximately 6 mg/km of absolute difference. The smallest difference is for the measurement from the mobile PEMS B system compared to the measurement from the laboratory system No. 1, and is 11%, which gives approximately 2 mg/km of difference.

Thanks to the obtained results, although the differences in the measurement of nitrogen oxides using the NDUV analyzer amounted to even several dozen percent, in reality, these values were at the level of a few mg/km, so we can state that NDUV analyzers installed in mobile systems are reliable.

Nomenclature

CLD	chemiluminescence detector	RDE	real driving emissions
NDUV	nondispersive ultra violet spectroscopy	WLTC	Worldwide Harmonized Light Vehicles Test Cycles
PEMS	portable emissions measurement system		

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