The presence of 1-naphthol in the urine of industrial workers exposed to naphthalene

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Abstract

1-Naphthol at concentrations ranging from 0.4 to 34.6 mg/l was found in urine collected directly after the end of the work shift from a group of industrial workers employed in distillation of naphthalene oil. The maximum excretion was found one hour after the end of the shift and the mean excretion rate was 0.57 mg/h. Coke plant workers exposed to naphthalene and other aromatic and polycyclic hydrocarbons also had 1-naphthol in their urine. Mean values were 0.89 mg/l (working with new technology) and 4.86 mg/l (working with old technology) and the excretion rates were 0.19 and 0.31 mg/h respectively. The maximum excretion was shifted to two to three hours after the end of the exposure. For non-exposed subjects the mean urinary 1-naphthol concentration was 120 µg/l and the excretion rate was 7.0 µg/h.

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1-Naphthol exists in animals as a metabolite of naphthalene.¹ It is excreted in urine as a sulphate or glucuronide conjugate.²⁻⁴ Keiser *et al* found 1-naphthol in the urine of people exposed to the insecticide "carbaryl".⁵

The presence of 1-naphthol was earlier found in urine collected from workers before and after exposure and its excretion seemed to be slowed under conditions of simultaneous exposure to aromatic and polycyclic hydrocarbons.⁶ This study investigates the excretion of 1-naphthol in more detail.

Materials and methods

The investigations were conducted under industrial conditions. All subjects were smokers.

Four groups of workers were investigated:

Group A: 75 operators exposed to naphthalene and other phenolic compounds during distillation of naphthalene oil.

Group B: 57 coke plant workers exposed to naphthalene, benzene, and other aromatic hydrocarbons, at coke plant I (old technology).

Group C: 66 coke plant workers exposed to naphthalene, benzene, and other aromatic hydrocarbons, at coke plant II (modern technology). In this case samples of air were taken constantly and naphthalene was measured in the air.

Group D: 24 subjects not occupationally exposed to naphthalene. Environmental exposure could not be excluded.

URINE SAMPLING

Samples of urine were collected as (1) voids of urine directly after the end of the work shift; (2) successive samples of urine collected for 24 hours from 26 workers.

ANALYSIS OF 1-NAPHTHOL IN URINE

The concentration of 1-naphthol in the hydrolysate of urine was determined spectrophotometrically after its separation by thin layer chromatography on polyamide gel with development in chloroform-methanol (99:1 v/v).⁷

Because of low concentrations of 1-naphthol in the urine of occupationally non-exposed workers gas chromatographic techniques were employed on these samples.

Values were corrected for a specific gravity of 1.024 and for creatinine content in the urine.

AIR SAMPLING AND ANALYSIS

Personal air sampling was performed with a battery operated pump (type AFC123 Casella Ltd, London) connected to a filter holder attached to the shoulder of the subject. Air was aspirated at a flow rate of 0.5 l/min through active carbon type H2. The naphthalene was released from the active carbon by treatment with 1 ml carbon disulphide in an ultrasonic bath for 15 minutes.

The content of naphthalene in the air samples was analysed by gas chromatography (Hewlett-Packard model 5890 II) with flame ionisation and a capillary column Ultra 1 (Lusiak T, Siwek A, unpublished data).

The error of the method was about 10% or higher for low naphthalene concentrations. For concentrations above 5 ng/µl the error was 5-6%.

STATISTICS

Geometric mean and geometric SD were calculated. Regression analyses were carried out with a program supplied by Statistical Graphics Corporation, US. Toxicokinetic calculations were carried out according to the method of Piotrowski.⁸

Results and discussion

The table presents values of concentration and excretion rate of 1-naphthol in urine collected directly after the end of the exposure

Concentrations and the excretion rate of 1-naphthol in urine

Group	No of subjects	Observed value (mg/l)	Values corrected for		
			Creatinine (mg/g)	Specific gravity 1.024 (mg/l)	Excretion rate (mg/h)
A	75	7.48 (2.187)	4.35 (2.734)	8.95 (2.745)	0.57 (2.068)
B	57	4.86 (2.465)	3.79 (2.128)	5.53 (2.084)	0.31 (1.954)
C	66	0.89 (1.783)	0.93 (2.293)	1.06 (2.502)	0.19 (2.454)
D	24	0.13 (1.868)	0.10 (2.514)	0.12 (2.464)	0.007 (1.786)

Values are geometric means (geometric SD).

