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Sensitivity Increase in Headspace Analysis of Hydrocarbons in Water by Using Online Selective Elimination of Gas Extractant

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Abstract: In this study, a novel approach in headspace gas chromatographic analysis using the selective absorption of the gas extractant during concentration of the analytes was developed. The carbon dioxide used as the gas extractant was removed from the sample flow by passing it through a column packed with microdispersed sodium hydroxide granules. The analytical capabilities of the suggested method were illustrated by the determination of aliphatic and aromatic hydrocarbons in water. We established that this method allows the preconcentration of analytes in the gas phase to be increased proportionally to the volume ratios of the gas extractant before and after absorption, while the analyte limits of detection decrease 30-fold. For example, benzene can be detected in water at a concentration of 0.5 μg/L.

Keywords: gas chromatography; aliphatic and aromatic hydrocarbons; headspace analysis; gas-phase extraction; carbon dioxide; gas-extractant absorption

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1. Introduction

The general method of determining volatile organic compounds (VOCs) in aqueous solutions is headspace analysis (HSA), which is based on various modes of the gas-phase extraction of analytes and their gas chromatographic (GC) determination [1–6]. HSA is a nonalternative method for the analysis of hydrocarbons, solving problems in the areas of sanitation and environmental control, in particular, the use of headspace analysis in the case of highly toxic aromatic hydrocarbons dissolved in water, the determination of which requires highly efficient concentration methods. By considering the partition of VOCs between the aqueous and the gas phase, the gas-phase extraction isolation of analytes enables an increase in the sensitivity of the analysis by one to three orders of magnitude compared to the direct injection of aqueous samples (without enrichment) into the gas chromatograph. Even so, it is not always sufficient to meet the maximum permissible level (several parts per billion) for the determination of benzene in natural and drinking water. Therefore, an additional preconcentration of analytes must be used for GC analysis. A combination of HSA with gas-phase adsorption is often used for the preconcentration of analytes. Additionally, the preconcentration of VOCs using static gas-phase extraction, known as headspace solid-phase microextraction (HS SPME) [7–11], dynamic [9,12,13], and continuous gas-phase extraction [14–16], can be achieved.

There are two common methods for the dynamic gas extraction of analytes. In the first, a flow of the gas extractant is passed through the stationary liquid phase, whereas in the second, continuous gas extraction, it is passed through the mobile liquid phase (so that the two phases are mobile). The dynamic gas extraction method used in this study is

known as purge-and-trap (P&T). The results from comparing the analytical capabilities of HS SPME and P&T [9] have not revealed any clear advantage of one method over the other. The advantage of P&T is the possibility of extracting VOCs in a continuous flow-through mode [17,18]. However, both methods experience a possible problem associated with the incomplete extraction of VOCs at the thermal desorption stage, causing poor precision in and uncertain validity of the analytical results [19]. However, this problem has been dealt with in various commercial systems.

The aim of the present work was the development of a new version of sensitive HSA exploring the additional preconcentration of VOCs using the selective trap of the gas extractant. Carbon dioxide was chosen as the gas extractant capable of selective absorption by solid alkali. Alternatively, other highly efficient absorbents can be used for carbon dioxide capture [20].

2. Materials and Method

2.1. Theoretical Background

During gas-phase extraction, a molar fraction n_i of the ith extracted component in the gas phase, which is in equilibrium with the source solution, can be expressed as:

$$n_i = \frac{p_i}{p_i + \sum p_j + p_L^0 + p_{EG}} \quad (1)$$

where p_i is the partial pressure of the ith extracted component; Σp_j is the sum of partial pressures of other volatile components from the analyzed solution and impurities in the gas extractant; ${p_L}^0$ is the saturated vapor pressure of the solvent at a given temperature; p_{EG} is the pressure of the gas extractant. In the headspace analysis of aqueous solutions, the value of p_{EG} has the main impact (>95%) on the denominator in Equation (1) under normal conditions, in the case of using pure-enough gas extractant. If gas-extractant flow containing the extracted analytes is directed to a column that is packed with material selectively absorbing the gas extractant, then a directly proportional increase in the molar fraction of analytes in the gas phase occurs according to a decrease in the denominator in Equation (1). An additional preconcentration effect can be obtained for the HSA of aqueous solutions due to the absorption of both the carrier gas and the solvent vapors, which are inevitably present in the flow of the gas extractant coming from the headspace of the analyzed liquid. As defined, the analytes that are not absorbed must stay in the gas-phase flow.

