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TO THE QUESTION ON METHYL TERT-BUTYL ETHER

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Nowadays fuel oxygenates are substances produced in the extremely high amounts worldwide. Methyl tert-butyl ether, the main agent among those is the most extensively used in fuel-processing industry and as result possesses the highest risks to the environment and human health. Studies conducted to date provide reasonable data on environment migration potential of MTBE and human health concerns.

Key words: *Fuel oxygenates, MTBE, environment, health.*

Introduction. In the end of the XX beginning of the XXI century, a number of countries in the world encountered a problem related to environmental protection from methyl tert-butyl ether (MTBE, 2-methoxy-2-methylpropane) [1, 2], which is one of the most common chemical compounds introduced in the industry instead of tetraethyl lead (TEL) in the 1970s to increase the octane number of fuel in carburettes, and later injection engines for motor vehicles.

The main oxygenator in Ukraine is now and will remain for the near future MTBE, which has been used in many countries around the world for almost half a century with consumption volumes up to 22 million tons per year in the early 2000s [1]. During this time, MTBE has become one of the most common pollutants of atmospheric air, soils, surface and groundwater. Taking into account the current needs of the Ukrainian fuel and processing industry in the MTBE, which is approximately 200 thousand tons annually [1] and the lack of monitoring of this substance in environmental objects, in particular groundwater and groundwater, it can be argued that the MTBE carries a hidden threat to environmental ecology , and hence the health of the population of Ukraine. It is known that soil is a leading component of the biosphere and is involved in the formation of the chemical composition of atmospheric air, underground and surface water and food products. This means that the ecological state of soil has significant impact on the state of human health [1, 7]. The hygienic study of the behavior of MTBE in soil is an important step in preventing the contamination of this exogenous chemical substance in neighboring environments and preserving public health. In Ukraine, for the standardization of exogenous chemicals in soil, the following parameter is used – the maximum allowable concentration (MAC), scientifically substantiated by conducting a series of experimental studies [1, 2]. At the same time, for the effective sanitary-hygienic control of MTBE in the environment, it is necessary to develop and improve methods of quantitative determination of the specified exogenous chemical in appropriate media (soil, water, air, plants).

Main part. Therefore, the relevance of the work is justified by the need to study the processes of migration of currently used gasoline oxygenators on the example of MTBE from the soil in neighboring environments for establishing ecological and hygienic monitoring of synthetic components of unleaded gasoline in environmental objects and preservation of public health.

The development of the fuel processing industry, the improvement of the detonation properties of unleaded gasoline as well as reduction of the environmental load by products of its combustion is a continuous process. Thus, at the current stage of the development of technologies for increasing the octane number of fuel the use of additives – oxygenators of gasoline can not be avoided. The main agent among mentioned is methyl tert-butyl ether, especially in the countries of Eastern Europe, Asia and the regions of South America. At the same time, the aggressive use of methyl tert-butyl ether in the US, UK and Western Europe over the 30 years, since the 1970s, has led to a widespread of this substance in the environment and especially pollution of underground sources of drinking water supply of the population [1, 5, 6, 12]. Studies on toxicological properties of MTBE indicated a low acute toxicity of this compound, but chronic exposure to it raised doubts about its absolute harmlessness for human health, as some of the experimental animals showed carcinogenic effects [8, 9, 16]. Based on this it can be argued that MTBE needs comprehensive ecological, hygienic and toxicological studies as well as the continuous monitoring of its content in water sources in order to prevent the potentially adverse effects of the MTBE on public health.

Methyl tert-butyl ether is volatile organic compound, which is synthesized by the reaction of methanol and isobutylene, which in turn are natural gas derivatives, or can be obtained as a result of the fuel-processing (isobutylene). Since MTBE is an artificially synthesized compound, this substance is not determined in the environment under natural conditions [1]. The main purpose of the MTBE is adding it to gasoline – thus increasing the oxygen concentration in the fuel, which contributes to its more complete and "cleaner" combustion, and also increases the detonation threshold (octane number), which is an important qualitative indicator of current unleaded gasoline [10] Also, MTBE is used in the production of isobutylene and in high-performance liquid chromatography – as an eluent, as well as in medicine, as a solvent for cholesterol stones of the gall bladder [1, 11], however, this share of the total use of MTBE is negligible .

