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ARTICLES

A Passive Chemical Dosimeter for Assessing Long-Term Exposure in Air Containing Aniline and Aniline Derivatives

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Abstract—A passive chemical dosimeter for assessing long-term exposure to toxic substances (aniline and its derivatives) in the atmosphere of inhabitable premises was described. The compounds to be determined were accumulated on an absorption filter due to a chemical reaction with a selective agent upon the many-hour exposure of the device. Analytical performance of chemical dosimeters (diffusion coefficients, chemisorption preconcentration rate, and detection limits) was evaluated. The concentrations of aniline, *p*-chloroaniline, 3,4-dichloroaniline, and *o*-toluidine in the air of chemical laboratories and smoking rooms were determined.

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The personal exposure to toxicants cannot be estimated by integrating the background contamination of outdoor or inhabited premises, because the environmental concentration of toxicants can change within hours or even minutes. Therefore, continuous and, what is important, personal assessments of exposure over a long time are necessary [1]. By exposure is meant any contact of an organism with a toxicant of a known concentration within a specified time [2]. Continuous analyzers cannot be used to solve these problems for economic reasons. Analytical technologies based on the principle of passive dosimetry, including their personal versions, are suitable for estimating long-term exposure to toxicants, their dose, and effect on humans [1, 3–7].

Aromatic amines and hydrazines are priority environmental contaminants. They belong to the most important classes of organic compounds and are widely used in chemical technology and pharmacy.

It was shown earlier that 4-chloro-5,7-dinitrobenzofurazan (BFZ) and 7-chloro-4,6-dinitrobenzofuroxan (BFO) are suitable for the selective and sensitive determination of amino compounds by HPLC, TLC, test methods, and flow-injection analysis [8–13]. These reagents can also be used as color agents in personal passive chemical dosimeters due to their high selectivity, sensitivity, and reactivity towards nucleophils.

The aim of this work was to develop a prototype and study the analytical parameters of passive chemical dosimeters for chemisorption preconcentration followed by the chromatographic determination of aniline and its derivatives in air based on the reaction of analytes with 4-chloro-5,7-dinitrobenzofurazan.

EXPERIMENTAL

A Hewlett-Packard HPLC 1100 chromatography system was used. The system includes an HPG1311A quaternary pump with a vacuum degasifier, a Reodyne 5525 HPG1328A manual sampler, a G1316A column thermostat, an HPG1315A diode-array detector, and an HPG1321A fluorescence detector with corresponding equipment and the 3D ChemStation G2170AA software for data processing. Components were separated on a Hypersil ODS column (4 × 250 mm ID) with a Hypersil ODS precolumn (4 × 50 mm ID). The sample volume was 20 μL.

Chromatographically pure acetonitrile and methanol (Kriokhrom, St. Petersburg) were used. Chromatographically pure water was obtained from a Simplicity 185 purification system (Millipore, France). If necessary, solvents were dried with 3A molecular sieves. 4-Chloro-5,7-dinitrobenzofurazan was synthesized by F.S. Levinson.

Commercial aniline, *p*-chloroaniline, 3,4-dichloroaniline, and *o*-toluidine were purified by distillation according to conventional procedures. Their purity was controlled by TLC and HPLC.

Silufol (silica gel fraction 0.1–0.3 mm) plates were used as the selective layer in passive dosimeters. To immobilize the reagents (BFZ and BFO), the absorbing layers of the filters were saturated with their acetonitrile solutions while controlling the reagent-to-adsorbent mass ratio. The adsorbent with the immobilized reagent was placed into the case of the dosimeter and fixed with a screw cap (Fig. 1).

