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The Use of Cured Atmospheric Moisture to Concentrate the Impurities in the Air Analysis.

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ABSTRACT

The new method of preconcentration of polycyclic aromatic hydrocarbons (PAH) from the air, which based on the use of solidification atmospheric moisture as a collector of the impurities was developed in this work. The recovery from the water condensed phase was executed by the microextraction. The integrated enrichment factor of PAH from the air to the extract was at the level $6.8 \cdot 10^{4}$–$1.4 \cdot 10^{5}$, the achieved limits of detection were at the level $(2–5) \cdot 10^{-5}$ µg/m^3. The analysis of the extract was carried out using gas-chromatography–mass-spectrometry.

Keywords: analysis of air, preconcentration by condensation, polycyclic aromatic hydrocarbons, liquid microextraction, gas-chromatography/mass-spectrometry.

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INTRODUCTION

The use of atmospheric moisture as a natural collector of impurities contained in the air, finds an increasing application in the assessment of the ecological state of the atmosphere. Studies of sorption of polycyclic aromatic hydrocarbons (PAHs) of atmospheric moisture in the form of rain [1], fog [2] and snow are described in the literature [1, 3-5]. The paper [5] has dealt with the establishment of the dynamics of atmospheric pollution with PAHs through studying the glaciers. The authors [6] carried out a correlation between the amount of PAHs in snow in city and the level of automobile emissions.

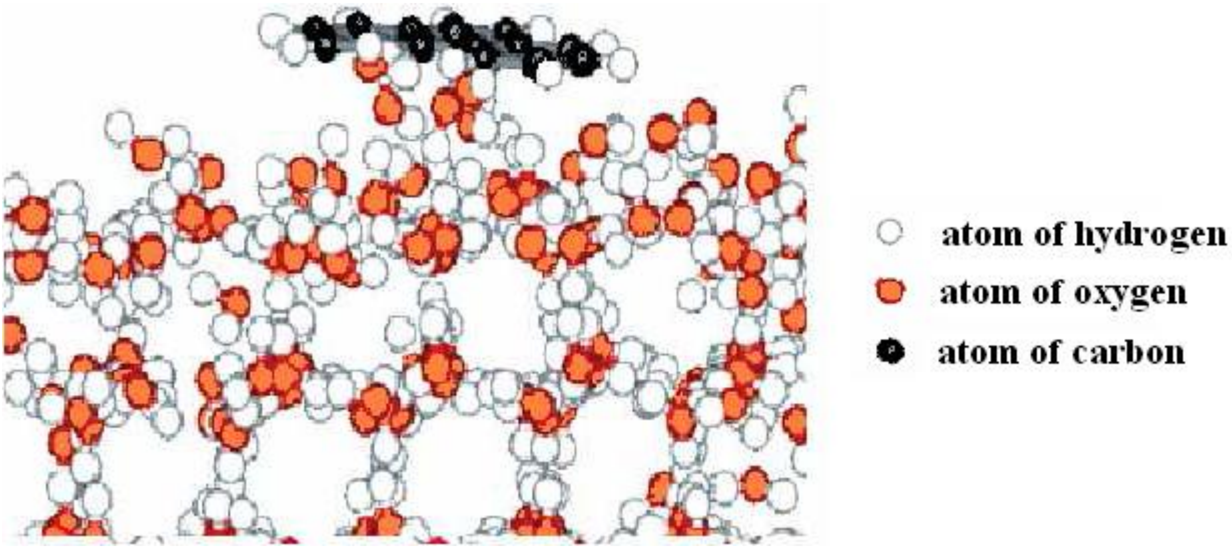

Figure 1: Phenanthrene sorption on the snow surface [3].

The development of such approaches is due to several advantages over the traditional methods for analyzing air such as high rates of concentration for nonvolatile impurities, refuse to utilize expensive synthetic sorbents, solution of problem with sorbent background, no desorption operations, drying, etc. [7]. However, the determination of the impurity composition of the air by means of condensed atmospheric moisture has some fundamental disadvantages. Firstly, there is no definite method of converting the impurity level in atmospheric moisture to the concentration in the air. Secondly, application of this method is limited by the geographic and seasonal factors.

