Occupational Exposure to Aromatic Hydrocarbons at a Coke Plant: Part II. Exposure Assessment of Volatile Organic Compounds

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Abstract: Occupational Exposure to Aromatic Hydrocarbons at a Coke Plant: Part II. Exposure Assessment of Volatile Organic Compounds: Grażyna BIENIEK, et al. Department of Molecular Biology, Biochemistry and Biopharmacy, Faculty of Pharmacy Medical University of Silesia, Poland—

The objective of the study is to assess the external and internal exposures to aromatic hydrocarbons in the tar and oil naphthalene distillation processes at a coke plant. 69 workers engaged as operators in tar and oil naphthalene distillation processes and 25 non-exposed subjects were examined. Personal analyses of the benzene, toluene, xylene isomers, ethylbenzene, naphthalene, indan, indene and acenaphthene in the breathing zone air allowed us to determine the time weighted average exposure levels to the aromatic hydrocarbons listed above. The internal exposure was investigated by measurement of the urinary excretion of naphthols, 2-methylphenol and dimethylphenol isomers by means of gas chromatography with a flame ionization detection (GC/FID). Urine metabolites were extracted after enzymatic hydrolysis by solid-phase extraction with styrene-divinylbenzene resin. The time-weighted average concentrations of the hydrocarbons detected in the breathing zone air shows that the exposure levels of the workers are relatively low in comparison to the exposure limits. Statistically significant differences between average concentrations of aromatic hydrocarbons (benzene, toluene, xylene isomers) determined at the workplaces in the tar distillation department have been found. Concentrations of the naphthalene and acenaphthene detected in workers from the oil distillation department are higher than those from the tar distillation department. Concentrations of naphthols, 2-methoxyphenol and

dimethylphenol isomers in the urine of occupationally exposed workers were significantly higher than those of non-exposed subjects. Concentrations of the 2-methoxyphenol and dimethylphenol isomers in urine were significantly higher for the tar distillation workers, whereas concentrations of naphthols were higher for the oil naphthalene distillation workers. Operators at the tar and naphthalene oil distillation processes are simultaneously exposed to a mixture of different hydrocarbons, mainly benzene and naphthalene homologues.

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Key words: Mixed exposure, Urinary metabolites, GC/FID analysis

Coke plants are known as sources of aromatic and polycyclic hydrocarbons and many other chemicals^{1–4}. Tar and naphthalene oil distillation processes emit a complex mixture of vapour and gases. The exposure to chemicals is usually assessed by both environmental and biological monitoring. Determination of volatile solvents and their metabolites in biological materials such as expired air, blood or urine, makes it possible to estimate the exposure levels to specific organic compounds that contaminate the environment. Biological monitoring was used to assess the exposure via both skin absorption and the gastrointestinal system. Biological monitoring of the mixed exposure is a growing field of interest in many occupational and toxicological investigative laboratories^{3, 5, 6}. Mixed exposure to aromatic hydrocarbons has previously been investigated by many authors^{7–12}.

The aim of the present study was to assess the mixed exposure of coke-plant workers to benzene and homologues, naphthalene, indane, indene and acenaphthene with air and biological monitoring. Biological monitoring was conducted by the analysis of urinary naphthols and phenols.

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Methods and Materials

1. Subjects

In this study, analyses were carried out in the summer months of 2001 and 2002. The investigated group comprised 69 workers, mean age 38 yr (range 20–65) exposed to aromatic hydrocarbons in a coke plant situated in Upper Silesia, Poland. Workers were engaged as operators in the tar distillation department (group A) and as operators in the naphthalene oil distillation department (group B). The survey was performed on the 5th day of a working week, by which time the metabolite excretion should have reached a plateau. The air and urine samples were collected on the same day during the day shift (6:00 AM–2:00 PM). To determine the physiological levels of urine phenols the 25 workers not occupationally exposed to aromatic hydrocarbons, mean age 28 yr (range 18–59) were investigated as a control. All subjects were smokers.

2. Air sampling and GC analysis of aromatic hydrocarbons

Air samples were collected in the breathing zone of the workers during the work shift. The sampling systems included a sorbent tube (SKC 226–01 charcoal tube, 100 mg/50 mg, SKC Inc., Eighty-Four, PA) and a low-flow sampling pump (type AFC 122 Casella Ltd, London, UK). The sampling flow rate was 0.5 l/min for 6 h (180 l). After sample collection, the analytes were released from the charcoal by treatment with 1 ml of carbon disulfide-methanol (60:1, v/v) in an ultrasonic bath for 15 min. The amount of the compound in the back-up showed no more than 10% of the compound in the sampling section. Otherwise the measurement was repeated.