Analyzing data on the toxic effects of MTBE, it should be noted that the main ways of coming MTBE into the human body is inhalation and alimentary. In this case, MTBE is rapidly absorbed in the body. In humans, this process proceeds similarly to it in rodents. It has been assessed that when contaminated by MTBE air is inhaled, on average 38 % of this compound is retained in the human body, and when intaken alimentary – about 30 % of ether is biodegraded [16]. At the same time, with percutaneous impact on the skin, MTBE does not remain on the skin due to high volatility [16].

MTBE is spreading extensively in the mammalian organism, has a moderate dissolution capacity in the blood, compared with adipose tissue, where this figure is 7–10 times higher. It is probable that the biosorption of MTBE depends on the sex of the biological species. It is assumed that when MTBE enters the body, it reacts with α2uglobulin (a specific type of protein synthesized in the kidneys of male rats) [13, 16].

The main stages of biotransformation of MTBE in rats and humans are through oxidation, MTBE is metabolized to tert-butyl alcohol (TBA) and formaldehyde (proven only *in vitro*). Formaldehyde, in turn, breaks down into formic acid and carbon dioxide [16]. TBA is metabolized to 2-methyl-1,2-propenediol and 2-hydroxybutyric acid, as well as a small amount of free TBA, TBA-glucorinate and another conjugate (possibly TBA-sulfate) is also identified in the urine. In MTBE inhalation, more than half of the detained ether biotransforms to metabolites of urine and less than half exhaled in unchanged form [16].

The excretion of MTBE from blood despite the route of administration of this substance to rats is carried out with exhaled air and by metabolism to TBA and occurs rapidly – within 24 hours after the onset of exposure. Metabolites are derived primarily from urine; less than 2 % of MTBE was found in faeces. The half-life (DT_{50}) of MTBE in the plasma is 0.45–2.3 hours. The results of kinetic experiments indicated that the total removal of MTBE from the body does not depend on the way of its receipt and sex of the person and passes to animals and humans alike [8, 9, 16]. It is shown that after the action of MTBE, its metabolite TBA remains in the blood longer and in higher concentrations than MTBE. The half-life of TBA from the blood is approximately 3 hours in rats and about 10 hours in humans [16].

Acute toxic effects of MTBE administered via intragastrical route to rats manifested in the following symptoms:

- reflex folding;
- occurrence of pleural effusion;
- development of hypoactivity;
- the appearance of hypernuclei;
- a state of prostrate and muscle weakness.

The high dose of MTBE also provoked inflammation of the stomach and intestines. [8, 16].

Administered via inhalation route MTBE caused the next clinical manifestations in rodents:

- Inflammation of the mucous membranes of the eyes and nose;
- loss of coordination;
- Irregular and rapid breathing;
- ataxia;
- tremor;
- tearing;
- restriction of movements;
- hypoactivity.

The blood clots in the lungs were found In animals that survived [8, 9, 16].

The percutaneous effect of MTBE on rats at a dose of 2 g / kg was manifested only in a slight erythema at the site of application, without a sign of systemic toxicity. In 2 studies in rabbits (6.8 and 10.2 g / kg), erythematous effects and weak to moderate edema were observed, however, mortality was not observed, therefore LD_{50} was set at > 10 g / kg [8, 16].

Purposeful studies in humans were not conducted, however, in those who received treatment for dissolution of stomachs of the gall bladder, or bile ducts, and who were administered MTBE intrahepatically, or through a noseblearn catheter for up to 7 days at doses of 30–480 cm^3 [11, 16] 5–25 % of patients had moderate complaints, including nausea, drowsiness, vomiting and local feelings of heat. Volunteers with inhalation of MTBE were shown to have symptoms of toxic effects on the central nervous system [16].

