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ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS AND ALIPHATIC HYDROCARBONS IN ACID TAR POND AND THEIR ENVIRONMENTAL AND HEALTH RISKS

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This article focuses on the chemical characterization of acid tars. The introduction describes the basic characteristics of acid tars as old ecological burdens and also it describes the pond Predajna I located in the Slovak Republic, which served as the point of delivery of acid tar. The methodology of the study points to the possibility of fractionation samples of acid tars using a Soxhlet apparatus and the subsequent use of gas chromatography with mass selective detector for the analysis of organic components in the sample. The results of the analysed samples indicate the presence of specific aliphatic hydrocarbons and PAHs which have a negative impact on human health and the surrounding environment.

Key words: acid tars, environmental burden, PAHs.

АНАЛІЗ ПОЛІЦИКЛІЧНИХ АРОМАТИЧНИХ І АЛІФАТИЧНИХ ВУГЛЕВОДНІВ У КИСЛОТНОМУ ГУДРОНОВОМУ СТАВКУ ТА ЇХ РИЗИК ДЛЯ ЗДОРОВ'Я І НАВКОЛИШНЬОГО ПРИРОДНОГО СЕРЕДОВИЩА

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Ця стаття присвячена хімічній характеристиці кислих гудронів. Вступ описує основні характеристики кислих гудронів як старих екологічних навантажень, а також описує ставок Predajna 1, розташований в Словацькій Республіці, який слугував місцем доставки кислого гудрону. Методологія дослідження вказує на можливість фракціонування зразків кислих гудронів із використанням апарату Сокслета, і подальше використання газової хроматографії з мас-селективним детектором для аналізу органічних компонентів у зразку. Результати аналізованих зразків вказують на присутність специфічних аліфатичних вуглеводнів і поліароматичних вуглеводнів, які чинять негативний вплив на здоров'я людини і навколишнє середовище.

Ключові слова: кислі гудрони, екологічна нагрузка, поліциклічні ароматичні вуглеводні.

PROBLEM STATEMENT. Acid tars are normally characterized as tars of high sulphuric acid content and arise from the refining of oils by the addition of sulphuric acid, thereby containing sulphonated organic compounds (Nancarrow, Slade, Streeds, 2001).They are semi-solid residues from petroleum refining produced due to inadequate processing technologies. This hazardous waste was placed into excavated or natural depressions in the ground surface and today they represent a serious environmental problem. They are characterized as old environmental burdens. Old environmental burdens of acid tars are noxious for soil, air, ground and surface water. One of the characteristics of hazardous waste is their corrosivity associated with low pH values. The chemical composition of acid tars can be referred to as another hazardous characteristic. It is diverse and contains a lot of toxic substances. It is necessary to characterize their composition in as much detail as possible to identify the environmental risk posed by acidic tars in the form of old environmental burdens. The acid tars composition can be different depending on the production process, therefore it is necessary to carry out a separate analysis of each location with an acid tar.

Polycyclic aromatic hydrocarbons (PAHs) are products of incomplete combustion or pyrolysis of various organic materials. Their ubiquity in the environment leads to measurable levels of exposure. However, such exposure varies strongly within different regions in Europe.

Some PAHs with four or more rings are suspected to be have a human-cancerogenic feature. Therefore the occupational and/or environmental exposure to PAHs may represent a significant health risk. Since PAHs are always present in complex mixtures consisting of up to 100 or more different PAHs, the related exposure has to be taken as a combined exposure in any case.

Traditionally, the human exposure to PAHs is assessed by air quality measurements. Therefore, biological monitoring is being used to evaluate the human health burden associated with exposure to PAHs.

Old environmental burden - Predajna I

The acid tar pond Predajna I is located in Central Slovakia in the cadastral area of the village Predajna (GPS coordinates: 48° 49' 14.12" N 19° 29' 00.4" E). The territory of the ponds is located in the Low Tatras National Park covering the area of 10,577 m^2 while the volume of acid tars represents 100,000 m^3 (Michaeli, Boltižiar,

2010). The present waste had been produced by Petrochema Dubová in the period 1964 – 1974. In 1974 the pond was closed down and another one – Predajna II - was built about 200 meters westward. In 1975 the pond Predajna I threatened to overflow to the surrounding environment. In order to ensure the pond against ingress of rainwater, certain precaution measures were taken to overlap the pond. Overlapping is currently inoperative; the coverage has been destroyed and submerged under the surface. (Samešová, Ladomerský, Hroncová, 2007).