Desorption efficiency for each target volatile compound was determined by analyzing three sorbent tubes. Each tube was spiked to the front section of the sorbent tube. Desorption efficiencies for benzene, toluene and xylene isomers were in the range 95–98%, whereas for naphthalene it was equal to 50%. The low desorption efficiencies for naphthalene were used for the concentration calculations.

The analysis of the charcoal extracts was performed with a Hewlett Packard, Model 5890 Series II gas chromatograph equipped with a flame ionization detector, an autosampler/autoinjector (HP7673) and an integrator (HP3396II) (Delaware, NY). Ethylbenzene, indan, indene and acenaphthene in air were analyzed gas chromatographically as previously described by Bieniek¹³.

Aromatic hydrocarbons (naphthalene, benzene, toluene, m+p-xylene and o-xylene) were analysed as previously described by Cisowska, Lusiak and Siwek [unpublished data]. In the abovementioned method, a capillary column Ultra 2 (25 m × 0.32 mm I. D., 0.52 µm film thickness (HP Part No. 19091 B-112) with injector and detector temperatures of 200 and 220°C, respectively,

was used. The following temperature program and GC parameters were applied: 40°C for 1 min, increased by 12°C/min to 140°C; held for 2 min; carrier gas, helium at a flow-rate of 2.5 ml/min; injection volume, 1 µl; splitless time, 1 min; split ratio, 1:30.

Ten duplicate analyses were performed at the lowest concentration of the calibrating curve, for all hydrocarbons, and the detection limit of the hydrocarbons was determined as three times the magnitude of the resultant standard deviation. For benzene, toluene, o-xylene, m+p-xylene and naphthalene the following detection limits: 0.75, 1.02, 0.47, 0.86 and 0.67 ppb, quantitation limits: 2.45, 3.57, 1.58, 2.85 and 2.22 ppb, and precision: 9.6, 3.5, 3.9, 3.3 and 3.7% were obtained, respectively.

3. Urinalysis

Urine samples were collected from the exposed workers during the last 4 h of the work shift (10:00 AM to 2:00 PM). Samples were kept at 20°C until analysis. Each sample was then thawed, and 10 ml was transferred to an Erlenmeyer flask. 1M hydrochloric acid solution was used to bring the sample to pH 5, and 5 ml of 0.1 M pH 5 acetate buffer was added. 25 µl of β-glucuronidase-arylosulfatase was added to each urine sample in order to hydrolyze conjugated metabolites. The solutions were incubated for 20 h at 37°C. 15 ml of the hydrolyzed sample was loaded onto SPE octadecyl (C₁₈) columns. The phenols were eluted with 3 × 0.5 ml of methanol-acetonitrile (10:1, v/v) into vials. The solvent was evaporated to dryness under a stream of nitrogen. The elute was dissolved in 1 ml of methanol-acetonitrile. The methanol-acetonitrile extract (1 µl) was subjected to GC analysis for quantification of phenolic metabolites according to the previous method described in a paper by Bieniek¹⁴. For urinary phenolic compounds, the following ranges, detection limit: 0.087 to 0.13 µmol/mol creatinine, quantitation limit: 0.18 to 0.32 µmol/mol creatinine, relative standard deviation: 3.2–18.4%, and accuracy: 1.6–26.4%, were achieved.

The creatinine content of each urine sample was analysed by the method based on the Jaffe reaction (Spinreact set, Spain) and determined spectrophotometrically.

4. Statistical methods

Statistical analyses were conducted with STATISTICA version 6.0 software. The parameters were characterized as median (measure of location), 5th percentile and 95th percentile (measures of spread) because the assumptions about the shape of the distribution could not have been set. Therefore, we decided to use nonparametric Mann-Whitney U test to make the comparisons between groups and the Spearman rank correlation coefficient to find the relationship between variables (toluene concentration in air and 2-methylphenol in urine). Only a few variables were log-normally distributed (Chi-Square Goodness—

Table 1. Median, and 5th and 95th percentile (unit ppb) of the hydrocarbons in air

Aromatic hydrocarbons					Personal air monitoring					<i>p</i> -value ^a
Group A (n=38)					Group B (n=31)					
Tar distillation department					Oil naphthalene distillation department					
	n ^b	Median	percentile		n ^b	Median	percentile			
			5 th	95 th			5 th	95 th		
Benzene	22	352.0	28.2	1046.1	24	129.4	17.5	415.1	<i>p</i> <0.01	
Toluene	38	227.1	14.9	820.0	20	16.1	2.4	289.1	<i>p</i> <0.001	
o-xylene	32	65.2	8.1	304.2	27	42.1	5.5	564.2	NS	
m+p-xylene	35	125.9	10.8	435.3	25	32.9	5.8	226.1	<i>p</i> <0.05	
Ethylbenzene	33	20.6	1.9	261.9	24	11.8	2.9	41.0	NS	
Naphthalene	27	120.2	11.4	392.2	31	316.2	16.4	1347.7	<i>p</i> <0.001	
Indane	22	4.4	1.4	135.1	26	9.2	1.7	34.1	NS	
Indene	32	4.5	1.7	40.0	27	6.7	1.5	34.3	NS	
Acenaphthene	20	1.4	0.6	6.3	26	2.5	0.8	8.9	<i>p</i> <0.05	