A feature of the developed method that should be taken into account is the longitudinal molecular diffusion of the concentrated analytes in the gas phase of the absorption cartridge. As a result of the gas-extractant elimination, analytes, which are present therein, tend to concentrate from the gas phase onto the first sections of the absorption cartridge, while diffusing toward the opposite end of the cartridge and outside of it. In the case of a one-dimensional model, the process of longitudinal diffusion in the gas phase of a column can be described by an equation well-known in the theory of chromatography:

$$C_i(x,t) = C_i^0 \exp\left(-\frac{x^2}{4D_i t}\right) \quad (2)$$

where $C_i(x,t)$ is the concentration of the ith component at a distance x from a column inlet at time t from the start of the diffusion process; ${C_i}^0$ is a concentration of the ith component at the column inlet (x = 0) at the initial time (t = 0); D_i is the diffusion coefficient of the ith component. Considering the high diffusion rates in the gas phase, for example, the concentration of benzene ($D \approx 0.25$ cm^2/s at 20 °C) at the column outlet (length, 15 cm) in 2 min will be 6.5 times less than the initial concentration at the inlet. For this reason, high flow rates of the gas extractant should be used and gas-phase extraction must be completed in the shortest possible time to minimize the negative effect of longitudinal diffusion on the preconcentration of the analytes in the gas flow exiting the absorption cartridge.

For the analysis of aqueous samples using the proposed method, the most convenient gas extractants include carbon dioxide, hydrogen, and steam. In addition to the technical difficulties involved in performing gas-phase extraction at high temperatures, the use of steam is limited by the absence of selective absorbents that do not retain polar organic substances. For example, popular desiccants such as $CaCl_2$ and $Mg(ClO_4)_2$ are not suitable, as they can retain lower alcohols and ketones together with steam [21]. Potentially, potassium fluoride, which is not soluble in polar organic solvents compared to ordinary dehydrators [22], might be used as a selective absorbent of water vapor. Hydrogen is widely used in gas chromatography (GC) in terms of its application with flame ionization detector (FID) and is readily absorbed by palladium, its alloys, and some other metals at room temperature [23]. Unfortunately, these metals are effective catalysts for hydrogenation in various organic substances [24], which makes their chromatographic identification difficult. Thus, carbon dioxide is the most suitable gas extractant for the proposed has method because of its low cost, operational safety, and availability. Moreover, various substances can efficiently absorb it [20]. Carbon dioxide absorption by alkali is well-known; for example, the application of widely available solid sodium hydroxide was described [25]. The interaction between carbon dioxide and sodium hydroxide is considered to be chemisorption, including both adsorption on the surface of solid sodium hydroxide and absorption in the aqueous liquid layer formed as a result of the reaction:

$$2\,NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

The release of water does not affect the retention of nonpolar analytes that are poorly soluble in water. Polar analytes (alcohols, ketones, and ethers) may react with alkali in the presence of water.

Among the possible variants of continuous HSA, chromatomembrane HSA with simultaneous movement of flows of an aqueous sample and a gas extractant through the cell with a biporous hydrophobic matrix is the most efficient and convenient one to be integrated into online analysis [26]. The main advantages of a continuous HSA mode are the high efficiency of mass transfer between the flows of the liquid and gas phases and the possibility of continuous isolation of VOCs from the analyzed aqueous phase flow into the gas-extractant flow. The application of 3D printing technology for making chromatomembrane cells creates new prospects in chromatomembrane HSA [27].

2.2. Reagents

In this study, a set of test substances including benzene, toluene, hexane, and heptane was used due to their chemical inertness toward alkali metal hydroxides used for carbon dioxide absorption. The choice of these substances was also connected with a strong need for their determinations in water at the trace level. Model aqueous solutions with a concentration of 5 mg/L were prepared by using chromatographically pure substances from unopened glass ampoules (Reachem, Moscow, Russia) and deionized water. High-purity, 99.8%, carbon dioxide was obtained from NII KM (Moscow, Russia). The main characteristics of the test substances are listed in Table 1.