As demonstrated by Ševčíková, Batošová, Soldán (2013), the pond is characterized by low pH in the top layer (about 1.2). The low pH value is conjointly dangerous to humans (causing skin corrosion) and to the surrounding fauna and flora.

Another risk is related to the chemical composition of acid tars. In the case of outpouring of acid tar pond or leaking into the groundwater, toxic substances can contaminate the environment and therefore knowing the composition of acid tars is crucial. This article focuses on the qualitative characterization of PAHs contained in the pond Predajna I.

EXPERIMENTAL PART AND RESULTS OBTAINED. In order to carry out a chemical analysis, the samples were taken from the bottom layer of the acid tar pond Predajna I from the depth pf about 2.5 meters. The bottom layer contains a dark resinous material with the density of 1780 kg/m^3.

Preparation sample

The sample of acid tars was prepared and extracted according to the procedure Kolmakov et al 2006. The weighed sample of acid tar was placed in a glassevaporating dishand heated to the temperature close to 100 °C. After transforming the sample into liquid, a fivefold (bymass) amount of distilled water was added and stirred for 30 min. The sample was cooled and aftwerwads separated into an organic phase and an aqueous phase. The main portion of water was decanted and the remaining sample was repeatedly heated and dried at 150–180°C until the complete removal of residual emulsified water (Kolmakov et al 2006).

Extraction sample

The fractionation sample of acid tar was performed by the method developed in accordance with Kolmakov et al in 2006. About the 5g preparation sample was weighed on an analytical balance. The cartridge with the weighed sample was placed into the extractor of a Soxhlet apparatus. A 250-ml flask of the Soxhlet apparatus was filled with 200 ml of petroleum attached to the extractor together with a bulb-type reflux condenser and heated to boiling. Soluble compounds overflow to the flask through the siphon and this process continues for about six hours (until the solvent becomes completely colourless). The extract collected in the flask is a mixture of hydrocarbons and resins and an insoluble residue in the cartridge contains asphaltenes, carbenes, carboids, and mechanical impurities. After the completion of the process the flask with a solution of hydrocarbons and resins in petroleum etheric is replaced by a flask with benzene. Benzene is taken at the same amount as in the previous step, and the process is repeated via the same scheme for about six hours until the extracting agent outflow becomes completely colourless. The procedure with benzene is used to extract asphaltenes. The benzene is used to extract asphaltenes. The petroleum ether and benzene are subjected to fractional distillation to recover solvents for their subsequent use in analysis. The concentrate of asphaltenes is placed in a preliminarily weighed flask and evaporated at 120–130°C. After cooling, the flask is weighed again and heating is repeated to constant weight. The mass fraction of asphaltenes in the sample is determined in terms of the mass of the starting sample of the acid tar product (Kolmakov et al 2006).

Carboids, carbenes and mechanical impurities were not separated. Their amount was determined by the difference in the mass of the cartridge with these components and the same cartridge before the experiment (Kolmakov et al 2006).

The solution of hydrocarbons and resins obtained in course of the first stage of extraction is evaporated to the formation of an oily dark brown liquid. The mass of the concentrate is determined by the difference in mass of the flasks and a concentrate of hydrocarbons and resins is poured into a beaker with an eightfold excess (by mass %) of alumina activated at 250°C. The resulting mixture is thoroughly stirred and left still for six hours. Resins are more readily adsorbed into alumina than hydrocarbons. Then, the contents of the beaker are transferred to a new, single-walled thimble (no weighing is required) which was loaded into Soxhlet apparatus. The flask is filled with petroleum ether. Then, the contents of the beaker are transferred to a new, single-walled thimble, which was loaded into Soxhlet apparatus. The flask is filled with petroleum ether. The hydrocarbon part is washed out of the sorbent during extraction and hydrocarbon extraction is completed when the extracting agent that outflows from the siphon of the extractor becomes absolutely colourless. This procedure usually takes 3–4 h. After the cooled apparatus is petroleum ether solution of hydrocarbons is removed from the flask, and the solvent is distilled off of this extract. The hydrocarbon concentrate is placed into a preliminarily weighed bottle and dried at 125°C to constant weight. Then, the percentage of hydrocarbons is determined (Kolmakov et al 2006).

