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Compositional surface-layered sorbents for pre-concentration of organic substances in the air analysis

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ABSTRACT

We juxtapose methods of synthesis of non-polar surface-layered sorbents on the platform of a carrier, which combines macro-porous coarse-dispersed polytetrafluoroethylene with micro-dispersed activated carbon. Further, we present data about the sorption properties of the said materials alongside perspectives of their analytical applications. Our study established that with respect to efficacy of dynamic sorption from gaseous phases these sorbents outperform bulk-porous analogues in their normal, granular form.

1. Introduction

Concentrations of organic contaminants in the atmosphere are measured to determine background pollution levels and their compliance with maximum permissive limits. Insofar as these values are small, the process of sampling is usually combined with pre-concentration. The low molecular weight organic compounds, which are in the focus of this paper, are typically present in the air in the state of vapors, while along an increase of analyte's molecular weight the plausibility of their aerosol state increases. The variety of methodologies employed for pre-concentration in the air analysis includes: cryogenic sample pre-concentration [1–3], solvent extraction (implemented in impingers [4] and denuders [5,6]), active [7,8] and passive [8,9] sample enrichment on solid adsorption badges and packed tubes and solid phase micro-extraction (SPME) [10,11]. The SPME and passive sampling in view of the inherent slow mass transfer are more relevant for long-term monitoring of the air, rather than for real-time control of its pollution. Solvent extraction is oriented towards usage of liquid analysis methodologies and does not fit to determining such volatile compounds as methanol. A substantial shortcoming of sample pre-concentration consists in formation of ice crystallites during analysis of the humid air. Active sample enrichment on solid sorbents (dynamic sorption) is among the most wide-spread and efficient methodologies employed in the stage of pre-concentrating in the air analysis [7,8,12,13]. In this approach a dramatic handicap of concentrating with the use of regular bulk-porous adsorbents is shaped up by relatively low rate of mass transfer. This circumstance limits the maximum allowed flow rate of the analyzed air through the sorption tube and elongates the time span of a pre-concentration stage [14,15]. Unlike fluid media, where to the end of getting higher efficacy of dynamic sorption one may employ fine-dispersed sorbents and high-pressure pumps, air analysis does not give such an opportunity, because pressure gradients provided by modern low-pressure pumps do not surpass 0.3 atm through sorption tubes.

A plausible way to enhance efficacy of the mass-transfer in sorption processes is to employ surface-layered sorbents (SLSs), where a fine-dispersed sorption-active material (SAM) is embedded in pores of a relatively coarse-dispersed carrier [16,17]. Despite of a long-going history of the SLSs development [18] and availability of evidences regarding their superior efficacy with respect to concentrating of volatile organic substances (VOS) from aqueous solutions [15], so far they have not been applied for VOS concentrating from the air.

The present study pursued a goal to work out composite surface-layered sorbents for express sorption concentrating of

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VOS in the air analysis. This goal was complemented by juxtaposing analytical capabilities of the mentioned sorbents with those of the regular charcoal under the same conditions. On the other hand, our work, we believe, validates the choice of carriers and SAMs for the development of non-polar SLSs. Ways of processing a non-polar SLS on the platform of a carrier combining porous polytetrafluoroethylene (PTFE) and activated carbon are compared below, their sorption properties being studied and analytical opportunities being estimated.

2. Experimental section

2.1. Materials

A pivotal feature for the choice of carriers and SAMs in molecular adsorption is polarity [17,18]; to put it definitely, the optimum combination of the material moieties matched in a SLS is as follows: both, the sorption phase and the carrier, should simultaneously be either polar or non-polar. A universal carrier of non-polar SAMs is porous PTFE, in which minimal polarity is complemented with relevant sizes of micro-pores (5–15 μm) [19]. The letter circumstance gives way to drawing down virtually any of the non-polar adsorbents on this material [20].