Table 1. Characteristics of analytes.

Analyte	Boiling Temperature, °C [28]	Solubility in Water (25 °C), g/L [28]	*K* [1], at 25 °C [29,30]	Maximum Allowable in Water, μg/L	
				WHO [31,32]	Russia [33]
Benzene	80.1	1.78	4.0 [29]	10	1.0
Toluene	110.6	0.531	3.6 [29]	700	24
n-Hexane	69.0	0.11	0.021 [30]		-
n-Heptane	98.4	0.024	0.019 [30]		-

[1] *K*—distribution coefficient is defined as the ratio of analyte concentrations in the aqueous and gas phases.

2.3. Instrumentation

A schematic diagram of the experimental setup used for dynamic HSA and absorption of the gas extractant is shown in Figure 1. A flow of carbon dioxide from a gas cylinder via a flow regulator (1) and a porous glass sparger (2) was passed through an aqueous solution of VOCs in the sample vessel (3) with a volume of 250 mL. The analyzed VOCs from the solution were transferred into a flow of the gas extractant according to their partition coefficients and passed via a switching valve (6) into an absorber tube (7) (120 × 14 mm ID) packed with sodium hydroxide granules (18 g) with a particle size ranging between 2 and 5 mm. The choice of this particle size range was defined by the necessity of having a uniform package of absorbing cartridges and the permeability sufficient for passing carbon dioxide at high flow rates. The absorbing cartridge was installed in the GC line where a gas sample loop is usually placed. After passing through a certain volume of the gas extractant, the sample valve was switched into the "inject" position as marked by the dotted lines in Figure 1, left. Meanwhile, a flow of the carrier gas (nitrogen) (8) transferred the VOCs concentrated in the absorbing cartridge into the GC instrument (9). The gas sparger (2) improved the mass transfer and efficiency of the gas extraction process by increasing the gas–liquid interphase area.

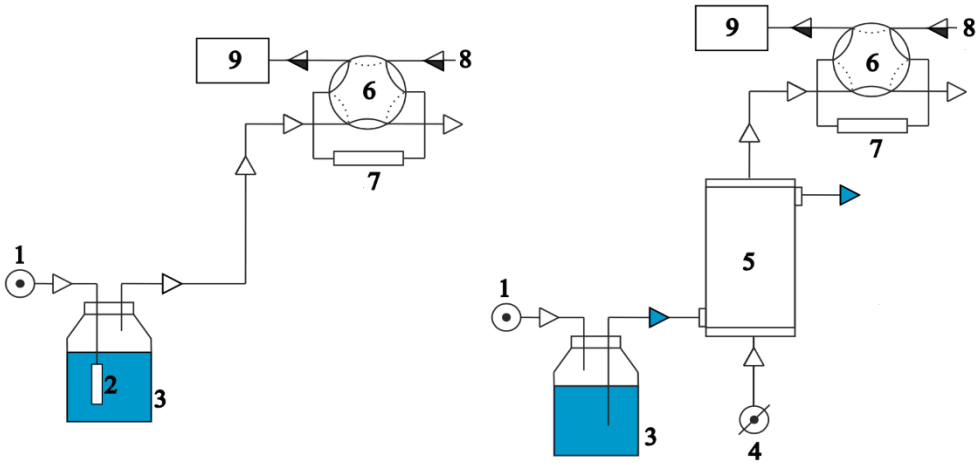

Figure 1. Schematic diagrams of the experimental setup used for dynamic HSA (**left**) and for continuous chromatomembrane HSA (**right**) with absorption of the gas extractant in both cases. 1: carrier gas flow regulator; 2: gas sparger; 3: sample vessel with an aqueous solution of VOCs; 4: gas-extractant flow regulator; 5: chromatomembrane cell; 6: switching valve; 7: CO_2 absorbing cartridge; 8: inlet for the carrier gas; 9: gas chromatograph.

