N_2O EMISSIONS FROM THE MOBILE SOURCES

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Summary: Nitrous oxide (N_2O) generally known for its anesthetic and hallucinogenic properties is oxide with the lowest valence of nitrogen among other oxides of nitrogen. In addition, it is the most stable nitrogen oxide in the environment. Measurement of the N_2O emissions from the mobile sources has recently come forward and there are only few data at disposal. Due this reason we make described experiment.

Keywords: Nitrous oxide, Greenhouse gas, Road vehicles, Emissions, IR analysis, Pollutions

1. INTRODUCTION

Nitrous oxide (N_2O) generally known for its anesthetic and hallucinogenic properties is oxide with the lowest valency of nitrogen among other oxides of nitrogen. In addition, it is the most stable nitrogen oxide in the environment. Formation and transformation of nitrogen oxides in the nature are parts of biogeochemical cycle of nitrogen. Nitrous oxide is mainly formed by the natural way during the denitrification processes under the anaerobic conditions in soils, other sediments, hydrosphere, primeval forests, etc.

Nitrous oxide of the anthropogenic origin is emitted into the atmosphere during the combustion of fossil fuels and biomass and owing to vehicles operation. Of course, the industrial productions of nitric acid or nylon as well as the agricultural activities such as transformation of the tropical forests into pastures contribute to nitrous oxide emissions, too. Various surveys differ substantially in the evaluation of the relative and absolute proportion of the particular sources of nitrous oxide.

The natural processes are still regarded as a principal source simultaneously with estimation of the 25 – 50% contribution of the anthropogenic sources to the total production. However, from the long view a volume of the emitted N_2O from the

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natural sources is more or less constant. On the other hand, the emissions of the anthropogenic origin are constantly increased.

The emissions of N_2O from the mobile sources are still considered as relatively low with regard to the total anthropogenic emissions. However, as it was shown Table , the specific emissions of N_2O are significantly increased by use of all types of devices serving for the emissions reduction – especially in the case of catalytic converters in cars. Although these equipments rather significantly reduce the emissions of CO, NOx and unburnt hydrocarbons simultaneously they cause the increase of the N_2O emissions.

With regard to their use in the increasingly measure the increased portion of the N_2O emissions from the transport can be expected. The following table documents the increase of the emissions of nitrous oxide due to use of the catalytic converters. It is worth meaning the interesting difference of the emission factors of N_2O in the case of three-way catalytic converters when comparing new and old converters (about quintuple).

Table 1 The N_2O emission factors of cars

	European data	**Canadian data**	**USA data**
Catalytic converter	mg/km	mg/km	mg/km
Without catalytic converter	5 - 20	20	1 - 3
Oxidative converter	75	75	2 - 40
3 - way converter, new	37 - 106	40	8 - 60
3 - way converter, old*	162 - 221	170	-

* 15 000 km running

2. EXPERIMENTAL PART

Measurement of the N_2O emissions from the mobile sources has recently come forward and there are only few data at disposal. Most values have come from the USA and Canada but, it is necessary to remark that the American and Canadian data exhibit relatively significant differences very often. At that time samples of emissions were analyzed only by means of gas chromatography (GC) as the results found by means of infrared (IR) spectrophotometry exhibited the significant error caused by CO and CO_2 interferences.

The interference of CO is apparent from the comparison of spectra of nitrous oxide, carbon oxide and carbon dioxide on Figure 1.