To solve the problems identified, the authors of this paper have developed for the first time a method of quantitative analysis of air using cured water as a collector of impurities from the air.

EXPERIMENTAL PART

Reagents. High purity carbon tetrachloride (OSCh 18-4) (TU 6-09-3219-84), further purified by high-efficiency rectification was used as an extractant for the PAH extraction from aqueous condensate [8]. Ethanol was used as a dispersing agent (OSCh 20-5), also additionally purified by rectification. A standard mixture of PAHs in PAH-16 Supelco # 4-7940-U acetonitrile was used as an individual impurity substances.

Equipment. The impurities were determined by using the gas chromatograph-mass spectrometer Focus DSQ II with a quadrupole mass analyzer, gas chromatograph-mass spectrometer management and XCalibur 1.4 data processing software, as well as the mass spectra library NIST-2005. Separation of impurities was carried out using the capillary columns with stationary phase FFAP (50 m × 0.32 mm × 0.5 µm), DB-5ms (30 m × 0.25 mm × 0.25 µm) and Rtx-5 (30 m × 0.25 mm × 0.1 µm). Ultrapure helium 60 (TU 0271-011-45905715-02) was used as the carrier gas.

The analyzed air was sampled with a portable aspirator PU-2E equipped with built-in thermometer and barometer. The humidity was determined with the use of hygrometer Center 310. When preparing reference samples the substances were weighted on the first order electronic balance Shimadzu AW-220. After microextraction the sedimentation was carried out with OPN-8 centrifuge.

Condensation extraction of aromatic hydrocarbons from the air into the ice structure.

The design of the concentrator. Concentration of impurities from the air was conducted with the flow concentrator (see. Fig. 2) which is U-shaped tube with a bend length of 500 mm, and a distance between the concentrator bends of 100 mm. The 7.5 mm diameter of the tube was defined as the optimum, since the smaller diameter leads to clogging of the tube lumen with the frost formed, and the larger diameter increases the probability of impurities slip. The concentrator tube was made of molybdenum glass. The inner surface of the cryoconcentrator tube has saliences made. They contributed to the increase in the rate of mass transfer of impurities to the walls of the concentrator due to the flow turbulence, as well as increase in contact area between the aspirated air and the surface of the concentrator tube, which improved the efficiency of heat transfer.

To improve the rapidness of the technique, a condensate collector was made of four tubes, which conducted aspiration of parallel air streams. The assembled system was immersed in a Dewar's vacuum flask so that the lower part of the concentrator was over liquid nitrogen. Dewar's vacuum flask was closed with a cap made of polyurethane foam, which served as a thermal isolator of the flask and a lock of tubes.