A scheme of the experimental setup used for continuous chromatomembrane HSA with the absorption of the gas extractant is shown in Figure 1, right. The excessive pressure of the carrier gas (nitrogen) was adjusted by the pressure regulator (1) and applied to the gas phase in the sample vessel (3) pushing an analyzed solution into the chromatomembrane cell (5). Simultaneously, a flow of the gas extractant (carbon dioxide) adjusted by the flow regulator (4) was also delivered into the chromatomembrane cell. Then, the flow of gas extractant containing extracted analytes came through the switching valve (6) into the absorbing cartridge (7) packed with sodium hydroxide. After this point, the same procedures were performed similarly to the scheme of dynamic HAS shown in Figure 1, left.

The chromatomembrane cell used in this work contained a 9 cm × 6 cm × 2 cm biporous PTFE parallelepiped as an extracting element. The aqueous phase flow entered through a 9 cm × 2 cm cross-section, which was perpendicular to the direction of the gas-phase flow through a 9 cm × 6 cm cross-section

In both versions of HSA, the dependence of peak heights and peak areas was studied as a function of the time of pass flow of carbon dioxide, as the gas extractant, through the absorber column packed with sodium hydroxide. The analysis was carried out using a gas

chromatograph Crystal-5000.2 (Chromatec, Yoshkar-Ola, Russia) equipped with FID and a 6-way injection valve for gas samples. A separation column (2 m × 3 mm ID) packed with Chromaton N-AW (60–80 mesh) coated with 5% OV-17 and a fused silica capillary column (10 m × 0.53 mm × 2.65 μm) coated with 100% dimethylpolysiloxane were used. The temperatures of the packed column and the fused silica capillary column were 100 and 70 °C, respectively, and the temperature of the detector was 160 °C. The flow rate of the gas carrier through the packed column was 20 mL/min. The Chromateck-Analytik 3 software complex was used for data acquisition and processing.

3. Discussion

As the results of the study showed, the absorbing cartridge packed with granular sodium hydroxide removed carbon dioxide from the gas phase, while hydrocarbons, which do not have acid properties, were not absorbed by alkali and stayed in the gas phase. The experimentally obtained dependences of the relative peak heights of benzene and toluene and the passage time of carbon dioxide from the solution (by dynamic HSA) through the absorbing cartridge are given in Figure 2. The peak height of the analyte after passing carbon dioxide through the absorbing cartridge for 15 s was taken as a unit of measurement.

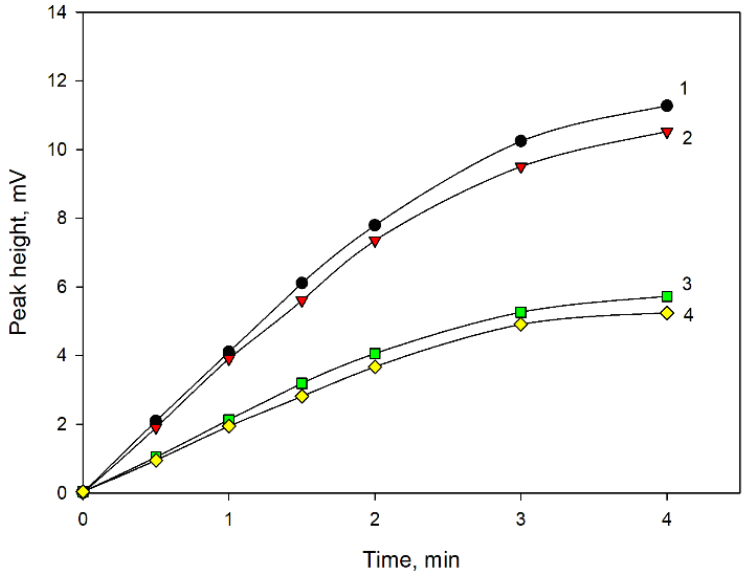

Figure 2. Dependencies of peak heights of toluene (1, 3) and benzene (2, 4) in dynamic HSA obtained for a series of model solutions at flow rates of 15 mL/min (3, 4) and 30 mL/min (1, 2).