MTBE may have an irritant effect on the skin, however, with no corrosive effect [8]. Despite the minor manifestations of the irritant effect of MTBE on the iris and conjunctiva of the eye, MTBE is considered as a chemical compound that does not have an irritating effect on the eye [8]. Studies on the sensitizing effect of MTBE were carried out on guinea pigs. The results led to the conclusion that the MTBE does not perform sensitization [8].

According to data [8, 9, 16], MTBE is not mutagenic – most studies of Salmonella typhimurium (both with and without metabolic activation); hepatocytes of rats; experiments with Drosophila melanogaster; a test for the detection of mutations in the genes of the lymphocytes of the spleen of mice; micronucleated erythrocytes of mice; cytogenetic rat bone marrow test and chromosomal abortion detection in rat bone marrow test were negative. Only the DNA method of comets on rat lymphocytes was positive, but the biological significance of the results of this test is questionable [8]. Instead, MTBE-formaldehyde and TBA-metabolizable products showed a positive reaction in some tests, such as the Ames test and experiments with lymphoma cells in mice.

In experimental studies on rats (Sprague-Dawley) with intramuscular administration of MTBE, the incidence of lymphoma and leukemia was increased in female rats with an increase in dose, however, no effects on lymphoid system were observed in other studies, suggesting a low significance of these results [1, 8]. The calculation of the background concentrations of MTBE for the average person showed that the person is exposed during the refueling of the car, and also if he lives at a distance of 50 m from the gas station. In this case, this person will receive a dose of 70–140 μg per day, which is equivalent to 1–7 μg / kg of body weight per day.

Assuming the worst-case scenario, a person can take about 30 micrograms of MTBE from drinking water per day, equivalent to 0.5 micrograms / kg per day. Based on the above, the background concentration of MTBE for the whole population was set at 0.004–0.005 mg / kg body weight per day [8].

It has been proved that the main oxygenator of gasoline is and remains for the near future is methyl tert-butyl ether, whose consumption in Ukraine as of today is more than 200 thousand tons per year, and content in gasoline of different grades varies from 12 % ("A-92") To 15% ("A-95" and "A-98").

It has been concluded that the priority sources of soil and groundwater pollution by methyl tert-butyl ether are the emergency leakage of gasoline as a result of depressurization of underground gas storage and gasoline spill during refueling of motor transport at gas filling stations. Despite the low accumulation capacity in the soil (0.01–0.06 %), methyl tert-butyl ether is capable of migrating rapidly into underground space, contaminating groundwater and spreading over long distances with water flow.

It has been shown that being in the soil 2-methoxy-2-methylpropane is very resistant to biodegradation, depending on the type of soil, its organic component, pH and concentration of oxygen in the soil. MTBE can undergo biodegradation in aerobic soil conditions, while it is almost resistant to decomposition under anaerobic conditions. The half-life of MTBE in the soil is 4–24 weeks, in underground waters 8-48 weeks. The main metabolites are: t-butyl formate, t-butyl alcohol, formaldehyde and acetone.

It has been revealed that methyl tert-butyl ether in the toxicological experiment when it enters the laboratory animal body is low toxic, with inhalation exposure – moderately toxic, has a weak irritant effect on the skin and mucous membranes, does not show allergenic activity and is characterized by weak cumulative properties. The values of the average deadly doses of methyl tert-butyl ether for rodents are: when administered in a stomach once in rats LD_{50} = 3800-4000 mg / kg, mice – 3665 mg / kg, when applied to the skin LD_{50}> 10,000 mg / kg, inhalation – LC_{50}> 85000–142000 mg/m^3. The maximum allowable concentration of methyl tert-butyl ether in the air varies from 0.5 to 2.6 mg / m^3 in different countries. The allowable daily dose of methyl tert-butyl ether is 0.3 mg/kg per day. The identification limit in the air on an organoleptic basis is 0.19 mg/m^3.