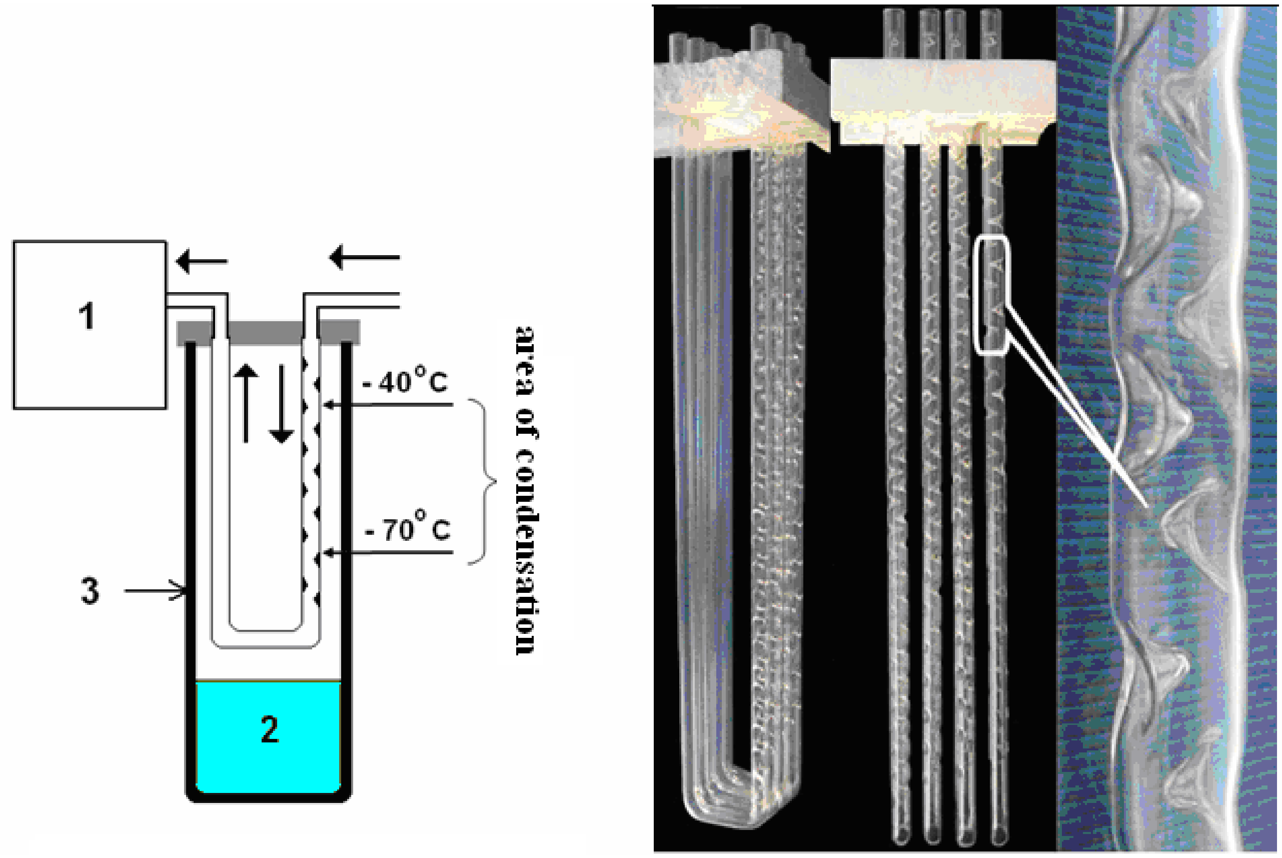

Figure 2: Assembly for the condensation concentration:

1 - aspirator, 2 - liquid nitrogen, 3 – Dewar's vacuum flask.

Concentration temperature. Condensation of atmospheric moisture in the form of frost occurred in the concentrator input bend. The temperature of the condensation zone ranged from -40 ° C (top) to -70 ° C (lower part). Temperature of the cryoconcentrator was determined with a chromel-copper and copel-copper thermocouples fixed on the concentrator tube. Temperature regulation was performed by moving vertically the tubes inside the Dewar's vacuum flask. The temperature gradient was 1 ° C/cm in the condensation zone and was kept constant during the entire period of aspiration by ensuring the stability of the temperature and the air flow.

The temperature of analyzed air ranged from 0 to + 35 °C.

The volume of air samples. Aspiration of analyzed air was conducted through the concentrator for 1 - 2 hours. The amount of volume sampled depends on the air humidity. To obtain the necessary volume of the aqueous condensate (minimum 5 ml), it is necessary to aspirate 250-500 liters of air. The increase in the volume of air sampled over 500 liters results in filling the tubes with frost, which makes further aspiration difficult.

After aspirating the air, the concentrator was removed from the Dewar's vacuum flask, ice was partially thawed in the concentrator and melted water was placed into a centrifuge tube. The tube was sealed with PTFE cap and ice was further melted.

Extraction of aromatic hydrocarbons from aqueous condensate.

The impurities were extracted from aqueous condensate (meltwater) through microextraction with the dispersion of an extractant [9]. For this purpose, an extractant (high purity carbon tetrachloride) in the dispersant (ethanol) was injected by 1mm syringe into water solution. The volume ratio of alcoholic solution and analyzed water was 1:6. The concentration of carbon tetrachloride in alcohol 1.5% (vol.).