As shown in Figure 2, there was an increase in the peak heights of the analytes directly proportional to the passage time of carbon dioxide within the first two minutes. Then, the growth slowed down and practically stopped after 3 min. The increase in the slowing down of the peak area occurred simultaneously with the continuous, quick absorption of carbon dioxide and stopped before the capacity of the absorbing cartridge ran out, which was equal to approximately 10 L, according to the stoichiometry of the chemical reaction. Apart from this, the time when this slowing down begins depends on the carbon dioxide flow rate. The absorbing cartridge should be replaced and repacked when carbon dioxide absorption declines, which occurs after passing approximately 3 L of carbon dioxide. Both factors prove the negative effect of longitudinal diffusion on the elution profile of the analytes out of the absorption tube. This diffusion is known to be dependent on neither the absorber capacity toward carbon dioxide nor its flow rate at the column inlet.

For the determination of aromatic hydrocarbons having distribution coefficients between the water and gas phases much higher than one (Table 1), the method chosen of carrying out gas-phase extraction is not essential. We revealed that the analyte concentration in a flow of the gas extractant in the cases of both dynamic and chromatomembrane

extractions remains constant for a long time and corresponds to an equilibrium saturation of the gas extractant with the analyte. For aliphatic hydrocarbons having distribution coefficients significantly less than one, a sharp decrease in the analyte concentration during the passing of the gas-extractant through the immobilized solution was observed for dynamic gas-phase extraction. This finding explains the declines in curves 3 and 4 after 2 min shown in Figure 3.

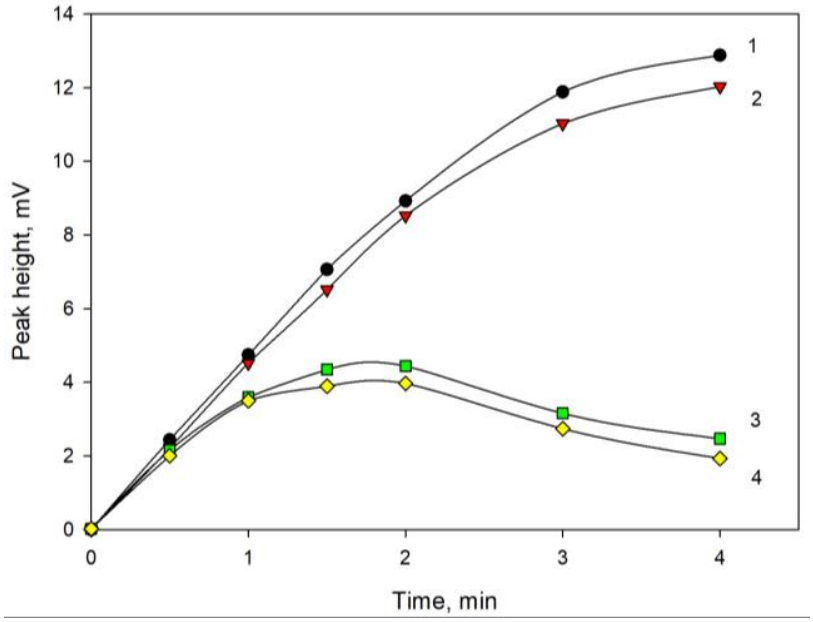

Figure 3. Dependencies of peak heights of n-heptane (2, 4) and n-hexane (1, 3) on the passing time of the gas-extractant (30 mL/min) through aqueous solution in the case of chromatomembrane (1, 2) and dynamic HSA (3, 4).

In contrast, in the case of the chromatomembrane version, the gas-extractant flow was always in contact with fresh portions of the solution, which enabled the analytes to be extracted into a smaller volume of the gas extractant and enhanced the sensitivity of HSA. Figure 3 is an illustration of this conclusion, showing the dependencies of the peak heights of n-hexane and n-heptane compared during the passage time of the gas-extractant flow (30 mL/min) with regard to dynamic HSA (curves 3 and 4) and chromatomembrane HSA (curves 1 and 2) with the passing of the aqueous phase sample through the chromatomembrane cell at a rate of 30 mL/min.

To demonstrate the advantages of the proposed HSA version, the gas chromatograms of aromatic hydrocarbons were obtained with and without selective absorption of the gas extractant. Figure 4 shows that the HSA version with the selective absorption of gas extractant provided a three-fold increase in sensitivity for GC determination of benzene and toluene using a packed column. A more profound positive effect of the application of the proposed method was obtained for the determination of alkanes by capillary GC. According to Figure 5, the selective absorption of the gas extractant resulted in a 10-fold increase in chromatographic peak heights. Two GC systems were tested to show the suitability of the bulky preconcentration scale (e.g., the sample vessels had a 250 mL volume). Clearly, a further decrease in limit of detection (LOD) values can be achieved with a more compact HSA system.

