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DETERMINATION OF VOLATILE ORGANIC COMPOUNDS FOR COMBUSTION ENGINES COMPLIANT WITH EURO 4 AND EURO 6

OZNACZANIE LOTNYCH ZWIĄZKÓW ORGANICZNYCH W SPALINACH SILNIKÓW SPEŁNIAJĄCYCH NORMY EURO 4 I EURO 6

Abstract: Volatile organic compounds are considered as one of the most harmful pollutants. Among them are hydrocarbons, which belongs to one of the chemicals groups monitored in the process of using vehicles. The article emphasized VOC toxicity in the light of the changes in the legislation on engine exhaust emissions. For the determination of volatile organic compounds, the exhaust gases of selected passenger cars were tested. Gas chromatography was used for the studies. The results have been verified with regard to the introduction of increasingly restrictive Euro standards. Furthermore this article discusses the issue related to the control of VOC emissions from internal combustion engines in cars as well as the attitude of vehicle users towards the adverse environmental conditions associated with the emission of toxins.

Keywords: VOCs, engine exhaust, Euro standards, chromatography

Introduction

European emissions standards include four groups of chemicals and specify the maximum allowable concentrations of these substances in the atmosphere. In addition to carbon monoxide, nitrogen oxides and particulate matter, hydrocarbons, including volatile organic compounds (VOCs), deserve special attention (Fig. 1). These are vapours of organic substances with an initial boiling point of 323-523 K, measured at normal pressure of 1013 hPa. Of the 200 identified engine components, the following volatile organic compounds can be identified: aldehydes, alcohols, ketones, aromatic hydrocarbons, paraffinic hydrocarbons, esters [1].

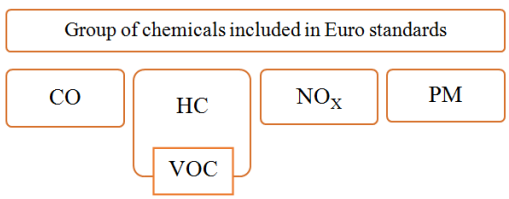

Fig. 1. Volatile organic compounds with respect to chemicals covered by Euro standards

Volatile organic compounds are a threat to human life through direct toxic effects [2] as well as through indirect action leading to the formation of secondary air pollutants

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(contributing to the formation of photochemical smog) [3]. Toxic effect is a harmful for living organisms, exerting a degrading effect on tissues, organs or biological processes [4]. VOCs penetrate the body through the respiratory system, digestive tract and through the skin. They can cause a number of side effects such as: headaches and dizziness, somnolence, mucosal irritation, permanent damage to the liver or nervous system [5]. Volatile organic compounds are listed as the second, after NO_X, most harmfulness air pollutant [6].

Anthropogenic sources are primarily responsible for VOC emissions [7]. Road transport is one of the three most common contributors to atmospheric pollution by volatile organic compounds [8]. The comparison of the industrial sources related to pollutant emission is shown in Figure 2.

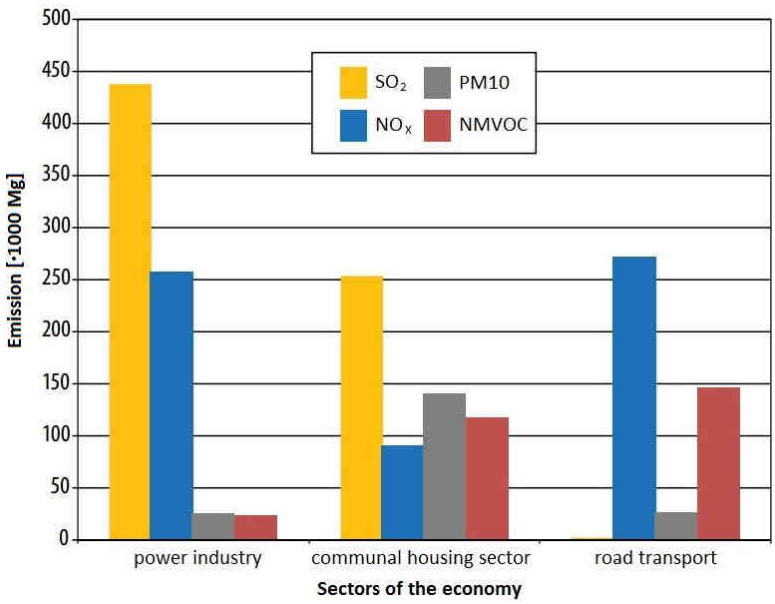

Fig. 2. The emissions of major pollutants in Poland in 2012 by sectors of the economy (NMVOC - non-methane volatile organic compounds) [9]