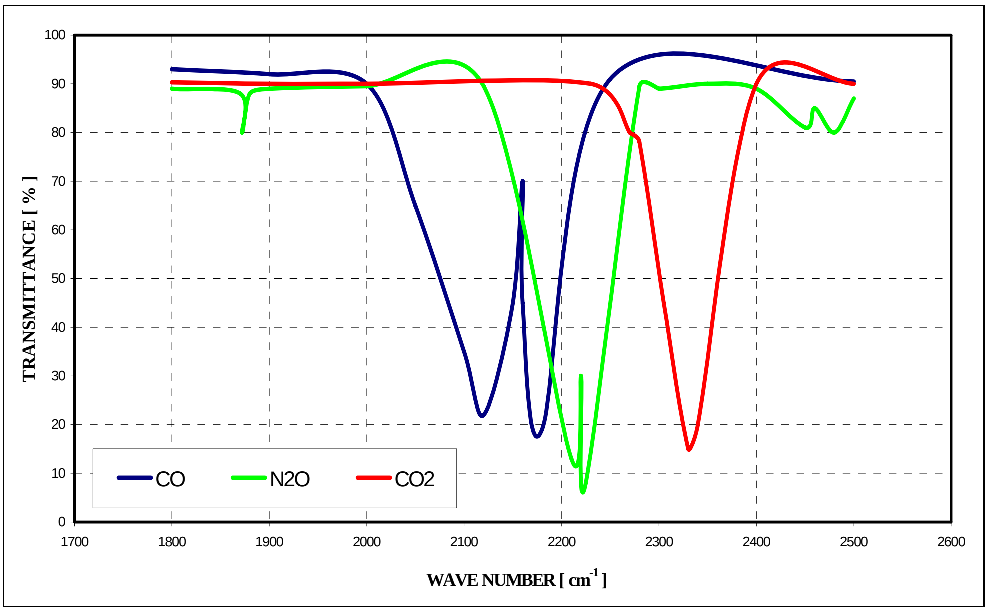

Figure 1 Infrared spectrum of N_2O, CO and CO_2 in the measurement region of N_2O

In order to reduce the negative CO influence on the IR analysis of N_2O the series of experiments focused on „washing out“ the component CO from the combustion products was performed.The further aim was to find an analytical method suitable and useful for standard authorized measurements of the emissions.

The second series of measurements of the emissions from the mobile sources was performed in last the years, nitrous oxide was analyzed by IR spectroscopy as well as by gas chromatography. The comparison of the results achieved by both methods of the N_2O analysis is presented on

Figure **2**.

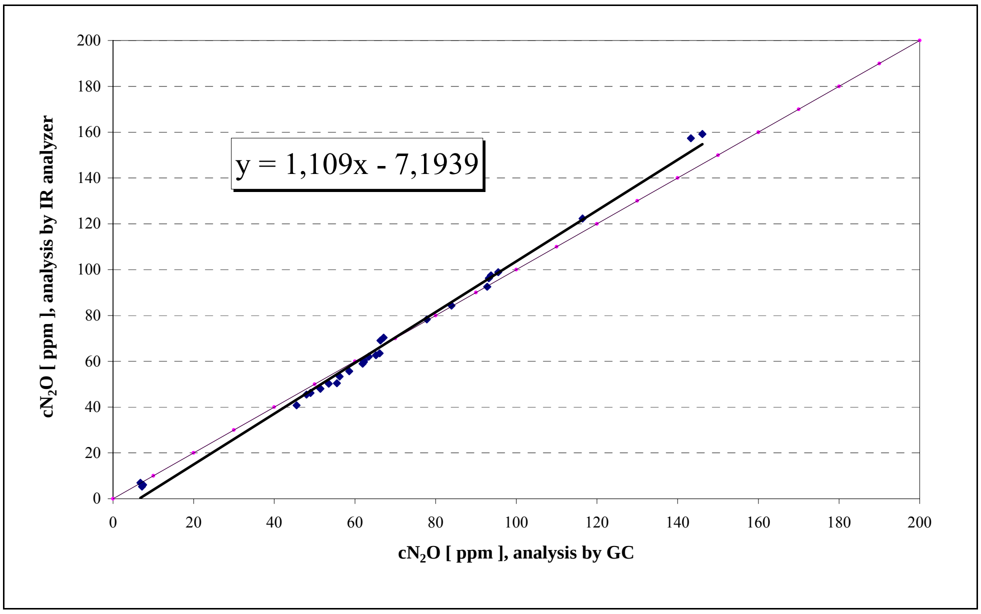

Figure 2 The comparison of the IR and GC analyses of nitrous oxide

The following criteria of the measured cars were monitored with regard to the concentration level of nitrous oxide:

- Type of engine
- Type of fuel
- Operation output – revolutions of engine
- With or without catalytic converter
- Age of catalytic converter

Two operation conditions were chosen for the measurement of the car N_2O emissions:

The neutral operation (about 900 min^{-1}) and the increased output of engine (3000 min^{-1}). This choice corresponds to the routinely used methodology of measurement of emissions from the mobile sources (cars).

The procedure of each test was as follows: before each measurement a car engine was heated by running about 10 km. When the operation temperature was achieved, a car was parked under the conditions of the permanent operation in the area of the Energy Research Center (VŠB – Technical University of Ostrava) where most of the measurements were performed. Figure 3 shows the results of the measurements of the emission factors from the combustion engines of the cars.