Activated carbons are among the most efficient and practically universal SAMs. Gaseous and easily volatile compounds with the boiling temperature below (50–80) °C can be recovered from these sorbents by thermal desorption [8,20]. If one uses the latter method for concentration of less volatile analytes, then it is expedient to employ either carbon sorbents having lesser specific surface as a SAM is, e.g. graphitized carbon blacks (CB), or polymer adsorbents [8,21]. Noteworthy is that the adsorbent on the platform of graphitized CB and PTFE carrier was historically one of the first SLSs and was used for gas-chromatographic separation of various organic substances [22]. The highest hydrophobicity along with the minimum catalytic activity is appropriate to a birch activated charcoal (BAC), synthesized from wood [23,24]. Unlike polar micro-porous adsorbents, activated carbons have relatively low adsorption affinity towards aqueous vapor and can be applied to extraction of organic substances from humid air. Nonetheless, while applying thermal desorption it would make sense to perform preliminary drying of the analyzed air by letting it pass through the pre-tube filled by a dryer, say, dehydrated K_2CO_3 [8,25].

We processed SLSs basing upon PTFE in two stages. In the first one we got granulated porous carrier [26]. To this end, a raw polymerized powder PTFE benchmarked F-4PN-20 (an analogue of Teflon 7) was exposed for baking at 380 °C (1 h duration). The gotten mass was ground out with subsequent fractionation of a produced PTFE sample on sifts. Note in passing, F-4PN-20 is a macromolecular polytetrafluoroethylene; at temperatures above 327 °C crystals of this polymer undergo melting, however the material does not transit into viscous-flow state up to the onset temperature of its decomposition (415 °C) [27]. The said properties of the material ensured that no artifact peaks showed up in the chromatograms below the temperature of 300 °C. In the second stage of processing SLSs the samples of PTFE and SAM having definite gravimetric contents were mixed up for producing homogeneous matter (mechanic method). Alternatively, small bits of PTFE in the form of a suspension in ethanol were added to a portion of SAM under constant stirring followed by evaporation of ethanol. The accomplishment of the latter process was verified by registration of a sorbent constant weight (henceforth we term this processing algorithm a suspension method). Upon finalizing these operations the sorbent was sifted out to the end of ridding it of SAM particulars, which failed to get affixed on the carrier surface. Eventually, a mass of an affixed SAM was determined by weighting the sorbent.

2.2. Apparatus

Determination of the test substances at the outlet of the studied sorption tubes was performed by a gas chromatograph "Cvet-500M" equipped with flame-ionizing detector and heated sampling valve. Gas-chromatographic registration was implemented using a packed tube 200 × 3 cm with Carbowax 20 M on Inerton. Liquid substances were injected into a chromatograph (1 μL) by a micro-syringe, whilst gaseous compounds were dozed by a valve with 1 mL volume of a sampling loop. A flow rate of a carrier gas was controlled either by a rate regulator introduced in a gas-preparation unit of the chromatograph or by a flow-regulating valve of a pump.

2.3. Reagents and preparation of solutions

All the chemicals used in this work were of analytical reagent grade (Vekton Co. Ltd, St.-Petersburg, Russia). All of the aqueous solutions were prepared by a volume–volume method. Aliquots of analytes were collected using a measuring pipette, administered into a volumetric flask, wherein the level was brought to a flask label by addition of the distilled water. If necessary, solutions prepared in such a way were diluted by water.

Model gas mixtures (MGMs) having concentration with an order of magnitude of some mg/m^3 were prepared in accord with the standard methodology by bubbling a gas-carrier through aqueous solutions having sufficiently big volume (over 1 L) and a given concentration of analytes C_0. The concentration of analytes in a MGM (C_G) was assumed to hold:

$$C_G = C_0/K, \tag{1}$$

where K stands for a distribution coefficient in a gas–liquid system [28].

Control concentration measurements of analytes in the prepared MGMs before and after experiments in all of the cases gave values, which differed only insignificantly, thereby providing evidence of virtually constant concentration of analytes.