The resulting emulsion of carbon tetrachloride in water, was demulsified in the centrifuge in 3 minutes at a rotor rate of 6000 rev / min. The extractant precipitated at the tip of the centrifuge tube (see. Fig. 3) was sampled with microsyringe Hamilton (P / N 20175) and injected into the chromatograph injector.

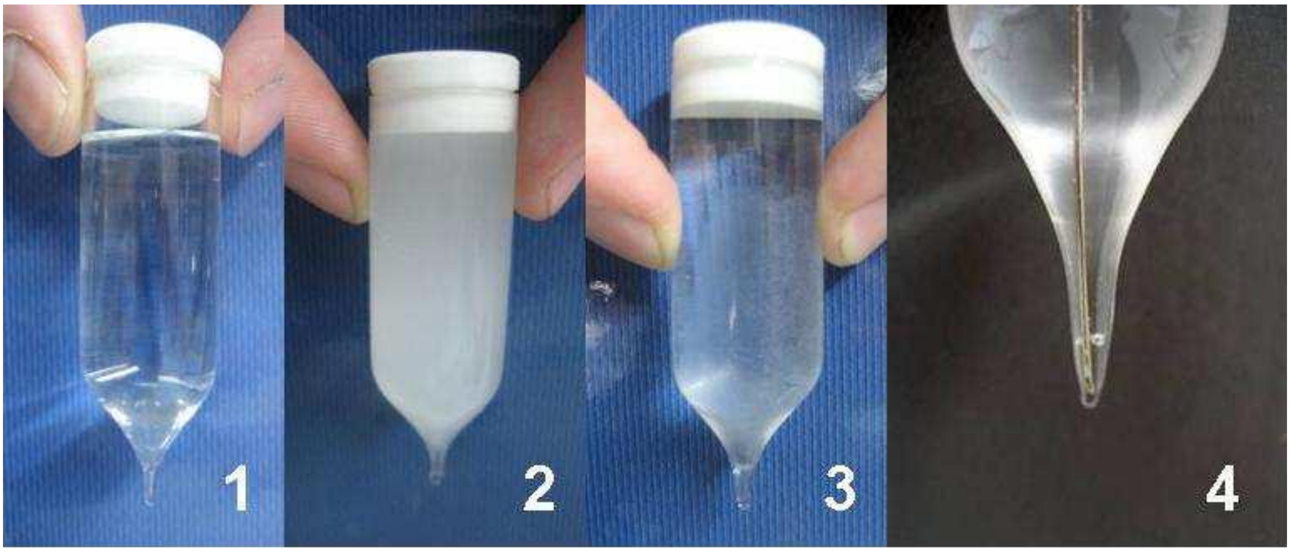

Figure 3: Scheme of microextraction concentration with dispersion of the extractant (1 - initial aqueous condensate analyze, 2 - emulsion in water after the addition of the extractant with a dispersing agent, 3 - extract isolated after centrifugation, 4 – sampling of extract).

Analysis of the extract. Gas chromatographic-mass spectrometric analysis of carbon tetrachloride was carried out under the following conditions: the energy of ionizing electrons - 70 eV, electron multiplier voltage - 1244 V, ion source temperature - 230°C, chromatograph-mass spectrometer interface temperature - 300°C.

Identification of impurities was carried out in total ion current mode in the mass range of 50-350 Da. Mass spectra of the obtained chromatographic peaks were compared with the mass spectra of the electronic database NIST-2005. Values of mass spectra similarity coefficients were 0.80-0.99. To determine the impurities of less than $1 \bullet 10^{-1}$ mg/L in the extract, a mode of selective ion monitoring (SIM) of the molecular ion peak was used. In this case the impurities in carbon tetrachloride were identified by the time of retention. At the recovery of the main component - carbon tetrachloride, the supply of cathode, lens and accelerating voltage was turned off to prevent the failure of the above elements of the detector.