To prepare amine vapor–air mixtures, analyte solutions in methanol with calculated concentrations were evaporated in a hermetic box. The homogeneous distribution of the compounds in the air was maintained

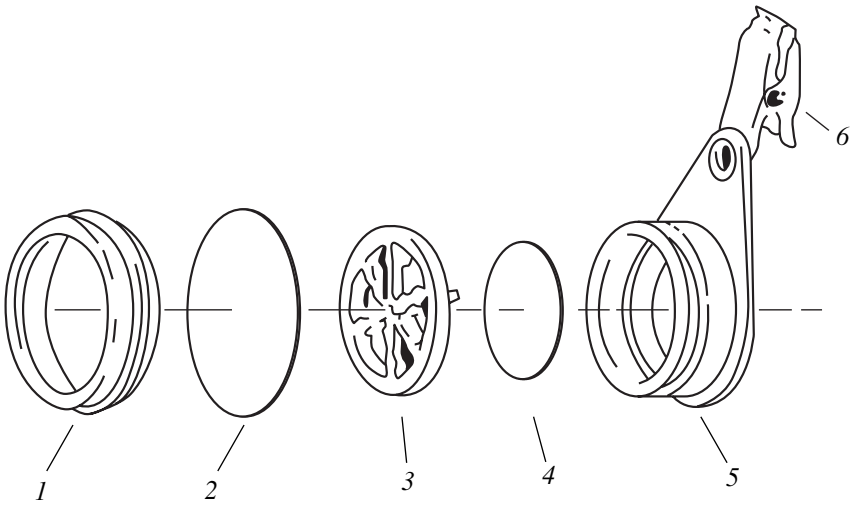


Fig. 1. Passive chemical dosimeter for determining the exposure to toxicants in air: (*1*) cap; (*2*) membrane; (*3*) diffuser; (*4*) absorption filter (adsorbent); (*5*) case; (*6*) clothespeg; geometrical parameters of passive chemical dosimeters: sorption surface area A, 3.8 cm^2; plate diameter D, 22 mm; diffusion path length L, 1 cm; dosimeter mass, about 20 g.

using a ventilator. The concentrations of compounds in the box were determined by chromatography using Rykhter absorption vessels.

In the long-term exposure of passive dosimeters (for more than an hour), constant concentrations of amino compounds in the air of the box were created by diffusing the analyte gas through a polymer tube. The analyte was introduced into a Teflon ampoule with an injection syringe and sealed. Nitrogen was passed through the thermostat to dilute the compound diffusing through the ampoule walls. The amount of the substance diffusing through the membrane was determined from the loss of the ampoule mass within the specified time [14, 15].

No data are available in the literature on the diffusion coefficients of amine compounds, except for aniline and *o*-toluidine; therefore, these coefficients were calculated from the equation for diffusion in air

$$D_i = \frac{0.001T^{1.75}\sqrt{\frac{1}{MWi}+\frac{1}{MWa}}}{P_a[(\Sigma V_1)^{1/3}+(\Sigma V_a)^{1/3}]^2},$$

where T is the temperature (K); MW_i and MW_a are the molecular weights of toxicants and air (28.8), respectively (g/mol); P_a is the pressure (atm); and ΣV_1 and ΣV_a are the molecular diffusion volumes of toxic amino compounds and air (20.1), respectively (cm^3/mol) [16].

The passive chemical dosimeters had the following geometrical parameters: sorption surface area A 3.8 cm^2; plate diameter D, 22 mm; diffusion path length L, 1 cm. The weight of the dosimeter was of about 20 g; therefore, it could be used as a personal dosimeter and worn, e.g., on the coat lapel. The dose of chemicals received by a human can be estimated from the amount of the inhaled air and the coefficient of toxicant absorption by the body.