2.4. Methodologies of estimation of sorbents regarding their analytical capabilities

To estimate analytical capabilities of the prepared sorbents we let pass MGMs with constant concentration of the test substances through tubes filled with these sorption materials. MGM flow rate was set constant by a regulator. Equal volumes of the gas phase were collected at the outlets of a tube with successive determination of test substances concentration. Further, retention curves were plotted in terms of reciprocals C/C_0 vs. V, where C_0 and C stand for concentration of a test substance in the gas phase at the inlet and the outlet of a tube accordingly; V is volume of a MGM sample, which passed through a tube. Basing on these curves the values of a breakthrough volume (V_B) and a retention volume (V_R) were determined for each of the test substances. A quantity V_B was assumed equal to such volume of a MGM passed through a tube, which corresponded to 95-% extraction of an analyte from a sample. A quantity V_R was set equal to such sample volume passed through the tube, which conformed to a constraint: $C/C_0 = 0.5$. A height of an equivalent theoretical plate (HETP) was used as a characteristics of mass-transfer efficacy. Its value was estimated from the length of a tube and a number of plates N complying with a relationship derived previously [29] for a frontal variant of chromatography:

$$N = V_R^2/(V_R - V_{0.16})^2 \tag{2}$$

V_R stands for a retention volume; $V_{0.16}$ is such volume of a sample passed through a tube, which corresponds to a constraint $C/C_0 = 0.16$.

MGMs with constant concentration of test substances were prepared by bubbling of a gas-carrier through aqueous solutions having given concentrations of test substances. An equilibrium distribution of test substances between phases was ensured in a chosen range of flow rates of a gaseous phase, *viz.*, (100–800) mL/min. Concentration of substances in model gaseous mixtures, C_G, was calculated in accord with a relationship:

$$C_G = C_L / K_{LG} \tag{3}$$

where C_L is a concentration of a test substance in an aqueous solution, K_{LG} is its distribution coefficient between the aqueous and gaseous phases.

3. Results and discussion

3.1. Choice of a method to process a non-polar SLS

The results of the studies performed are summed up in Table 1. As is well seen therein sorbates retention parameters and efficacy of mass-exchange on the SLSs manifest virtually no dependency on the method of their preparation.

Further, it is established that the suspension method of processing SLSs provides a material with a content of SAM, which exceeds several times the one obtained by the mechanical method. Say, in case of the suspension method maximum content of active BAC may reach up to 50% of PTFE carrier mass, while mass fraction of coal in the mechanical method does not surpass 10%. One may explain this difference by operation of capillary forces, which retract organic solvent along with carbon micro-particles residing in it into PTFE pores. So, despite of a higher workload one, possibly, should prefer a suspension method of producing a SLS. Henceforth we did employ it.

Table 1
Specific volumes of sorbate retention (V_R) from the air flux (250 mL/min) and values of HETP on the non-polar SLS (10% BAC on PTFE; particular sizes 0.45–0.9 mm), processed by different methods.

Sorbate	Method of processing	V_R, L/g	HETP, mm
Acetone	Mechanic	9.5 ± 0.7	3.1 ± 0.3
	Suspension	11.0 ± 0.8	2.8 ± 0.3
Ethanol	Mechanic	7.8 ± 0.6	2.5 ± 0.2
	Suspension	7.5 ± 0.5	2.3 ± 0.2

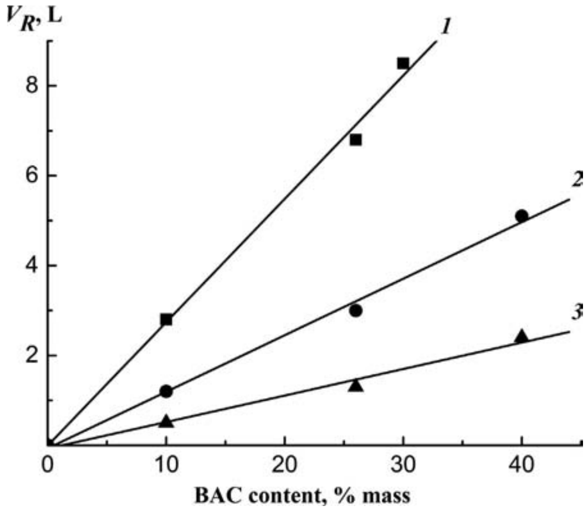

Fig. 1. Volumes (V_R) of retention from the air flux of some substances on the SLS with varying content of BAC (the tube 4 cm × 0.3 cm): (1) methyl acetate; (2) acetone; (3) methanol.