^aNS-not significant, ^bNumber of workers in whom the aromatic hydrocarbons were detected above the analytical detection limits

Table 2. Results of biological monitoring of workers: median, 5th and 95th percentile (unit ppb)

Metabolites in urine	Group A (n=38)				Group B (n = 31)				<i>p</i>	Group C (n=26)					
	Tar distillation department				Oil naphthalene distillation department					Control					
	n ^b	Median	percentile		n ^b	Median	percentile			n ^b	Median	percentile			
			5 th	95 th			5 th	95 th				5 th	95 th		
		μmol/mol creat.					μmol/mol creat.					μmol/mol creat.			
1-naphthol	27	215.3	23.9	736.5	31	321.4	36.3	901.7	NS	25	3.6	0.8	15.3		
2-naphthol	27	126.5	11.5	345.5	31	204.6	19.5	654.3	NS	25	2.3	0.2	11.3		
2-methylphenol	38	21.4	4.6	113.6	20	13.6	7.6	56.2	<i>p</i> <0.001	25	3.4	0.5	35.6		
2,4-+2,5-dimethylphenol	29	21.3	6.8	77.6	25	11.3	5.6	17.7	<i>p</i> <0.001	25	3.1	0.3	27.9		
3,4-dimethylphenol	25	21.8	5.6	44.6	23	8.6	2.3	31.6	<i>p</i> <0.001	25	3.2	0.3	19.7		
3,5-dimethylphenol	23	15.6	5.7	36.5	24	7.7	1.7	17.5	<i>p</i> <0.001	24	3.5	0.2	28.9		

creat.-creatinine, ^bNumber of subjects in whom the naphthols and phenols excreted were above the analytical detection limits, *p*-value for group A vs B

of—Fit Test), so analyses on correlations were also carried out after logarithmic transformation of these data, with the Pearson correlation coefficient (naphthalene in air and naphthols in urine). The results were accepted as statistically significant with a *p*-value <0.05.

Results

The time weighted average concentrations of benzene, toluene, xylene isomers, naphthalene, ethylbenzene, indan, indene and acenaphthene detected in the breathing zone air of the exposed workers are summarized in Table 1. It is apparent, that the workers are exposed to relatively low concentrations of aromatic hydrocarbons. For A-group of workers, concentrations of benzene, toluene,

m+p-xylene in air are higher (*p*<0.05) than for B-group, whereas concentrations of naphthalene and acenaphthene in air are higher for B-group than for A-group (*p*<0.05). For groups A and B, no statistically significant differences between average concentrations of o-xylene, ethylbenzene, indane and indene detected in the breathing zone, have been found.

Table 2 summarises the results for urinary naphthols, 2-methylphenol and dimethylphenol isomers for exposed workers (groups A and B) and non-exposed subjects (group C). Urinary metabolite levels were corrected against the creatinine concentration¹⁵⁾. In Table 2, significant differences (*p*<0.05) between average concentrations of urinary metabolites of non-exposed and

Fig.1. Relation between naphthalene in breathing-zone air and the sum of 1-naphthol and 2-naphthol in shift-end urine of operators of the naphthalene oil distillation.

exposed workers, can be seen. In the exposed group A urinary concentrations of 2-methylphenol and dimethylphenol isomers are significantly higher than in group B ($p < 0.001$), whereas the differences between concentrations of 1-naphthol and 2-naphthol are not statistically significant.

The correlation between the time-weighted average naphthalene exposure and the urinary naphthols level, during the shift, were examined by regression analysis. Figure 1 shows the correlation between the concentration of naphthalene in air and the sum of 1-naphthol and 2-naphthol concentrations in shift-end urine of operators of the naphthalene oil distillation. The correlation between the summary concentration of naphthols in urine and the naphthalene concentrations in the breathing zone air are statistically significant at $p < 0.001$.

It has been found that concentrations of urinary 2-methylphenol and dimethylphenol isomers for groups A are higher ($p < 0.05$) than for group B (Table 2). No significant association was found between urinary 2-methylphenol and toluene in air.

Discussion

During the tar and naphthalene oil distillation processes many chemicals are produced, which can contaminate the environment, e.g. benzene, naphthalene and its homologues, and phenols. According to the current standards of the occupational risk assessment, selected compounds, e.g.: benzene, naphthalene or phenol, have been assigned to study the levels of exposure to different

toxic chemicals^{1, 12, 16}.