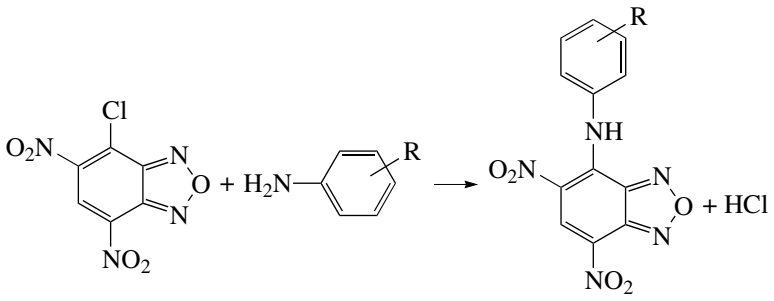
RESULTS AND DISCUSSION

The mass of an analyte migrating through the passive dosimeter to the adsorbent under chemisorption accumulation conditions can be found from the first Fick equation

$$m_i = D_iA/l(c_i - c_0)t,$$

where m_i is the mass of compound i found on the adsorbent (pg), D_i is the diffusion coefficient of compound i in the air (cm^2/min), A is the dosimeter cross-section (cm^2), l is the length of the diffusion zone (cm), c_i is the concentration of compound i in the ambient air (μg/m^3), c_0 is the concentration of analyte on the adsorbent surface before the exposure, and t is the time of exposure (min). D_iA/l is the effective chemisorption rate (ECR). In the presence of an ideal adsorbent ($c_0 = 0$), it can be calculated theoretically if the diffusion coefficient is known. The prototype of a personal passive chemical dosimeter for determining toxicants used in this work is shown in Fig. 1.

The chemisorption accumulation of toxicants as 5,7-dinitrobenzofurazan derivatives on the absorption filters of passive dosimeters occurred under operating conditions. The chemisorption preconcentration of analytes with these analytical devices can be described by the following reaction:



After the exposure, the round adsorbent plate was removed from the passive dosimeter, and 5,7-dinitrobenzofurazan aniline derivatives formed on the porous adsorbent were desorbed with methanol or acetonitrile under laboratory conditions. At this step, toxicants can also be determined visually from the substrate color if their concentration is at a level of several MPC. When present in concentrations of 0.05–30 mg/m^3, toxicants in the air can be determined by scanning the colorimetric properties of the adsorbent layer (integral intensities of red, green, and blue colors). For example, for toluidine, the inverse integral intensity of the above colors (1/RGB) was related to the toxicant concentration in the air by the regression equation

$$Y = 1.311X \text{ (mg/m}^3\text{)} + 0.042 \quad (r = 0.995 \text{ for } n = 12).$$

Desorption of amino compounds. The desorption of nonvolatile amine derivatives formed on the substrate surface is an essential step for the subsequent quantification of these compounds in the air by HPLC. To minimize the loss of analytes, the conditions for the elution of analyte derivatives from the silica gel layer with different solvents were studied. For this purpose, the synthesized analyte derivatives and the reagent used were immobilized on silica gel by saturating the adsorbent with their acetonitrile solutions. The mass of silica gel and the concentration of the saturating solution were controlled. After the solvent was evaporated, compounds immobilized on the substrate were washed off with three portions of methanol. The total solvent volume was 2 mL. The solutions obtained were filtered through a Teflon membrane and chromatographed; the mass of aryl amine derivatives on the absorption filter was determined. The recovery of the chemisorbed aryl amines was almost complete for all analytes and came to 97 ± 3%.

Effective chemisorption rate. The effective rate of chemisorption depends on the geometric parameters of the dosimeter and the diffusion coefficient of the amine to be determined. We found this value using the procedure described in [3]; it was calculated by the equation $U = DA/L$, where U is the effective rate of chemisorption in a passive dosimeter, D is diffusion coefficient (cm^2/s), A is the surface area of the adsorption plate in the dosimeter (cm^2), and L is the diffusion path length (cm). In the physical sense, sampling (absorption) rate is the volume of air from which the analyte diffuses into the adsorbent in a unit time.

The actual effective chemisorption rate was calculated from the equation $U = m/(ct)$, where m is the mass of the absorbed component (g), c is the component concentration in the air (g/cm^3), and t is the time of exposure (s). The calculated effective chemisorption rates are given in Table 1. The effective chemisorption rate varied from 9.3 mL/min for aniline to 6 mL/min for *o*-toluidine. The effective chemisorption rates were used to calculate toxicant concentrations in the air.