The engine is one of the member of entire vehicle, having most unfavourable effect on the environment. Other structural components of vehicles also have an undesirable effect on the environment. For example abrasion of the tire's surface causes pollution as well, as do oil leaks from the gearbox and main transmission and abrasion of friction linings of brakes and clutches, etc. Due to the visible negative effects of the engine on the environment through emission of harmful pollutants, the environmental protection has been started from reducing the effects of the engine's negative impact on the air quality, and significant progress is being made in this area. It is however, unrealistic to entirely reduce the pollutants, which is why it is important to control the level of toxins emitted by the exhaust system of a vehicle [10].

Due to the harmfulness of volatile organic compounds in atmospheric air, it has become mandatory to assess their levels [11, 12], as well as the permissible level of factors harmful to health in the work environment [13, 14]. Among the VOCs, benzene and its derivatives are considered to be of particular concern, both for man and for the environment [15, 16]. Benzene belongs to the group of chemicals that can cause cancer and hereditary genetic damage [17].

The volatile compounds deliberated here are not considered as a separate group of compounds in the European legislation on emission limits. However, due to their high toxicity [18], it was decided to check, with aid of an appropriate analytical method, the VOC emission in the exhaust fumes of the vehicles in relation to the Euro standards. Although the overall value of toxic emissions and the introduction of ever more stringent Euro standards are declining, for petrol engine vehicles, hydrocarbons (HC) emissions remain at the same level since 2005 (Table 1). It is therefore worth analyzing the value of volatile organic compounds in selected vehicles.

Table 1

Emission values for new petrol-powered vehicles [19]

	Valid since	**CO [g/km]**	**HC [g/km]**	**NO_x [g/km]**	**HC+NO_x [g/km]**	**PM [g/km]**
Euro 1	12/92	2.72	-	-	0.97	-
Euro 2	01/97	2.20	-	-	0.50	-
Euro 3	01/00	2.30	0.20	0.15	-	-
Euro 4	01/05	1.00	0.10	0.08	-	-
Euro 5	09/09	1.00	0.10	0.06	-	0.005*
Euro 6	08/14	1.00	0.10	0.06	-	0.005*

*with direct injection

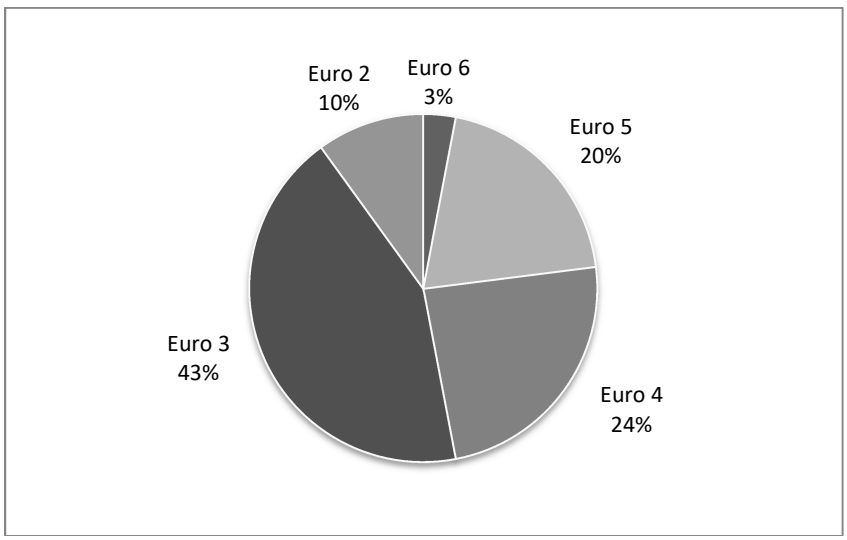

Fig. 3. The number of cars in Poland in 2016 that fulfil specific emission standards [20]

The requirements for modern engines seem to be very high. On the one hand, one can see a continuous increase in the number of vehicles on the roads and traffic related to it, the construction of new roads, widening of existing streets, and on the other hand the need to reduce the amount of fuel consumed and exhaust emissions. Taking into account the fact that on Polish roads vehicles that meet the latest standards will not dominate for a long time (see Fig. 3), it is worth noting that the more important is the continuous monitoring of all emitted toxic substances. Therefore, despite the ever lower emission of toxins from fuel combustion of newer vehicles, its overall level in the atmosphere is not diminishing at all.