Next, the concentration of resins in the analysed sample of the acid tar is determined. For this purpose, resins from the adsorbent are extracted with an alcohol–benzene solvent (4:1 by volume ethanol–benzene). The blend from Al_2O_3 remaining in the cartridge after the previous operation. Desorbed resins are well soluble in an ethanol–benzene mixture. (Kolmakov et al 2006)

Adsorption Separation of Hydrocarbon Fractions

The sample of hydrocarbon fraction was prepared of method SPE Application Guide Sample Preparation by Solid Phase Extraction, Application 130, Macherey-Nagel. We have applied about 250µl sample hydrocarbons to the column (filling: unmodified, weakly acidic

silica) and aspirate or force it into the adsorbent with 2 x 1 ml n-hexane. Then an extract was analysedby GC/MS.

PAHs and aliphatic hydrocarbons analysis

PAHs and aliphatic hydrocarbons were analysed by GC / MS. For the determination we used the sample of hydrocarbon fraction.Method EPA8270C - Semi-volatile organic compounds by GC/MS was adapted for the analysis. The analysis was performed using a Agilent Technologies 7890 A gas chromatograph coupled to a Agilent Technologies 5975C mass spectrometer equipped with a split/splitless injection. Helium gas was used as the carrier gas and as analytical column was used Agilent Technologies HP- 5MS (5% phenyl-95% methylsiloxane) 30 m x 0.250 mmID x 0.25 µm.The column was programmed at 40°C for 6min and then ramped to 320 °Cat10°C/min, after which it washeld at 320°C for 6min, for a total running time of 40min. The attempts were made to identify unknown compounds using the library software of the GC/MS by comparing unknown spectra with the library of known spectra.(Sunday, Stegemann A, Amitava, 2010)

Results and discussion

As follows from the data presented in Table 1, anacid tar contains considerable share asphaltenes, carbenes, carboids and hydrocarbons.The sample in addition contains much lower amounts of resins and mechanical impurities. Kolmakov et al (2006) indicates that relatively high proportion of hydrocarbons in the starting acid tar is beneficial to the preparation of asphalt compositions. The representation of hydrocarbons in the sample of acid tars is relatively high. From this point of view it would be a suitable material to the preparation of asphalt compositions. Besides the sample acid tar contains a high amount of carbenesand carboids and these components, as argued by Kolmakov et al (2006), can excerce a negative effect on the quality product. Carbenes and carboids in course of thermal treatment of the starting acid tar; as a result, their relative amount in the final product decreases sharply (Kolmakov et al 2006).Carbenes and carboids components can be eliminated by using the thermal cracking method.

Table 1 – Fractional composition of the acid tar in pond of Predajna I

Fraction	Content [%]
Asphaltenes	35.85
Carbenes andcarboids	30.65
Hydrocarbons	24.45
Resins	1.38
Mechanical impurities	0,43

As disclosed by Nancarrow et al. (2001), PAHs are complex, multi-ringed hydrocarbons of moderate to high molecular weight, moderate to high toxicity and moderate to low mobility in the environment. From the results of the chromatogram (Fig. 1), it can be assumed that acid tars contain PAHs and aliphatic hydrocarbons bearing an ecological and human health risk (Table 3). As reported by Hao and Smith (2008), acidic tars are able to migrate across the surface or through cracks within tens of meters from their original locations.

This fact along with the results confirming the presence of PAHs and aliphatic hydrocarbons, demonstrates high risk exposure to the surrounding environment and human health. Hazardous substances and the risks posed are described in Table 2. Generally speaking, theses substances can irritate eyes and respiratory system; they can cause cancer and they are very toxic to aquatic organisms.