To study the chemisorption of aryl amine on the adsorbent as a function of the time of exposure, a series of similar chemical dosimeters was prepared. These dosimeters were placed in a box with a constant concentration of aryl amine. The time of exposure was varied from 10 min to 8 h. After exposure to the corresponding amine for different times, the chemisorption layers of dosimeters were subjected to desorption with solvents. From the chromatographic analysis of the extracts obtained, the mass of aryl amines chemisorbed on the absorption layer was determined. From the data obtained, the mass of aniline absorbed by the dosimeter was plotted as a function of exposure time; the plot was a linear function (Fig. 2). Similar studies were performed for other aromatic amines.

The mass of chemisorbed aniline as a function of its concentration in the air in testing the dosimeter for 1 h is shown in Fig. 3. The dosimeter response is linear in a wide concentration range (from 0.05 to 5 mg/m^3), which points to the possibility of determining aniline in the main ecological situations.

Selectivity of determination. In developing and manufacturing personal passive chemical dosimeters, special attention was given to their selectivity. The

Table 1. Main analytical parameters of the passive chemical dosimeters studied

Analyte	Diffusion coefficient, $D \times 10^{-2}$ (cm^2/s)	Effective chemisorption rate (mL/min)	Determination limit (μg/m^3)
Aniline	7.59	9.3 ± 0.8	3
p-Chloroaniline	6.92	8.8 ± 0.7	3
3,4-Dichloroaniline	6.44	8.1 ± 0.8	3
o-Toluidine	6.97	5.9 ± 0.6	5

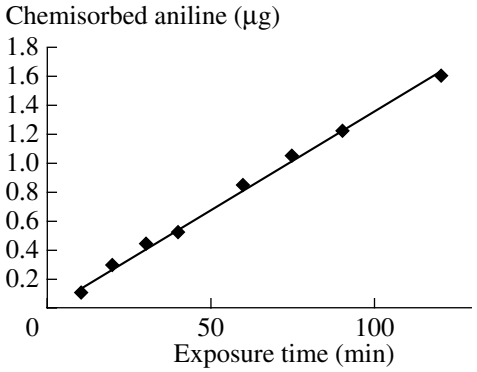


Fig. 2. Mass of aniline chemisorbed by a passive dosimeter vs. the time of exposure to toxicant in air.

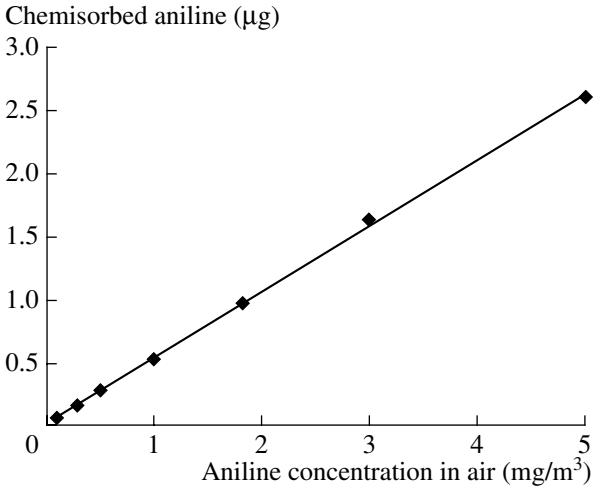


Fig. 3. Mass of aniline chemisorbed by a passive dosimeter as a function of its concentration in air for an exposure of 60 min.

effect of different atmospheric components on the determination of aniline, *p*-chloroaniline, 3,4-dichloroaniline, and *o*-toluidine was studied. Usual concentrations of alkanes, halogenated hydrocarbons, alcohols, and sulfur and nitrogen oxides in the air did not interfere with the chemisorption preconcentration of aromatic amines. Alkyl amines and ammonia present in the air also reacted with the reagent to form corresponding derivatives. The potential effect of these compounds can be eliminated using chromatographic separation. Under the conditions corresponding to the typical concentrations of alkyl amines and conventional air humidity, no effect of the above-mentioned compounds on the chemisorption preconcentration of aromatic amines followed by HPLC determination was found.