Gas chromatographic separation of impurities was carried out under the following conditions: initial column temperature was maintained at 50°C for 1 minute, then the column temperature increased at a rate of 40°C·min^{-1} up to T = 120°C and then heating was performed at a rate of 10°C·min^{-1} up to T = 280°C and this temperature was maintained for 15 min. The linear velocity of the carrier gas was 27-37 cm · s^{-1} in the column. The volume of the sample introduced into the column was 1 µl. Injector temperature was 300°C. Dosing of samples was performed with microsyringe Hamilton.

Determination of the rate of recovery substances from the air.

The rate of recovery water from the air was determined as the ratio of the mass of water condensed in the cryocondensator to the mass of water contained in the air, passed through the cryocondensator. The mass of the condensed water was determined by weighing the tube of the cryocondensator prior to and after the cryocondensation.

The mass of water contained in the air was calculated subject to humidity, which was determined by a hygrometer.

The rate of PAHs recovery from the air to the $R_{\text{air}\rightarrow\text{water}}$ condensate was determined from the ratio of the mass of the impurity in the resulting aqueous condensation to the mass of the impurity in the model gas mixture passed through the cryocondensator.

Introduction of PAHs into the flow of aspirated model gas (high purity nitrogen) was performed by passing the gas stream through a glass filter placed at the inlet of the cryocondensator and filled with glass wool coated with a known quantity of PAHs. High purity nitrogen containing maximum 0.0005% vol. oxygen was used instead of air to avoid oxidation of PACs during heating. The filter temperature of 300–350°C was maintained by using an electrical heating element. Heat is required to evaporate high-boiling PAHs and entrain them with gas flow. To create a model gas mixture with the content of moisture approximate to the air, flow of nitrogen was saturated with water vapor by bubbling through a twice-distilled water. Relative humidity of nitrogen was controlled by a hygrometer and was 97.0 ± 2.5%.

RESULTS AND DISCUSSION

Rate of recovery. Table 1 shows values of the rate of PAHs recovery ($R_{air\rightarrow water}$) from the air into condensed water. They ranged from 80 ± 10% for "light" PAHs up to 100 ± 20% for five-ring PAHs. Thus, the results of determining the rate of recovery of the aromatic hydrocarbons and water from the air indicate insignificancy of a slip of the impurity components at the aspiration of air flow through the cryoconcentrator. Both the rate of impurities recovery from air into water and the rate of water recovery from the concentrator tube are important for practice. It was established that the rate of recovery of aromatic hydrocarbons from the concentrator ($R_{\text{out cond}}$) ranged from 60 to 90%.

The enrichment factor. We have determined the *enrichment factor* of aromatic hydrocarbons from air to aqueous condensate $K_{air\rightarrow water}$ (see Table 1). This value shall mean the ratio of the concentration of impurity C_{water} (wt%) in the aqueous condensate to the concentration of impurity C_{air} (wt%) in air:

$$K_{\text{air}\rightarrow\text{water}} = C_{\text{water}} / C_{\text{air}} \qquad (1)$$

To increase the limiting possibilities of the technique, the impurities were concentrated from the aqueous condensate into the extract using a liquid phase microextraction with the dispersion of the extractant. In this case, the indicator of the concentration performance is an integral factor of the impurity concentration K_{sum}, which is the ratio of the concentration of impurity C_{extr} (wt%) in the extract to the concentration of impurity C_{air} (wt%) in air:

$$K_{\text{sum}} = C_{\text{extr}} / C_{\text{air}} = K_{\text{air}\rightarrow\text{water}} \cdot K_{\text{water}\rightarrow\text{extr}} \,, \qquad (2)$$

Where $K_{water} \rightarrow_{extr}$ – is a factor of impurities concentration from aqueous condensation into the extract during microextraction. This value ranged from 520 for naphthalene to 1020 for the five-ring PAHs.

As Table 1 shows, the values of the integral concentration factor reach the values 10^4-10^5, that are on a level with the best results obtained when using conventional sorption techniques.

Table 1: Characteristics of condensation concentration.

