Occupational exposure to polycyclic aromatic hydrocarbons in various technological processes i

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) occur as needles, plates, crystals, leaflets, or prisms ranging from colourless to pale yellow to golden yellow. Solubility characteristics vary for each PAH, but in general, they are slightly soluble to insoluble in ethanol, and are soluble to slightly soluble in acetic acid, benzene, acetone, toluene, xylene, 1,4-dioxane, and other organic solvents. PAHs are insoluble in diethyl ether and petroleum ether, and most are insoluble in water.

PAHs are used only in biochemical, biomedical, laboratory and cancer research. They are present in coal tar, coal tar pitch, creosote, bitumens and asphalt. PAHs form as a result of incomplete combustion of organic compounds. The primary source of PAHs in air is the incomplete combustion of wood and fuel for residential heating. PAHs are found in gasoline or diesel motor vehicle exhaust, by-products of open fires or refuse burning, coke tars or coke oven emissions, mineral oils, industrial smoke and soot, cigarette and cigar tobacco and smoke, tar, or smoke condensates, and charcoal-broiled foods.

Polycyclic aromatic hydrocarbons belong to group of compounds that have been classified by International Agency for Research on Cancer (IARC) as suspected carcinogenic to human. The value of Polish Maximum Admissible Concentration (MAC) – 2 $\mu g \cdot m^{-3}$ was established for nine gas phase and particle PAHs: anthracene, benzo[a]pyrene, benzo[a]anthracene, dibenzo[a,h]antracene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, benzo[g,h,i]perylene and indeno[1,2,3-c,d]pyrene. This MAC value refers to the sum of the concentrations of particular PAHs multiplied by their relative carconoogenic factors (Table 1).

The primary routes of potential human exposure to PAHs are inhalation of polluted air, wood smoke, and tobacco smoke, as well as ingestion of contaminated water, and foods normally containing microgram quantities of PAHs.

There is potential occupational exposure to PAHs for workers at coal tar production plants, coking plants, coal gasification sites, smoke houses, foundries, aluminium production plants, bitumen and asphalt production plants, road and roof tarring operations, municipal waste incineration sites, other facilities that burn carbonaceous materials, and cooking fume sources in the food and catering industries.

Due to PAHs carcinogenic and mutagenic properties researches have been taken concerning of assessment of occupational exposure in various technological processes in Central Institute for Labour Protection-National Research Institute.

TABLE 1. Physical and Chemical Properties of Determined Polycyclic Aromatic Hydrocarbons (PAHs) and Their Carcinogenic Factors

PAHs	Molecular Weight	Number of Rings	Boiling Point (°C)	Relative Carcinogenic Factor (Niebst & Lagoy, 1992)
Naphthalene	128.2	2	217.7	0.001
Acenaphthene	154.2	3	96.2	0.001
Fluorene	166.2	3	295.0	0.001
Phenanthrene	178.2	3	340.0	0.001
Fluoranthene	202.3	4	375.0	0.001
Pyrene	202.3	4	404.0	0.001
Chrysene*	228.3	4	448.0	0.010
Benzo[g,h,i]perylene*	276.3	6	500.0	0.010
Anthracene*	178.2	3	342.0	0.010
Benzo[a]anthracene*	228.3	4	437.5	0.100
Benzo[b]fluoranthene*	252.3	5	481.2	0.100
Benzo[k]fluoranthene*	252.3	5	480.0	0.100
Indeno[1,2,3-cd]pyrene*	276.3	6	530.0	0.100
Benzo[a]pyrene*	252.3	5	310.0–312.0	1.000
Dibenzo[a,h]anthracene*	278.4	5	269.0–270.0	5.000

Notes. *—PAHs for which a Polish Maximum Admissible Concentration (MAC) value has been established

METHODOLOGY

Air sampling was performed according to principles enabling the assessment of agreement of working conditions with MAC values given in Polish Standard PN-89/Z-04008/07.

For polycyclic aromatic hydrocarbons determination HPLC was used. Separation of PAHs were ensured by the column: Supelcosil^{TM} LC-PAH column with gradient mobile phase - acetonitrile : water and fluorescence detector, which wavelengths was programmed.

For sampling glass fibre filters and solid sorbent ORBO-43 tubes with the flow rate below 100 L min^{-1} was used. The filters and ORBO-43 were extracted ultrasonically with dichloromethane. The extract was then evaporated to dryness in nitrogen atmosphere. Purification of PAHs was achieved by the use solid phase extraction method on J.T.Baker-SPE Instrument. The lowest detection limit for each of fifteen PAHS was 0.001 μg·m^{-3} during sampling about 0.8 m^3 of air.