It has been found that methyl tert-butyl ether in the soil in concentrations up to 15 mg / kg is indifferent to sanitary-indicative microorganisms and has a low ecotoxicity level compared with DDT – $8.4 \cdot 10^{-5}$ ecotoxic.

It has been shown that methyl tert-butyl ether is capable of accumulation and translocation in concentrate plants, which are determined at a concentration of 0.015 mg/kg and more in the soil.

It has been proved that methyl tert-butyl ether is actively migrating from the ground to atmospheric air. Especially readily these processes occur in chernozem, where at the same time at the concentration of oxygenator of gasoline at the level of 0,05 mg/kg, the amount coming into the air reaches 0,5 mg/m^3, that is, the MAC of MTBE in the atmospheric air established in certain countries, in particular Russia.

It has been found that methyl tert-butyl ether disrupts the processes of self-purification in water, inhibits nitrification activity and reduces biochemical oxygen consumption. In high concentrations, MTBE has an inhibitory effect on certain sanitary-indicative bacteria of seawater.

Based on the results of the conducted research, the amount of the maximum allowable concentration of methyl tert-butyl ether in the soil at the level of 0,05 mg/kg is scientifically substantiated, and the limiting indicator of harmfulness is migratory and air.

The analytical practice of the methods of the vapor phase gas chromatographic analysis of soil, water and plants on the content of MTBE was developed and implemented. The methods are selective, highly sensitive and in line with current requirements for methods for the determination of exogenous chemicals. The limits of the quantitative determination of MTBE are: 0.09 mg/m^3 in the atmospheric air, 0.017 mg/dm^3 in water, 0.02 m /kg soil, 0.6 mg/kg in plants.

Given the lack of a unified view of the possible impact of methyl tert-butyl ether on human health, it is necessary to introduce continuous monitoring of this exogenous chemical in the environment, in particular in the soil of land plots adjacent to gas stations, to prevent the pollution of sources of drinking water supply and to prevent the migration of methyl tert-butyl ether to the human body.

CONCLUSIONS

Thus, during the thorough analysis of the peculiarities of the toxic properties of methyl tert-butyl ether, when conducting own research, the peculiarities of the behavior of methyl tert-butyl ether in the soil and neighboring media, the levels of accumulation in the tissues of the investigated plants, the effect on the processes of soil and surface water self-purification allowed to scientifically substantiate the MAC of methyl tert-butyl ether in the soil. Compliance with this standard will make it impossible to contaminate 2-

methoxy-2-methylpropane of the environmental objects, in particular atmospheric air and groundwater, and will also contribute to the preservation of public health.

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К ВОПРОСУ О МЕТИЛ ТРЕТ-БУТИЛОВОМ ЭФИРЕ

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На сегодняшний день, оксигенаторы бензина являют собой вещества производимые в екстремально огромных количествах во всем мире. Метил трет-бутиловый эфир, будучи основным из таких агентом и наиболее экстенсивно используемый в нефте-перерабатывающей промышленности, как результат несет наивысшие риски окружающей среде и человеческому здоровью. Исследования проведенные раннее дают обоснованную информацию о возможностях миграции МТБЭ в окружающей среде и обеспокоености касательно его влияния на здоровье человека.

Ключевые слова: *оксигенаторы бензина, МТБЕ, окружающая среда, здоровье.*

ДО ПИТАННЯ ПРО МЕТИЛ ТРЕТ-БУТИЛОВИЙ ЕФІР

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На сьогоднішній день, оксигенатори бензину являють собою речовини, що виробляються в екстремальних знаних кількостях в усьому світі. Метил трет-бутиловий ефір, будучи основним з таких агентів, найбільш екстенсивно використовується в нафто-переробній промисловості і, як результат, несе найвищі ризики навколишньому середовищу і людському здоров'ю. Дослідження

проведені донині дають обґрунтовану інформацію про можливості міграції МТБЕ в навколишньому середовищі і стурбованість щодо його впливу на здоров'я людини.

Ключові слова: *оксигенатори бензину, МТБЕ, навколишнє середовище, здоров'я.*