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Experimental Study of the Absorption Dynamics of Harmful Admixtures in Hermetic Chambers under Normal and Hyperbaric Conditions

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Activated charcoal is a traditional component of filters that purify a gaseous environment of harmful admixtures in inhabited hermetic chambers. However, its utilization in chambers saturated with moisture markedly decreases its sorption capacity. Moreover, several volatile compounds forming as a result of urine decomposition and endogenous biochemical reactions (ammonia, amines, low aliphatic acids, and aldehydes) are poorly absorbed by charcoal at ordinary temperatures [2,4].

In order to overcome the above difficulties, ion-exchange fiber materials are increasingly being used to purify gaseous environments. These materials absorb acidic or alkaline compounds depending on the nature of the functional groups [1,6]. Volatile bases and acids react with the active centers of the fibers to form stable ion bonds. When used as a purifying filter in hyperbaric diver complexes, these materials have an important advantage over ordinary filters: moist gaseous environments do not impair sorption on such fibers, and the absorbed compounds will not be desorbed in an emergency temperature rise or in the decompression accompanying the diver's exit from the hyperbaric complex.

In this context, the combined utilization of activated charcoal and ion-exchange materials as a sorbent for the purification of a gaseous environment from noxious admixtures in inhabited hermetic chambers, as well as its possible application in hyperbaric systems, may be promising.

For this purpose we investigated the purification efficiency and sorption capacity with respect to a variety of chemical compounds (pentane, hexane, heptane, benzene, toluene, acetone, methanol, ethanol, butanol, ammonia) under normal and hyperbaric conditions.

MATERIALS AND METHODS

A sample of cation-exchange fiber (Na-form, VION™) and activated charcoal (BAU™) in a fine-meshed metallic container were placed in the chamber pictured in Fig. 1. The saturation of the hermetic space accounted for 1 cm^2/liter for fiber, 1.482 g for charcoal mass, and 0.4-0.8 mm for granule size. The temperature was kept at 20-21°C.

The samples were thermovacuumized at 80°C for 2 hours in a rotary evaporator to a constant weight, followed by saturation with water vapor by 20% of their dry weight in an exsiccator. After the test the fiber sample was dried as described and weighed to an accuracy of ±0.15 mg. The amount of ammonia irreversibly bound to cationite and the chemosorption dynamics was estimated by the difference of sample weight before and after the test.

The charcoal was washed with acetone and placed in helium flow (30 ml/min, 240°C, 24 hours).

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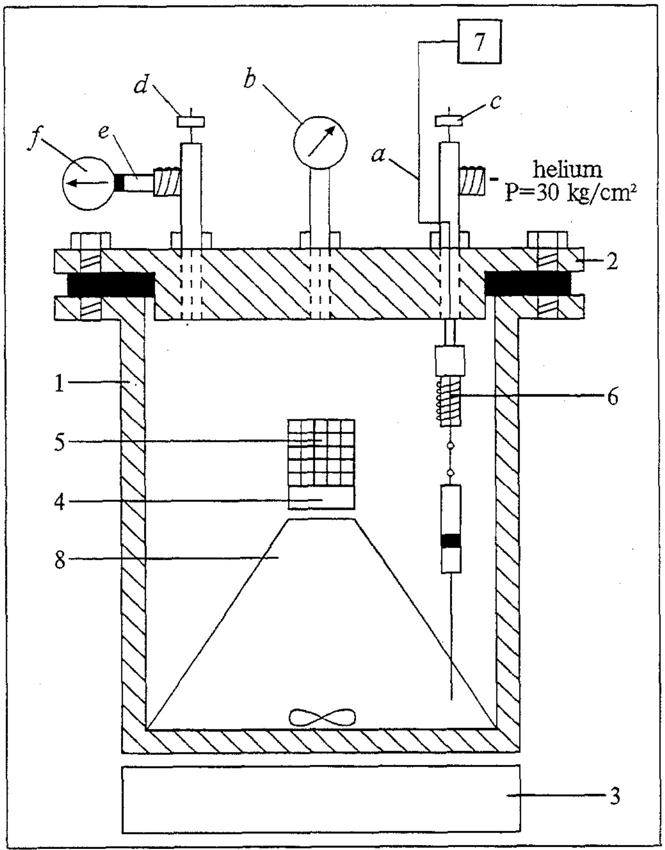

Fig. 1. Scheme of hyperbaric stand for study of volatile substances sorption dynamics: *1*) steel chamber of volume 3.23 liter; *2*) cover equipped with electrohermetic inlet (*a*), pressure-gauge (*b*), pressure lock tap (*c*), fine adjusting tap (*d*), silicone tube (*e*), and rubber cylinder (*f*); *3*) magnetic mixer; *4*) fiber sample; *5*) activated charcoal in container; *6*) syringes with electromagnetic drives; *7*) control panel of syringes supplied with 3 V battery, *8*) support for sorbent placement.

The container with charcoal was weighed before and after each test.