Determination of aniline and its derivatives. Personal passive samplers were tested under real conditions for determining aniline, 4-chloroaniline, and 3,4-dichloroaniline in the air of a chemical laboratory and a smoking room without active ventilation (Fig. 4).

The presence of aniline, *p*-chloroaniline, and 2,5-dichloroaniline in the air of the chemical laboratory after the exposure of the analytical device for 9 h was assessed by chromatography using the standard addition method (Fig. 4). Within this time, experimental studies with aniline, 4-chloroaniline, and 3,4-dichloroaniline were carried out in the laboratory. After the exposure, passive dosimeters were placed in a sealed desiccator. The compounds accumulated in the chemisorption layer of passive dosimeters were chromatographed the next day.

Our results indicate that the highest concentration of amines was observed near the ventilator, which was due to the observance of safety measures. Taking into consideration the effective rate of the chemisorption preconcentration of toxicants, the weighted average concentration of the above aromatic amines in the air was in the range from 9 to 30 μg/m^3 (Table 2).

Aromatic amines in tobacco smoke form because of the pyrolysis of tobacco amino acids under smoking conditions [17–20]. Tobacco smoke is usually divided into two flows (mainstream and sidestream), differing in composition and consequences for human health, and humans inhaling smoke are divided into active and passive smokers [17]. The mainstream smoke forms in the burning and hot zones of cigarettes and cigars during deep inhalations. About 35–40% of the cigarette tobacco burns down upon the smoker's inhalations. During an inhalation, a large volume of oxygen passes through the cigarette, which results in intense oxidation

Table 2. Determination of aniline and its derivatives in the atmosphere of laboratory and smoking room after a many-hour exposure of an analytical device ($P = 0.95$; $n = 6$)

Analyte (time, h)	Test atmosphere	Added (μg/m^3)	Found, $X \pm \Delta X$ (μg/m^3)
Aniline	Box	3.5	3.9 ± 0.9
Aniline, *p*-chloroaniline, 3,4-dichloroaniline (14 h)	University compartments	–	Not detected
Aniline (14 h)	Chemical laboratory	–	30 ± 2
p-Chloroaniline (14 h)	Chemical laboratory	–	21 ± 2
3,4-Dichloroaniline (14 h)	Chemical laboratory		9.1 ± 0.8
Aniline (8 h)	Cigarette smoke	–	15 ± 2