Table 2 – Results PAHs and aliphatic hydrocarbons analysis(ECHA 2014)

PAH	Molecular formula	Hazards
benzene, 1,3dimethyl-	C_8H_{10}	Causes serious eye damage. May cause respiratory irritation. Suspected of damaging fertility or the unborn child. Harmful to aquatic life with long lasting effects.
anthracene	$C_{14}H_{10}$	Causes skin irritation. Causes serious eye irritation. May cause cancer. Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
naphthalene	$C_{12}H_{12}$	Harmful if swallowed. Suspected of causing cancer. Very toxic to aquatic life with long lasting effects
benzene, 1-ethenyl-2-methyl-	C_9H_{10}	Flammable, Harmful: May cause lung damage if swallowed
Aliphatic hydrocarbons		
tetradecane	$C_{14}H_{30}$	Harmful by ingestion, inhalation or skin absorption. Irritant. May significantly bioconcentrate in fish and aquatic organisms.
dodecane	$C_{12}H_{26}$	May be fatal if swallowed and enters airways. Repeated exposure may cause skin dryness or cracking

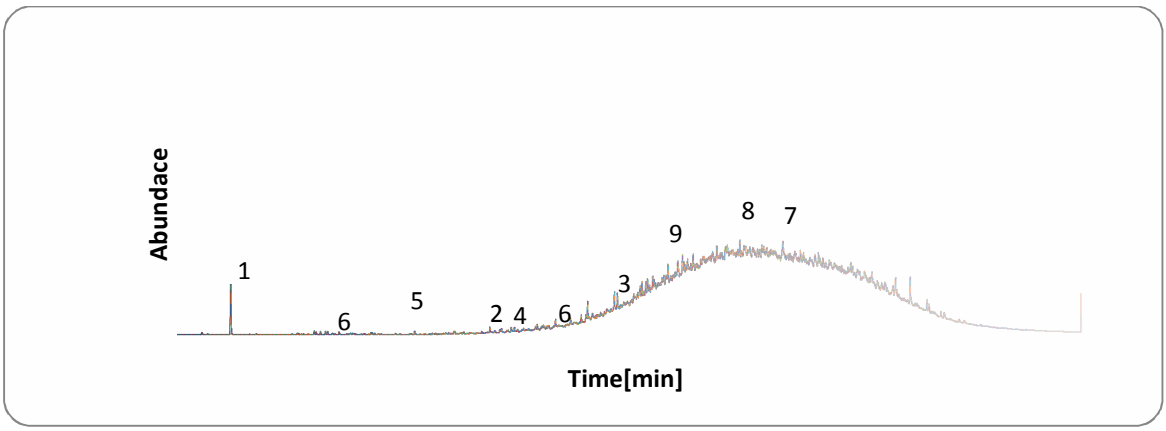

Figure 1 – Chromatograph for aliphatic fraction of acid tar in Predajna I
1 – benzen, 1,3dimethyl-, **2** – tetradecane, **3** – anthracene, **4** – naphtalen, **5** – dodecan, **6** – benzene, 1-ethenyl-2-methyl-, **7** – 7,8-epoxylanostan-11-ol,3acetoxy-, **8** – phorbol, **9** – 1-Heptatriacotanol

CONCLUSIONS. Based on the measurement results, it can be conclude that the pond in stores contains chemicals that are hazardous to the environment and human health. From the ecotoxicological point of view, appears as the most dangerous contaminating the aquatic environment, which could be fatal to aquatic organisms. Since the area has the tailings present a real risk is necessary to select a permanent and sustainable remediation option for the site. Based on these results it is possible to determine the appropriate processing method of acid tars as the method of thermal cracking. Such modified acidic tars can be used as additives for asphaltenes.

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АНАЛИЗ ПОЛИЦИКЛИЧЕСКИХ АРОМАТИЧЕСКИХ УГЛЕВОДОРОДОВ И АЛИФАТИЧЕСКИХ УГЛЕВОДОРОДОВ В КИСЛОТНОМ ГУДРОНОВОМ ПРУДУ И ИХ РИСК ДЛЯ ЗДОРОВЬЯ И ОКРУЖАЮЩЕЙ СРЕДЫ

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Эта статья посвящена химической характеристике кислых гудронов. Введение описывает основные характеристики кислых гудронов, как старых экологических нагрузок, а также описывает пруд Predajna 1, расположенный в Словацкой Республике, который служил местом доставки кислого гудрона. Методология исследования указывает на возможность фракционирования образцов кислых гудронов с использованием аппарата Сокслета и дальнейшее использование газовой хроматографии с масс-селективным детектором для анализа органических компонентов в образце. Результаты анализируемых образцов указывают на присутствие специфических алифатических углеводородов и ПАУ, которые оказывают негативное влияние на здоровье человека и окружающую среду.

Ключові слова: кислые гудроны, экологическая нагрузка, полициклические ароматические углеводороды.

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