RESULTS and CONCLUSION

Assessment of occupational exposure to polycyclic aromatic hydrocarbons have carried out during production and using of bitumens, production of coal electrodes, for diesel engine equipments operator and in rubber industry. One hundred and twenty six full-shift personal samples were collected. The range of concentration of individual PAHs and range of exposure factors are presented in Table 2.
The investigation indicated that all of workers of our experiments were exposured to polycyclic aromatic hydrocarbons. Exposure factors – time-averaged weighed concentrations calculated on the basis of 9 individual PAH (anthracene,dibenzo[a,h]anthracene, benzo[a]pyrene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, chrysene, indeno[1,2,3–c,d]pyrene) concentrations. The highest concentrations of PAHs were determined in the breathing zone of vibratory press operator in coal electrodes production. The range of exposure factors in this industry was 2.13 – 3.81 μg/m^3, what exceed the MAC value. During production and using of bitumen's the range of exposure factors was 0 – 20.88 μg/m^3, in rubber industry - 0.003 – 0.13 μg/m^3, for diesel engine equipments operator - 0.006 – 0.43 μg/m^3.

Benzo[a]pyrene, for which the relative carcinogenic factor is 1, was detected in the air of 110 workplaces. The highest exposure factor (time-averaged weighed concentration) for this compound was 1 μg·m^{-3} and it was about 2 times lower than the Polish MAC value for benzo[a]pyrene.

TABLE 2. Average Concentrations of Individual Polycyclic Aromatic Hydrocarbons (PAHs) in various technological processes

PAHs	Concentration (µg/m^3)							
	production and using of bitumens		diesel engine equipments operator		coal electrodes plant		rubber industry	
	min - max	Range of exposure factors (µg/m^3) min-max	min - max	Range of exposure factors (µg/m^3) min-max	min - max	Range of exposure factors (µg/m^3) min-max	min - max	Range of exposure factors (µg/m^3) min-max
Naphthalene	0.09 – 5.5		0.106 – 84.37		1.74 – 4.18		0.535 – 18.99	
Acenaphthene	0.05 – 17.3		0.192 – 55,97		9.64 – 50.43		0 – 9.60	
Fluorene	0 – 0.23		0 – 0.20		9.40 – 15.74		0.002 – 0.01	
Phenanthrene	0 – 5.17		0.002 – 0.152		36,70 – 42.30		0.003 – 0.013	
Fluoranthene	0 – 0.35		0.003 – 0.441		19,50 – 21.63		0.005 – 0.099	
Pyrene	0 – 0.24		0 – 0.386		29.96 – 31.91		0.016 – 0.016	
Anthracene	0 – 0.27		0.002 – 0.041		17.07 – 15.07		0.002 – 0.014	
Benzo/a/anthracene	0		0 – 0.071		7,27 – 7,80		0.002 – 0.09	
Chryzene	0 – 0.078		0.003 – 0.032		3.37 – 3.55		0.004 – 0.009	
Benzo/b/fluoranthene	0 – 0.117	0 – 20.88	0.0004 –0.059	0.006 – 0.43	0.64 – 0.92	2.13 – 3.81*	0.0006 – 0.007	0.003 – 0.13*
Benzo/k/fluoranthene	0 – 0.064		0.0003 – 0.075		0.35 – 0.44		0.0002 – 0.005	
Benzo/a/pyrene	0 – 0.48		0.008 – 0.063		0.67 – 1.01		0.0006 – 0.011	
Dibenzo/a,h/anthracene	0 – 4.16		0 – 0.011		0.089 – 0.34		0.0004 – 0.002	
Benzo/g,h,i/perylene	0 – 0.56		0 – 0.115		0.53 – 1.24		0.008 – 0.01	
Indeno/1,2,3-c,d/pyrene	0		0 - 0.34		0.18 – 0.30		0.001 – 0.002	

Notes - *calculated value for 9. PAHs

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Frequently, in different technologies in Polish industry where PAHs might be present, concentration of benzo[a]pyrene only is measured, and its concentration is considered an exposure factor in assessing exposure to PAHs.

The results of our investigation confirm that measurements of only benzo[a]pyrene for occupational assessment of workers' exposure to PAHs is not correct and does not indicate the hazard to human health.

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