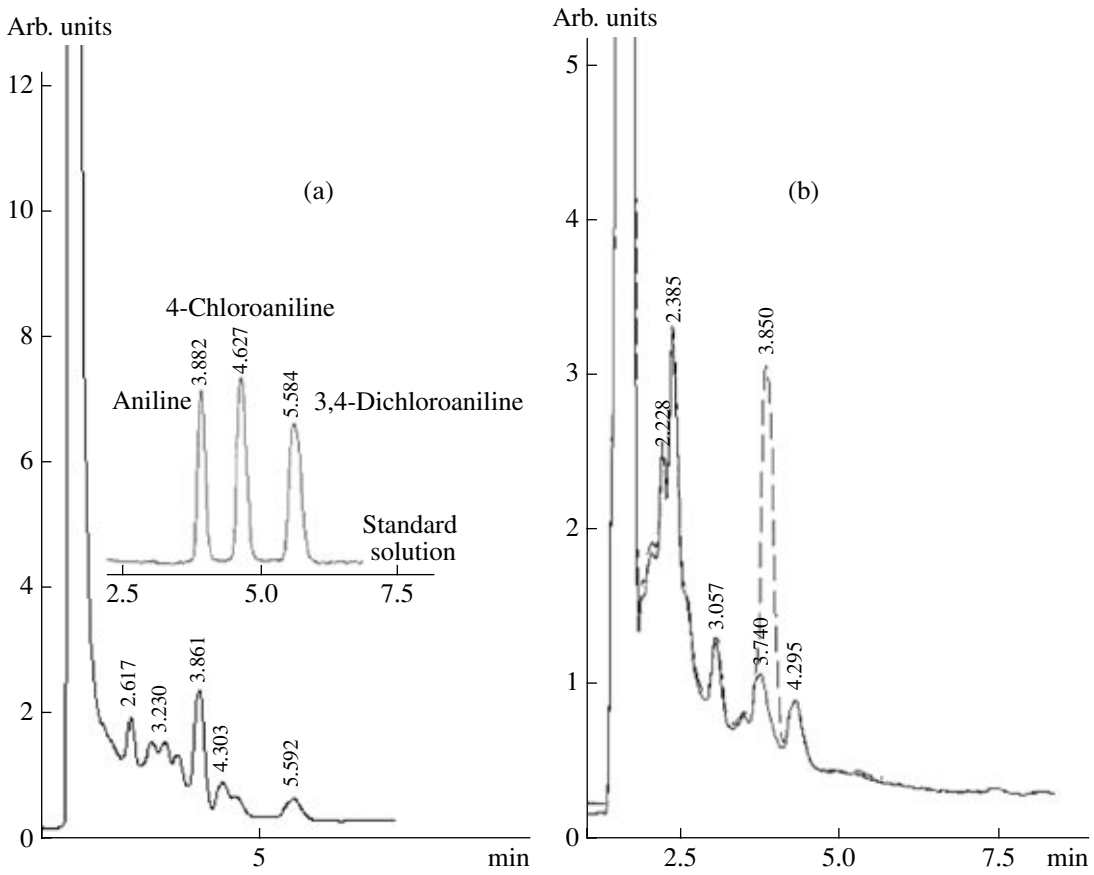


Fig. 4. Chromatograms of compounds accumulated in passive dosimeters (a) in the atmosphere of chemical laboratory and (b) in sidestream smoke.

[18]. Sidestream (environmental) smoke forms between the inhalations and is released to the ambient air from the carbonized end of the cigarette. During the smolder between the inhalations, 60–65% of cigarette tobacco burns out. During this time, the access of oxygen to the hot zone of the cigarette is lower; therefore, oxidation reactions proceed less actively. The aromatic amines are formed during smoking by the pyrolisis of amino acids, which are present in the tobacco. The sidestream smoke, which is inhaled by passive smokers, contains much more ammonia, carbon monoxide, benzopyrene, and aminobiphenyls (including aromatic and volatile carcinogenic ones). For example, the concentration of 4-aminobiphenyl, which is responsible for the development of bladder cancer, in sidestream smoke is 30-fold higher than in the mainstream smoke [20].

In view of the aforesaid, it was interesting to study the detection of aniline in the cigarette smoke (so-called environmental smoke) using passive chemical dosimeters. For this purpose, passive dosimeters were installed in smoking rooms of the institute for 6 h. At the end of exposure, the chromatographic analysis of their chemisorption layer was performed. A comparison of the standard solution chromatogram with that of the solution obtained after the desorption of aniline derivatives from the absorption layer of a passive dosimeter revealed the presence of aniline in the cigarette smoke inhaled by passive smokers (Fig. 4b). The concentrations of aniline and its derivatives were calculated from calibration curves similar to those shown in Figs. 2 and 3. On the absorption layer, 0.083 μg of aniline was found, which corresponded to a toxicant concentration in the air equal to 15 μg/m^3. In ventilated indoors (e.g., in disco clubs), the concentration of aromatic amines usually increases to 10 μg/m^3 [20].

Thus, the results obtained suggest that the device studied can be used as a personal passive chemical dosimeter for determining aromatic amines and assessing the risk of their impact.

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