The volatile compounds studied (within a concentration range of 7.9-16.2 mg/m^3, adjusted to normal conditions) were injected into the chamber by means of a special sparksafe device with syringes cinematically connected to a low-voltage electromagnetic relay (Fig.1). The injections were performed in a volume of 1-2 μl in the liquid phase with one or several syringes depending on the task at hand. The pressure inside the chamber was increased to 30 atm with helium. Under hyperbaric conditions the chemical compounds were injected into the chamber after temperature equilibrium was established. A propeller-shaped magnetic mixer was used to mix the vapors of the substances studied and to create a constant gas flow through the sorbents.

The content of organic compounds in the chamber and the purification dynamics were studied with a Khrom-41gas chromatograph (Czechoslovakia) equipped with a flame-ionization detector. The conditions of the analysis were the following: column 2.5 m long, internal diameter 3 mm, packed column Chromaton N-AW with 15% Carbowax 1500, rate of helium flow 30 ml/min, hydrogen flow 30 ml/min, air flow 450 ml/min, temperature of evaporator 150°C, of columns 100°C, and of detector 150°C. Calibration was performed by the absolute method using pure standards and an automatic integrator. The minimal concentrations detectable for hydrocarbons and alcohols were 0.1-0.12 mg/m^3 and 0.4-0.6 mg/m^3, respectively.

The sampling of the gas under hyperbaric conditions was performed through a fine adjusting tap (*d*) coupling with a silicone rubber tube (*e*) for piercing by needle and a small rubber cylinder (*f*) producing a slight pressure gradient to avoid an admixture of room air (Fig. 1). During gas sampling under normal pressure, a rubber membrane and metal lid with a needle hole were mounted instead of the fine adjusting tap (*d*).

The content of ammonia in the chamber was controlled with a Miran-80 infrared spectrophotometer (Germany), equipped with a 20-meter-long sen-

TABLE 1. Purification Efficiency and Time of Complete Purification of Chamber from Harmful Admixtures at 1 atm and 30 atm

Compound	Purification efficiency, P (% of initial concentration), (*M*±*m*) in 6 h		Time of complete purification (hours), (*M*±*m*)	
	at 1 atm, *n*=3	at 30 atm, *n*=3	at 1 atm, *n*=3	at 30 atm, *n*=3
Pentane	100	94.9±1.7	3.67±0.25	10±0.85*
Hexane	99.9±0.1	89.4±1.7*	6.2±0.85	15±2.6*
Heptane	87.6±0.5	61±8*	>24	>24
Benzene	100	99.4±0.9	2.3±0.2	56.3±1.3*
Toluene	99.9±0.1	86.3±3.7*	6.5±1.1	20±3.9*
Acetone	99.9±0.1	83.6±1.9*	6.2±0.85	16±4.4
Methanol	91±2.1	64±2.1*	>24	>24
Ethanol	94.3±2.1	70.9±5.6*	16±1.5	20±2.7
Propanol	99±0.5	81.2±6.2*	9±0.85	12.3±2.1
Butanol	99.9±0.1	89±3.7*	6.5±0.74	8±0.85
Ammonia	100	100	2.5±0.43	4.3±0.65

Note: *: *p*...0.05

TABLE 2. Sorption Capacity of Charcoal and VION for Organic Compounds and Ammonia, Respectively, under 1 and 30 atm, 1 and 6 Hours after Injection ($M \pm m$)

Compound	E, mg/g, after 1 hour		E, mg/g, after 6 hours	
	at 1 atm, n=3	at 30 atm, n=3	at 1 atm, n=3	at 30 atm, n=3
Pentane	17.07±0.08	15.4±0.07	17.93±0.11	17.65±0.05
Hexane	17.17±0.041	15.8±0.06	17.87±0.23	17.65±0.1
Heptane	17.43±0.18	14.55±0.15	18.3±0.17	17.45±0.1*
Benzene	27.13±0.041	24.85±0.16	27.07±0.041	27.05±0.09
Toluene	25.5±0.07	22.85±0.15	26.27±0.33	25.65±0.21
Acetone	22±0.14	19.65±0.35	25.27±0.1	24.45±0.1*
Methanol	18.5±0.07	14.7±0.17	22.1±0.07	19.6±0.1*
Ethanol	23.27±0.164	20.7±0.09	24.8±0.19	24.5±0.1
Propanol	25.6±0.07	22.35±0.08	26.93±0.22	25.9±0.2*
Butanol	25.47±0.08	22.45±0.07	27.3±0.07	26.35±0.3*
Ammonia	23.97±0.07	16.8±0.07	25.03±0.15	25.05±0.1

Note: *: changes in all compounds reliable, $p<0.05$.

sitive gas cuvette. The minimal concentration detectable was 0.4-0.5 mg/m^3.