Our results show that the time-weighted average concentrations of benzene, toluene, naphthalene, o-xylene, m+p-xylene, ethylbenzene and indene in the breathing zone air (Table 1) are relatively low in comparison to the exposure limits given by ACGIH¹⁷. The tar distillation process brings about higher exposure to benzene and its homologues, while higher risk of exposure to naphthalene and acenaphthene has been found at the naphthalene oil distillation process.

Occupational risk from aromatic hydrocarbons of the coke plant workers has been also estimated by the simultaneous determination of 2-methylphenol, dimethylphenol isomers, and naphthols in urine. As can be seen in Table 2, concentrations of the remaining phenol derivatives in urine are also estimated to be low. Nevertheless, significant differences ($p < 0.05$) are found between the concentrations of urinary metabolites detected in the urine of exposed workers (group A and B) and the reference group C. It has been found, that the concentrations of the dimethylphenol isomers in the urine of workers employed at naphthalene oil distillation are lower than in operators at the tar distillation process ($p < 0.05$).

A statistically significantly higher concentration of 2-methylphenol in the urine ($p < 0.01$) of workers employed at tar distillation process suggests a higher exposure to toluene or 2-methylphenol in this group than in group B. A survey of the literature shows, that the quantitative relation of urinary 2-methylphenol with time-weighted

average intensity of exposure to toluene has been investigated by several authors^{18–21}. In our work no statistically significant association was found between urinary 2-methylphenol and toluene in. This result can be partially explained by the metabolism of toluene under conditions of simultaneous exposure of coke plant workers to many chemicals present in large amounts in coal tar. Urinary 2-methylphenol is a very minor metabolite of toluene, accounting for as little as one thousandth of the amount to toluene adsorbed¹⁹. According to Inoue²², the urinary 2-methylphenol level is significantly reduced by smoking, drinking, and the two habits combined, therefore it cannot be considered reliable as a biological indicator of low-level exposure to toluene. The presence of 2-methylphenol in the urine of workers might be due to the exposure to toluene^{21, 23, 24} as well as to 2-methylphenol. Phenolic compounds comprise approximately 5% of naphthalene oil and 33% of carbolic oil²⁵. It is hard to determine the amounts of urinary 2-methylphenol deriving from exposure to toluene and to 2-methylphenol present in air.

Metabolites 2-methylphenol, dimethylphenols and naphthols, were present in the urine of non-exposed subjects. All subjects were smokers and smoking is a known source of naphthols⁸ and fenols^{26, 27}. The phenolic compounds found in the control group may reflect the uptake of small amounts of phenol derivatives from environmental sources. The reference group (C) comprises subjects who live in the same area as the workers, but who are not occupationally exposed. Phenols in ambient air have been extensively monitored in the highly industrialized Upper Silesia region of Poland²⁸. In 1997–1998 they ranged from 1.3 to 3.9 ppb, the highest values being recorded in the areas of greatest industrial concentration. Aromatic hydrocarbons are most often present in the environment as components of complex mixtures. Aromatic hydrocarbons from the petrochemical effluents ranged between 77 and 93%¹¹.

Naphthalene tends to be the predominant airborne compound in the processing and handling of coal tar products^{1, 16}, in iron foundry²⁹ and in creosote impregnation plants^{30, 31}. Naphthalene is metabolized almost exclusively to 1-naphthol and 2-naphthol¹⁶. Detection of naphthols in the urine is the most widely used indicator of naphthalene exposure^{32, 33}.

As seen in Table 2, concentrations of naphthol isomers are higher in the urine of workers engaged in the naphthalene oil distillation than in the tar distillation departments, but are not statistically significant. Differences between the concentrations of 1-naphthol and 2-naphthol detected in the urine of exposed and non-exposed subjects are statistically significant. Earlier investigations were able to determine simultaneously the presence of 1-naphthol and 2-naphthol in the urine of workers employed at the naphthalene oil distillation

process in a coke plant³². It was found that the concentrations of the naphthols were significantly higher than in the present results.

The data have shown that for most of the biomarkers studied, significant differences are found between the non-exposed subjects and those occupationally exposed to low concentrations of hydrocarbons. Biological monitoring of hydrocarbons provides better estimation of the absorbed substances than measurements of the corresponding contaminants in air, because the skin can be an alternative route of exposure.

Conclusions

In conclusion, the GC/FID analysis is useful for environmental and toxicological studies. Operators at the tar and naphthalene oil distillation processes are simultaneously exposed to a mixture of aromatic hydrocarbons. Concentrations of the hydrocarbons have been found to be relatively low in comparison to the exposure limits. Occupational risk from aromatic hydrocarbons in coke plant workers seems to result mainly from the diversity of the compounds identified in an occupational environment.

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