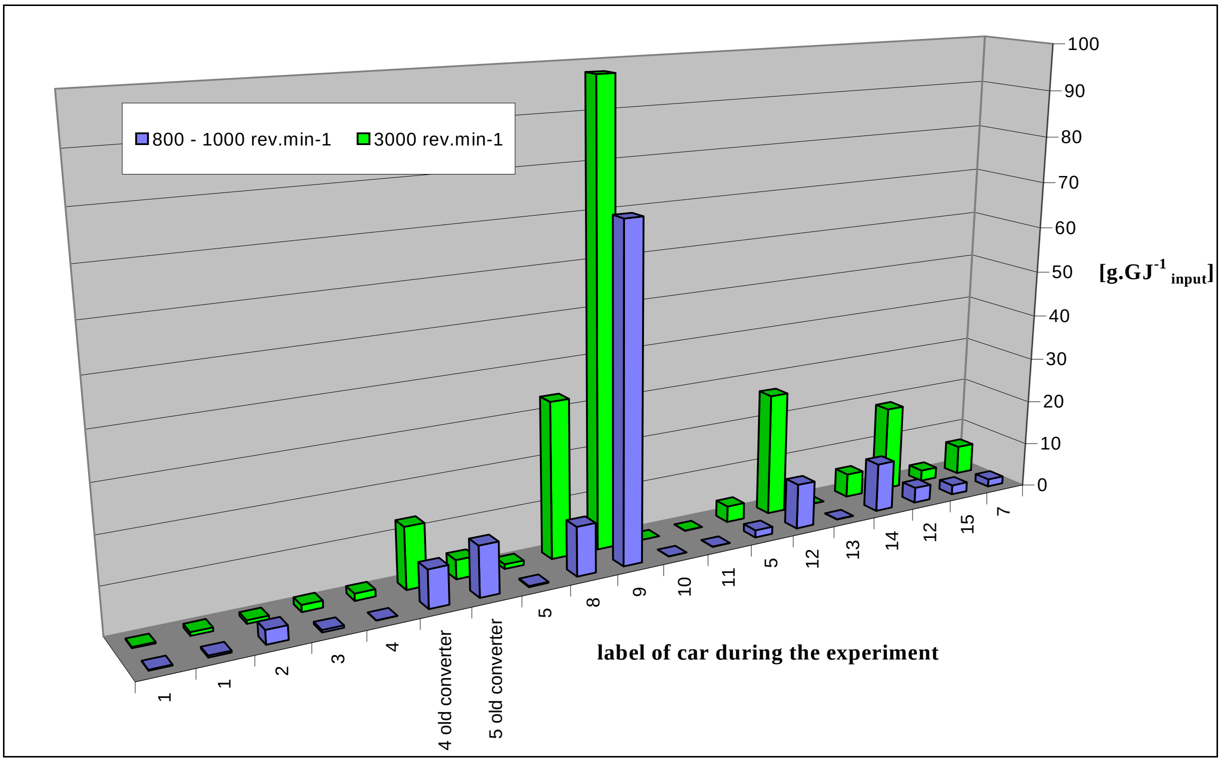

Figure 3 The N_2O emission factors of the mobile sources in the dependence on their type

1, 2, 3, 8, 9   engine without catalytic converter

4 engine with one-way catalytic converter
5, 10-14 engine with three-way catalytic converter
12 LPG

The results were used for calculation of the emission factors of N_2O related to the invested energy from the fuel, see below.

Table 2 The emission factors of N_2O in the combustion products

Engine/number	**Fuel**	**Revol. min^{-1}**	**Emission factor N_2O**	
			g.GJ^{-1}$_{input}$	**St. deviation**
no catalyst/6	gas	900	14,3	28,3
no catalyst/6	gas	3000	22,4	39,2
1-way converter/2	gas	900	4,1	5,7
1-way converter/2	gas	3000	7,4	8,2
3-way converter/8	gas	900	4,2	5,3
3-way converter/8	gas	3000	5,1	9,0
3-way converter/1	LPG	900	1,0	-
3-way converter/1	LPG	3000	18,9	-
Diesel/4	diesel	1000	1,0	1,1
Diesel/4	diesel	3000	2,2	3,0

The survey of the measured emission factors gives evidence about their significant dependence on the amount of the runned kilometers: The new catalytic converter (especially three-way) exhibit the low emissions of N_2O but these values increase significantly after running about 20, 000 km. The increase is more significant in the case of one-way catalytic converter.

Table 3 The N_2O in the dependence on the age of three-way catalytic converte

ENGINE WITH THREE-WAY CONVERTER	AFTER RUNNING 500 KM	AFTER RUNNING 20 000 KM	AFTER RUNNING 66 500 KM
	N_2O [G.GJ^{-1}]		
900 REV.MIN^{-1}	0,23	10,9	1,61
3000 REV.MIN^{-1}	1,01	4,11	2,50

Table 4 The N_2O in the dependence on the age of one-way catalytic converter

ENGINE WITH ONE-WAY CONVERTER	AFTER RUNNING 5 000 KM	AFTER RUNNING 25 000 KM
	N_2O [G.GJ^{-1}]	
900 REV.MIN^{-1}	0,1	17,2
3000 REV.MIN^{-1}	3,1	24,7

A content of the fuel nitrogen is one of the factors influencing an amount of emissions in the combustion products. Similarly as combustion in the stationary sources it is supposed that nitrous oxide is particularly formed from the fuel nitrogen. In order to clarify these presupposition five samples of gas with various additives of the various nitrogen content were prepared in the laboratory.