3.2. An impact of SAM content in SLS upon retention parameters and permeability of the sorption tube

Our measurements show that retention parameters of sorbates increase proportionally to an increase of carbon content in the SLSs (Fig. 1). However, permeability of a sorption layer steadily decreases with an increase of carbon content. Consequently, an air consumption decreases given a fixed gradient of the air pressure through the sorption tube. Fig. 2 shows reciprocals of the air consumption against the pressure gradient through the sorption tubes filled with SLSs having various carbon contents. Exploiting SLSs with contents of carbon exceeding 40% of a carrier mass does make appearance as a sensible method. It is so, because for a maximum gradient of pressure (0.3 atm), which is attainable by industrially produced pumps, one cannot provide sufficiently high consumption of air along the sorption tube.

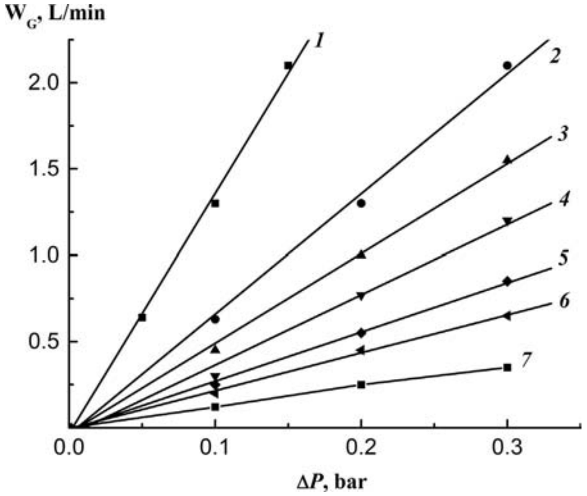

Fig. 2. Air flow rate vs. pressure gradient through the sorption tube (4 × 0.3) cm, filled with various sorbents with particular sizes 0.5–1.0 mm. Curve (1) BAC; (2) porous PTFE; lines (3)–(7) SLS with different contents of BAC: (3) 11%; (4) 19%; (5) 30%; (6) 41%; (7) 49%.

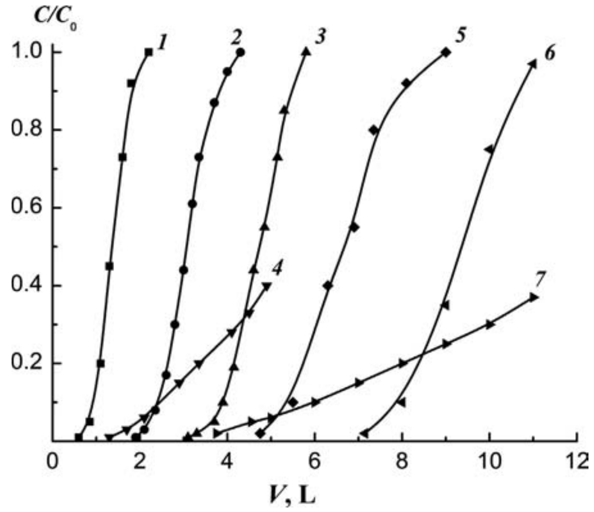

Fig. 3. Output curves of vapor retention of acetone (curves 1–4) and methylacetate (5–7) from the air flow (rate 500 mL/min) in the tube 4 cm × 0.3 cm filled with BAC (lines 4,7) and SLS with varying content of BAC: curve (1) 11%; (2) and 5–25%; (3) and 6–35%.

3.3. Regularities of organic substances vapor retention on the SLS

Owing to a higher efficacy of mass-transfer, SLSs with mass fraction of carbon above 20% provide a quantitative extraction of analytes from big amounts of the analyzed air in contrast to bulk-porous BAC of the same volume and granulometric content, given all the rest conditions identical. Fig. 3 exemplifies the output retention curves of organic substances vapors on the same tubes, filled with BAC and SLS with varied content of BAC.