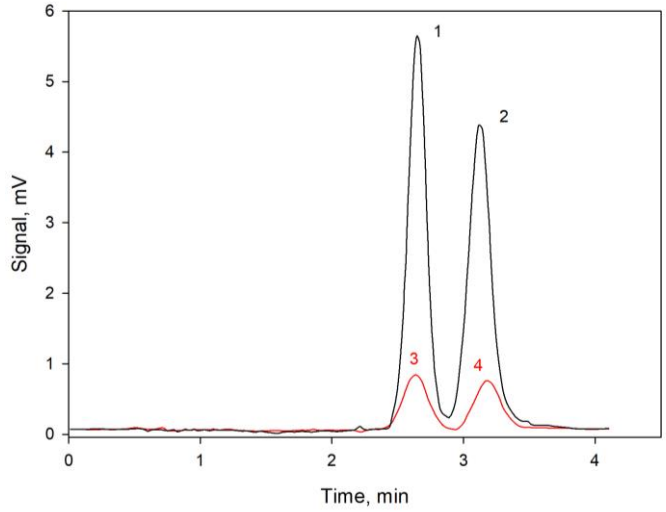

Figure 4. GC determination of benzene (1, 3) and toluene (2, 4) in a model solution (5 mg/L) with preconcentration by a selective adsorption of the gas-extractant (1, 2) and without it (3, 4). CO_2 flow rate—30 mL/min, time—2 min. Separation column—Chromaton N-AW (60–80 mesh) coated with 5% OV-17.

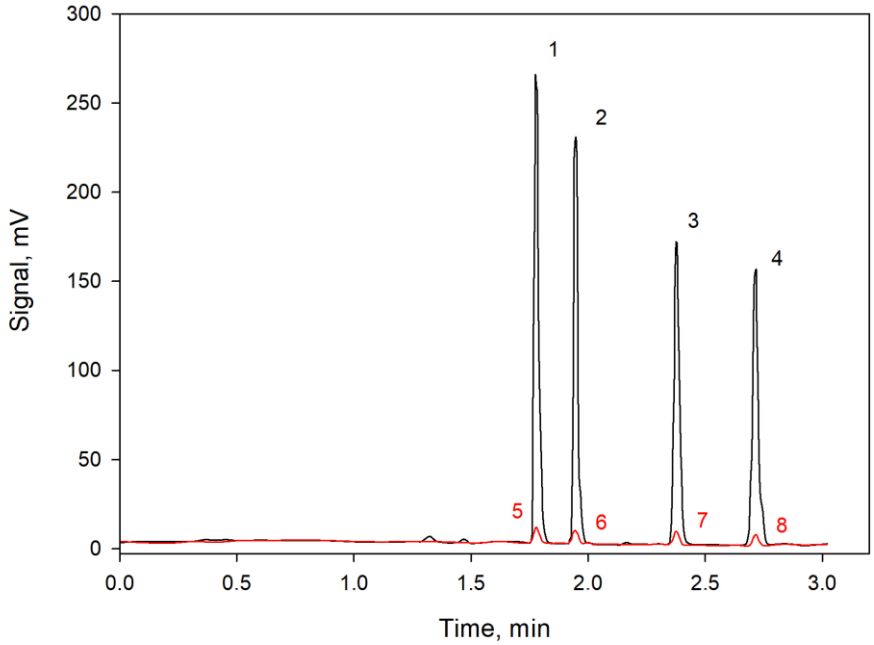

Figure 5. Gas chromatograms obtained with capillary GC column used for the determination of n-hexane (1, 5), benzene (2, 6), n-heptane (3, 7) and toluene (4, 8) in a model solution after preconcentration via selective adsorption of the gas-extractant (1, 2, 3, 4) and without it (5, 6, 7, 8). Concentrations of n-hexane and n-heptane—0.2 mg/L; benzene and toluene—5 mg/L. CO_2 flow rate—30 mL/min, time—2 min. Fused silica column with dimethylpolysiloxane coating.