Group A = operators of the distillation of naphthalene; group B = cokers of coke plant I (old technology); group C = cokers of coke plant II (modern technology); group D = non-exposed workers.

from operators of naphthalene oil distillation (A), coke plant workers (B, C), and subjects occupationally non-exposed to naphthalene (D). The results were log normally distributed. Concentrations of 1-naphthol presented in the table were the highest in the operators of the naphthalene oil distillation. This presumably results from the fact that naphthalene is the main component of naphthalene oil (73.6%).

Figure 1 presents the relation between the average naphthalene concentrations in breathing zone air during exposure and 1-naphthol

Figure 1 Correlation between naphthalene in breathing zone air and 1-naphthol in urine of coke plant workers. Lines and curves are calculated regression line (solid line in centre), 95% CIs (dotted curves close to regression line), and 95% CIs of individual samples (outermost dotted lines).

Figure 2 Urinary excretion of 1-naphthol as a function of time. (A) workers employed in distillation of naphthalene oil; regression equation for $t \leq 9$, $c(t) = 8.5(1 - e^{-0.18t})$; for $t > 9$, $c(t) = 8.5(1 - e^{-0.18t})e^{-0.18(t-9)}$; $k = 0.18/h$, $t_{1/2} = 4.0$ hours. (B) Coke plant workers; regression equation, $c(t) = 4.5(e^{-0.05t} - e^{-0.15t})$; $k_1 = 0.05/h$, $t_{1/2} = 14.0$ hours; $k_2 = 0.15/h$, $t_{1/2} = 4.6$ hours. c = concentration of 1-naphthol in urine; t = time from the start of exposure.

concentration in the urine of coke plant workers (group C) collected just after the end of the work shift. A linear dependence between the time weighted average naphthalene concentration in the air and 1-naphthol concentration in the urine for the original measured value, corrected for specific gravity 1.024 and corrected for creatinine content, was noted.

The urinary excretion of 1-naphthol as a function of time calculated from the beginning of exposure was examined (fig 2). Figure 2A presents data on 1-naphthol excretion in the urine of operators of naphthalene oil distillation during and after exposure. The excretion coefficient $k = 0.18/h$ indicates a half life of about four hours. The presented model gives a similar shape of excretion curves for 1-naphthol as found earlier for phenol.⁹ It is assumed that 1-naphthol in the urine of naphthalene oil operators is the result of exposure to naphthalene as well as low amounts of 1-naphthol which are found in the naphthalene oil.

In the group of coke plant workers exposed to naphthalene (in the absence of 1-naphthol) the excretion of 1-naphthol in urine (fig 2B) is described by a kinetic equation more appropriate for the "metabolic" model. The kinetic coefficients, 0.05 and 0.15/h may represent the metabolic conversion of naphthalene and rate of excretion, respectively. The numerical values of these coefficients were obtained as the best fits from computer imaging.

A comparison of the time course of 1-naphthol excretion in fig 2A and B may indicate differences between the kinetics of 1-naphthol and naphthalene respectively; naphthalene requires metabolic conversion before excretion. This process may be much slower compared with excretion alone and therefore some accumulation in the body under conditions of occupational exposure to naphthalene cannot be excluded.

For given concentrations of naphthalene in breathing zone air one would expect higher concentrations of 1-naphthol in urine than those obtained in our studies. This may be explained by the relatively low metabolism of naphthalene to 1-naphthol under conditions of simultaneous exposure of coke plant workers to chemical compounds present in large amounts in coal tar.

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