Material and method

The study was carried out for exhaust gases derived from two passenger cars of different brands equipped with petrol engines. Vehicles had a valid periodical inspection and met certain exhaust emission standards - the first Euro 4 standard, the second Euro 6 standard. The concentrations of individual volatile organic compounds were determined in the exhaust gases. Three samplings were made for each car (Fig. 4). Gases were taken to the test bags at a distance of approximately 20 cm from the exhaust pipe of the idling vehicle. An aspirator with a gas flow rate of 30 dm^3/min was used for sampling for activated carbon sorbent (20 min intake time). The qualitative and quantitative analysis of volatile organic compounds was performed with aid of gas chromatography. This is the only method that separates the individual hydrocarbons in the exhaust gases. It is characterized by a small amount of dosed sample, rapid analysis, and good repeatability.

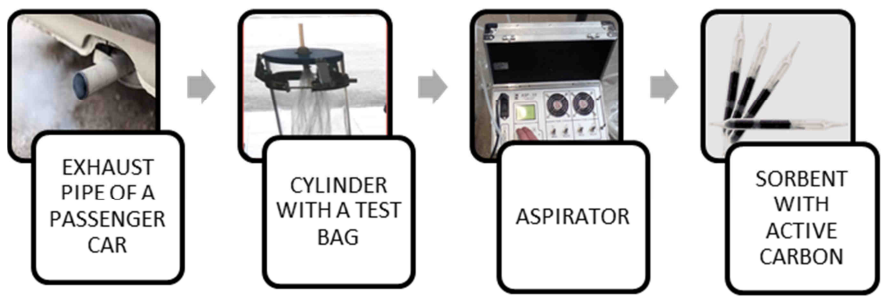

Fig. 4. The flow of the tested gases in the measurement system

Results and discussion

The results are shown in Table 2. Twelve different volatile organic compounds were identified. For each car, the results are given for 3 trials. The individual concentrations were averaged and the total number of concentrations of detected compounds was presented.

Based on the below data, it can be concluded that the average concentrations of individual chemicals for Euro 6 compliant engines are lower than those of Euro 4. The emission values of all compounds, except for n-pentane, slightly differ between the two vehicles. For the n-pentane a significant decrease in the exhaust gas concentration in the Euro 6 engine has been observed, resulting in a significant difference between the total concentration of all chemicals in the exhaust gases.

Table 2

Concentrations of volatile organic compounds in passenger car exhausts compliant with Euro 4 and 6 standards (± 30%)

No	Chemical compound	Concentration [ppm] (Euro 4)				Concentration [ppm] (Euro 6)			
		Test 1	Test 2	Test 3	Average	Test 1	Test 2	Test 3	Average
1	n-pentan	156.00	164.42	172.85	164.42	3.73	3.60	3.67	3.67
2	2-propanol	1.85	1.90	1.93	1.89	2.07	1.98	1.67	1.91
3	2-butanol	0.31	0.35	0.21	0.29	0.17	0.26	0.23	0.22
4	toluen	0.47	0.46	0.41	0.45	0.42	0.44	0.40	0.42
5	1-butanol	0.34	0.27	0.24	0.28	0.30	0.27	0.20	0.26
6	etylobenzen	0.48	0.46	0.46	0.47	0.43	0.39	0.39	0.40
7	p-ksylen	0.44	0.43	0.41	0.43	0.26	0.23	0.17	0.22
8	kumen	1.84	1.73	1.57	1.71	1.23	1.43	1.31	1.32
9	propylobenzen	0.24	0.23	0.24	0.24	0.18	0.22	0.22	0.21
10	mezytylen	0.20	0.16	0.20	0.19	0.12	0.11	0.19	0.14
11	p-cymen	0.78	0.71	0.72	0.74	0.70	0.75	0.67	0.71
12	butylobenzen	0.20	0.17	0.20	0.19	0.12	0.15	0.14	0.14
Sum:		163.15	171.29	179.44	171.29	9.73	9.83	9.26	9.61

Taking into account the average difference in vehicle concentrations, it can be concluded that the results of the tests confirm the general assumptions of the legal norms on improving the quality of exhaust gas. However, the presented concentrations of toxic compounds show minimal average differences in tested vehicles. In addition, it can be seen that in the exhaust emissions of Euro 6 compliant engines there are measurement points where the concentrations are higher than the concentrations of compounds present in the exhaust gas of Euro 4 compliant engines.