In HSA, the dependences of peak area on the concentration of analytes present linear plots with zero intercepts (Figure 6). As for dynamic HSA combined with capillary GC application, the calculated limits of detection (LODs), according to the 3σ rule, are 0.5 (0.05) μg/L for benzene, 0.6 (0.06) μg/L for toluene, 0.030 μg/L for n-hexane, and 0.035 μg/L for n-heptane. The values in brackets are approximate values for the mass spectrometry detector (MSD). According to the literature, when MSD was used in the case of benzene, the LOD was 0.2 μg / L for static HSA [34]; for HS-SPME, 0.04 μg/L [9]; and for P&T, 0.06 μg/L [9]. Thus, the sensitivity of the proposed method is not inferior to the most

effective concentration methods. This method can be used to determine other analytes that do not interact with alkalis, for example, permanent gases dissolved in water (oxygen, nitrogen, hydrogen, helium, etc.). The relative standard deviation (RSD) for all analytes did not exceed 6% for a value of n = 5. Moreover, the sensitivity of this method is in line with the WHO guidelines and the Russian sanitary requirements [31–33].

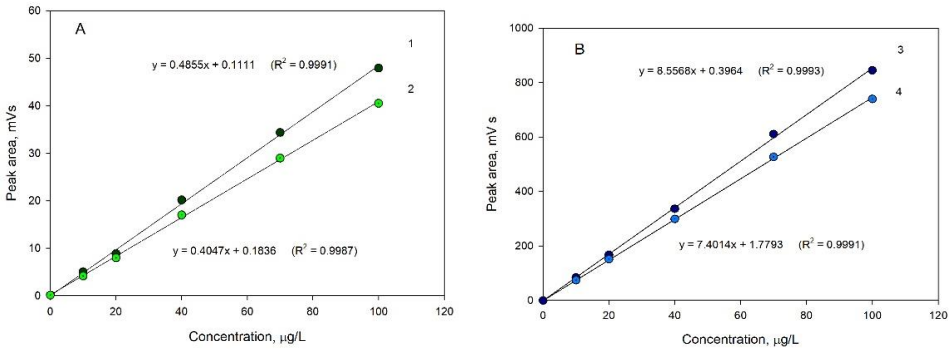

Figure 6. Peak area of dependencies on preconcentrations of aliphatic (**A**) and aromatic (**B**) hydrocarbons found by using dynamic gas extraction combined with capillary GC. 1—benzene, 2—toluene, 3—n-hexane, and 4—n-heptane.

Considering the strong dependence of distribution coefficients on temperature and the sample composition [29], the standard addition method should be used for quantitative analysis. This method is performed by recording the signals of the sample and of the sample with a known amount of standard addition. The result of the replicate measurement is calculated using the formula:

$$c = \frac{c_{ad} V_{ad} S}{V_s (S_{ad} - S)} \quad (3)$$

where c_{ad} is the concentration of analyte in the solution of standard addition (mg/L); V_{ad} is the volume of the solution of standard addition in the sample (mL); V_s is the sample volume, mL; S and S_{ad} are the peak areas of analyte signals recorded for the original sample and the sample containing standard addition (mVs), respectively. The set of model solutions with known standard additions of benzene and toluene in the range from 10 to 500 μg/L was analyzed. We determined that the effect of systematic error was negligible.

In the case of aliphatic hydrocarbons, the standard addition method leads to significant bias. It is assumed that this is due to the very small distribution coefficients of the analytes and, consequently, their significant volatilization during the preparation of the solution.

4. Conclusions

A new method of headspace GC analysis was proposed with the selective absorption of the gas extractant. The analytical capability of the suggested method was illustrated by an example of the determination of aromatic and aliphatic hydrocarbons in aqueous solutions with the absorption of carbon dioxide as a gas extractant in a cartridge packed with dispersed sodium hydroxide. The proposed method of headspace analysis can be carried out both in the conventional dynamic gas-phase extraction mode by surging the gas extractant through the liquid sample, and in the chromatomembrane mode of this process by continuous passage of flows of the gas extractant and the liquid sample through the chromatomembrane cell. A further enhancement in the sensitivity of the HSA method is connected to the optimization of conditions and using smaller absorption cartridges for the absorption of the gas- extractant.

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