The efficiency of purification of the chamber from each compound was calculated as the difference between the initial and the final (6 hours later) concentration related to the initial concentration and expressed in %. The sorption dynamics was also estimated by the time interval between the injection and first negative results of the analysis for the given compound. This interval was assumed as the time of maximal sorption or full removal of the particular substance injected in a given initial concentration. Gas-chromatography analysis of the absorption of harmful substances on charcoal and VION was performed every 30 min.

The sorption capacity (E, mg/g) of charcoal and VION for each compound was determined gravimetrically and expressed as the ratio of the amount of absorbed compound (mg) to the sorbent constant weight (g).

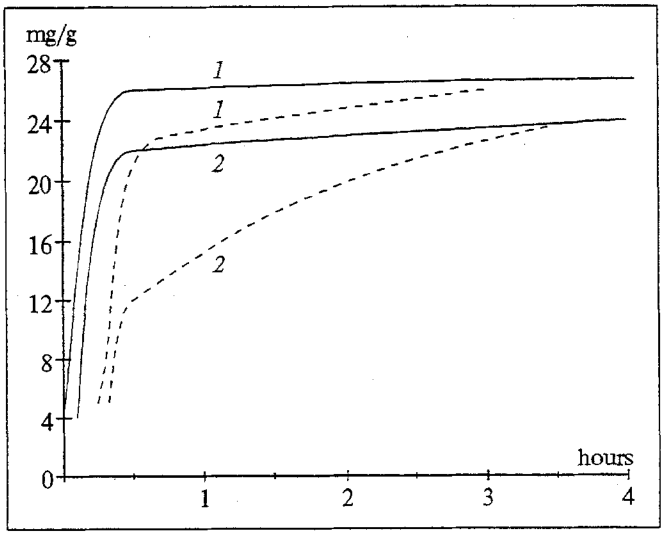

Fig. 2. Dynamics of sorption capacity (E): *1*) sorption of benzene on charcoal; *2*) sorption of ammonia on VION under 1 atm (solid line) and 30 atm (dotted line).

Additionally, to evaluate the sorption dynamics under elevated and normal gas pressure the amount of ammonia and benzene injected in an equal mass quantity and sorbed on VION and charcoal, respectively, was determined gravimetrically after the hyperbaric and normobaric experiments. The sorption capacity was determined at 2, 5, and 10 min and then every 30 min.

RESULTS

A comparison of the purification efficiency under normal and hyperbaric conditions (Table 1) indicates that the adsorption rate under elevated pressure was lowered for an equal mass amount of volatile compound injected. During the 6-hour period the concentration of the substances decreased more slowly under 30 than under 1 atm. The maximum sorption was reached under elevated pressure later than under normal pressure.

A comparison of the sorption capacity actually reached under 30 and 1 atm (Table 2) also revealed a delayed saturation under hyperbaric conditions. Moreover, for several compounds the sorption capacity under high pressure did not reach the value obtained under normal pressure even after 6 hours (Fig. 2). Sorbent saturation with benzene and ammonia occurred 3 hours and 1 hour later, respectively, under 30 atm than under 1 atm. Further exposure up to 6 hours resulted in a gradual equalization of the sorption capacities and in the removal of the majority of harmful admixtures from the chamber. Some substances (heptane, methanol) remained present in the chamber in trace amounts even after 24 hours.

The data obtained are in accordance with other observations concerning the inverse proportion between the diffusion rate for some compounds and the gaseous environment pressure, which suggests the need to make an allowance for pressure [3,5]. From the practical point of view, this offers the possibility of extending the service life of the gaseous environment filters under hyperbaric in comparison with normobaric conditions. On the other hand, this can lead to an underestimation of the concentrations of harmful admixtures measured by sorption methods (indicator tubes, concentration traps with solid sorbents) in hyperbaric inhabited chambers compared to normobaric conditions.

The sorption dynamics differs quantitatively and qualitatively for various substances. For the family of hydrocarbons both the purification efficiency and sorption capacity decreased in the following order: pentan→hexane→heptane. The maximum sorption was also delayed (Tables 1 and 2). In the aromatic series, the sorption capacity and purification efficiency were higher for benzene than for toluene. In the alcohol series the maximal sorption capacity and purification efficiency were observed for butanol and the minimal for methanol.

Thus, the chamber was purified of the aliphatic and aromatic hydrocarbons, acetone, and ammonia with the maximal efficiency. The purification efficiency and sorption capacity decreased with increasing molecular weight of the hydrocarbons. The opposite relationship was observed in the alcohol series. The sorption did not change qualitatively with the pressure, despite the quantitative impairment of the dynamics, efficiency, and capacity of sorption.

Under hyperbaric conditions, the relations between the sorption characteristics in homologous series remained the same those under normal pressure. Essentially pentane, hexane, benzene, toluene, acetone, and ammonia were completely removed from the chamber within 6 hours under normal pressure. Heptane and alcohols remained in trace amounts. Under hyperbaric conditions, only ammonia was completely removed from the chamber within 6 hours, which can be explained by its irreversible sorption on the fiber. For other compounds the absorption on charcoal was reduced with the pressure elevation.

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