The determination of volatile organic compounds during standard road tests was not carried out. However, bearing in mind that the compounds tested are highly toxic and that they are subject to legal monitoring, their importance in total emissions to the atmosphere is becoming increasingly important. The study showed a minimal difference in concentrations of most of the chemical compounds in the tested vehicles. Therefore, it is important to consider the emission of volatile organic compounds from engine exhaust during vehicle approval tests.

Moreover, a high percentage of older vehicle models (i.e. most with Euro 3 and Euro 4 standards compliance) and a general increase in the number of cars on the roads, cause that the degree of air pollution does not improve in satisfactory level. According to the latest report of the European Environment Agency, air pollution significantly affects the health of Europeans, especially in urban areas. Although air quality has been improving steadily for years, air pollution remains one of the most serious environmental health hazards, decreasing the quality of life due to diseases and causing, according to estimates, 467 thousand premature deaths per year [21].

60 years ago, there were only 40 000 cars on Polish roads. Today, there are about 20 million of them. The fashion for having more than one car for a household appeared only a few decades ago. Passenger cars permanently integrated into the surrounding landscape, from a gigantic city to a small village. At the moment it is not possible to eliminate them at all. Transport by private passenger cars enabled cities to grow more easily and more dynamically. At the moment, only a reasonable, long-term plan, implemented in

cities and villages, which would limit the traffic of cars (including speed limits, closing individual streets, blockade of entry, for example, to the city centre) is able to improve air quality at large scale. However, note that the car can be reached everywhere, but not everywhere it is reached quickly enough.

Summary and conclusions

Volatile organic compounds as a group of toxic compounds that can cause serious disturbances in the functioning of a living organism should not be ignored during environmental emission testing. Presented results of the preliminary investigation should prompt researchers to discuss on include the determination of volatile organic compounds in engine exhaust to standard tests carried out prior to the admission of vehicles to the market.

The emission requirements for internal combustion engines are becoming more and more stringent. However, despite the emergence of new standards for the vehicles, the majority of vehicles authorized for road traffic are older car models, and besides, their number per year increases significantly. That is why every car user should pay attention to how to reduce unnecessary vehicle driving, in order to improve both his own health and contribute to the overall improvement of the atmosphere in the environment.

We can improve the condition of our environment, by controlling of toxins emission exhausting from internal combustion engines of passenger cars, including volatile organic compounds and also by the increase of the empathy of vehicle users on the problem of air pollution from mobile emitters.

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OZNACZANIE LOTNYCH ZWIĄZKÓW ORGANICZNYCH W SPALINACH SILNIKÓW SPEŁNIAJĄCYCH NORMY EURO 4 I EURO 6

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Abstrakt: Lotne związki organiczne wymieniane są jako jeden z najbardziej szkodliwych czynników zanieczyszczających powietrze. Wśród nich znajdują się węglowodory, które stanowią jedną z grup związków chemicznych, monitorowaną w procesie eksploatacji pojazdów. W artykule zwrócono szczególną uwagę na toksyczność LZO w aspekcie wprowadzanych zmian norm prawnych dotyczących emisji spalin silnikowych do atmosfery. W celu oznaczenia lotnych związków organicznych przeprowadzono badania gazów wylotowych

wybranych samochodów osobowych. Do badań wykorzystano metodę chromatografii gazowej. Wyniki zweryfikowano pod kątem wprowadzania coraz bardziej restrykcyjnych norm Euro. Podjęto dyskusję na temat kontroli emisji LZO z silników spalinowych przed wprowadzeniem samochodów do obrotu oraz postawy użytkowników pojazdów wobec niekorzystnego stanu środowiska związanego z emisją toksyn z emitorów mobilnych.

Słowa kluczowe: LZO, spaliny silnikowe, normy Euro, chromatografia