Substance	$R_{air\rightarrow water}$, %	$R_{out\ cond}$, %	$K_{air\rightarrow water}$	$K_{sum} \times 10^{-3}$	C_{min}, μg/m^3
Naphthalene	90 ± 20	80 ± 20	130 ± 30	68 ± 15	$3\cdot10^{-5}$
Acenaphthylene	90 ± 20	80 ± 20	130 ± 30	77 ± 16	$3\cdot10^{-5}$
Acenaphthene	90 ± 20	80 ± 20	130 ± 30	88 ± 18	$3\cdot10^{-5}$
Fluorene	90 ± 20	80 ± 20	130 ± 30	68 ± 15	$3\cdot10^{-5}$
Phenanthrene	90 ± 20	80 ± 20	130 ± 30	68 ± 15	$3\cdot10^{-5}$
Anthracene	90 ± 20	80 ± 20	130 ± 30	98 ± 21	$5\cdot10^{-5}$
Fluoranthene	90 ± 20	80 ± 20	130 ± 30	78 ± 17	$5\cdot10^{-5}$
Pyrene	90 ± 20	80 ± 20	130 ± 30	78 ± 17	$5\cdot10^{-5}$
Benz[a]anthracene	100 ± 20	90 ± 20	140 ± 30	84 ± 18	$2\cdot10^{-5}$
Chrysene	100 ± 20	90 ± 20	140 ± 30	84 ± 18	$2\cdot10^{-5}$
Benzo[b]fluoranthene	100 ± 20	90 ± 20	140 ± 30	140 ± 30	$3\cdot10^{-5}$
Benzo[k]fluoranthene	100 ± 20	90 ± 20	140 ± 30	140 ± 30	$3\cdot10^{-5}$
Benzo[a]pyrene	100 ± 20	90 ± 20	140 ± 30	140 ± 30	$3\cdot10^{-5}$
Dibenz[a,h]anthracene	100 ± 20	90 ± 20	140 ± 30	140 ± 30	$3\cdot10^{-5}$
Benzo[g,h,i]perylene	100 ± 20	90 ± 20	140 ± 30	140 ± 30	$3\cdot10^{-5}$
Indeno[1,2,3-cd]pyrene	100 ± 20	90 ± 20	140 ± 30	140 ± 30	$3\cdot10^{-5}$

The detection limit. The detection limit of the technique (in wt.%) was calculated by dividing the direct limit of detecting the aromatic hydrocarbons into the integral concentration factor:

$$C_{min}\,(wt\ \%) = C_{min\ direct} / K_{sum}, \qquad (3)$$

The detection limit (g/m3) was calculated by the formula:

$$C_{min}\,(g/m^3) = C_{min}\,(wt\ \%)\cdot\rho_{air}, \qquad (4)$$

where $[rho]_{air}$ - air density, g/m^3.

The developed method has solved the problem of efficiency of air sample preparation. Conventional methods of PAH determination require aspiration of considerable volume of air, which leads to a substantial reduction both in the rapidness of sampling and in necessity to use high-performance aspirators. For example, authors of the paper [10] collected volume of 50832 m^3 of air for 24 hours, where the PAH detection limits were at the level of values obtained in the present paper. This is due to the fact that only a small proportion of PAH, in terms of the total air sampled, enters into the analytical instrument. The proportion of sample entering the device when using conventional techniques ranges from 1/100 to 1/10000, while the method described in this article allows introducing 1/5 of sample in terms of the total air sampled.

Only the use of desorption in the injector allows implementing lower detection limits (with an equal volumes of aspirated air) than those obtained by the authors of this article. However, the direct desorption in the injector is rarely used due to the difficulty of thermal desorption of high-boiling PAHs.

SUMMARY

We have developed a new efficient method of concentrating the polycyclic aromatic hydrocarbons from the air, based on the use of the cured water. The method can be used to monitor air pollution. The combination of PAHs concentration by atmospheric moisture and liquid microextraction allowed implementing high coefficients of concentration equal to those in traditional methods of sample preparation, as well as solving the problems associated with the background of the sorbent. The implemented detection limits of PAHs are 2-5 order less than the norm for the air in populated areas that allows monitoring the state of the atmosphere long before the occurrence of an emergency.

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