- gas without additive
- pyridine, content of N_2 = 0,2 %
- butyl amine, content of N_2 = 0,2 %
- propionitrile, content of N_2 = 0,2 %
- pyridine, content of N_2 = 1,0 %

The studied dependence is shown on Figure 4.

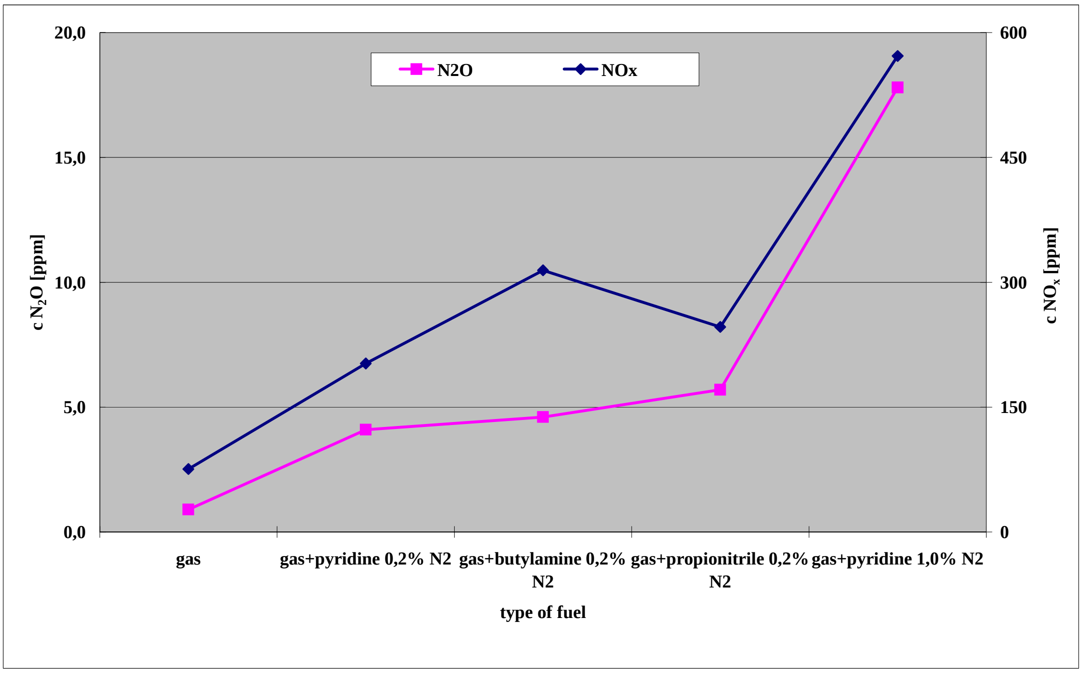

Figure 4 The influence of the fuel nitrogen amount on the N_2O and NO_x emissions

3. CONCLUSIONS AND DISCUSSION

According to the found results these facts can be stated:

- There were found no measurable concentrations of nitrous oxide in the case of the new Diesel engines. The concentrations on the level of ppb or ppm were found in the case of the old Diesel engines. These concentrations are not surely negligible with regard to a composition of the car fleet in the Czech Republic.

The results found for the spark ignition engines exhibit the following facts:

- The lowest average values of the emission factor can be found in the case of cars without the catalytic converter (they use unleaded gas called „natural“). This conclusion presented also in the literature (for example (2)) would be true if the results obtained on the older cars did not be included. It is clear (Fig. 3) that the contribution of such devices is significant (tens g.GJ-1input). Due to a great number of such cars operating in the Czech Republic (hundred thousands) the fact presented in the reference is rather inaccurate.
- The average levels of the emission factors in the case of cars equipped with catalytic converter (one-and three-way) fluctuate. In practice, the new cars exhibit the immeasurable concentrations of nitrous oxide in the combustion products. On the contrary, the cars with ten thousands run kilometers appear to be a significant source of the N_2O emissions.

- The content of nitrogen in the fuel positively influences the concentration of nitrous oxide in the combustion products from cars. The emissions of nitrous oxide increase with its increasing content.

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