Advantageous impression about SLS against the bulk-porous sorbents is the more tangible, the bigger is the increment of mass-transfer retardation into the broadening of a zone of analytes, which are being extracted. As is inferred in the diffusion-kinetic theory of chromatography [30], a contribution of this term increases alongside a decrease of sorbate diffusion coefficients. The latter phenomenon results from a growth of a sorbate molar mass as well as from an increase in consumption of a volatile phase through the sorption tube. It also benefits from an increase of particular sizes of a sorbent applied. Fig. 4 collates reciprocals of HETP vs. consumption of mobile phase through the tubes, filled with sorbents having various particular sizes. As is seen in the figure altering of the above mentioned conditions actually results in an increase of a positive effect following the application of SLSs.

Unlike a bulk-porous BAC, SLSs basing on BAC provide HETP and break- through volumes V_B of the extracted substances (Table 2), which are relatively weakly dependent on a linear flow rate through the sorption tube. It gives benign pre-requisites for working out express methodologies of sorption pre-concentration in determining volatile organic substances in the air basing upon SLSs.

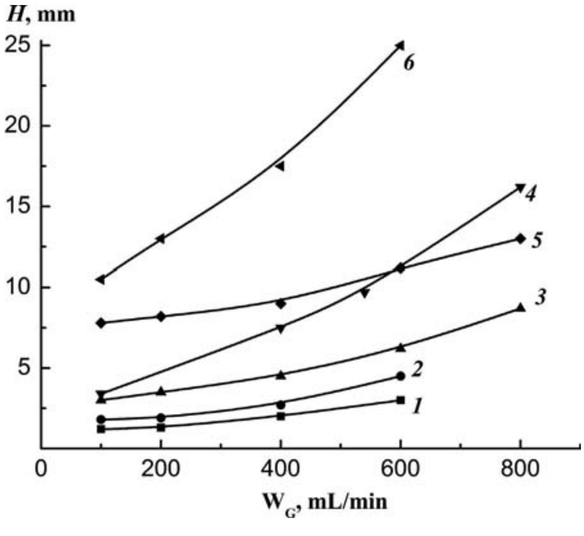

Fig. 4. HETP (H) for ethanol against air flow rate in case of various sorbents: a column (3 × 0.3) cm. Curves (1), (3), (5) SLS with BAC content of 35%; curves (2), (4), (6)—BAC; particular sizes of sorbents are: (1), (2) 0.25–0.5 mm; (3), (4) 0.5–1.0 mm; (5), (6)—1–2 mm.

3.4. Gas-chromatographic determination of organic vapors in the air using pre-concentration on the non-polar SLS and its validation

A MGM was passed through the tube filled with a studied sorbent during fixed time and with a given rate. After accomplishment of this stage the sorption tube (3) (see the flow-chart in Fig. 5) was placed into position of a batching loop of the heated batcher-valve (2). The sorption tube was heated (duration 90 s) by a slot-like oven (4) proving a given temperature. Thereafter the batching valve was set into a position designated by dashed lines in Fig. 5 for 30 s. Over this time analytes desorbed by heating were blown out from the sorption tube into the gas-chromatographic one (5) and further into the detector (6). After that the batching valve was set its into an initial position. The studies performed give evidence that quantitative (above 95%) thermal desorption from the surface of BAC into gas-carrier takes place in the temperature range (280–300) °C for thermo-stable organic substances having boiling temperatures below 80 °C. Sufficient completeness of desorption is corroborated by negligibly small peaks of analytes on the chromatograms upon the repeated thermal desorption (see Fig. 6). Owing to the smaller coal content the volume of gas-carrier required for quantitative desorption from the SLS of pre-concentrated substances is 1.5–2 times smaller as compared with the pure coal. This circumstance additionally enhances the degree of pre-concentration.

To verify the devised methodology a series of experimental determination of analytes was performed regarding MGMs with known concentrations (Table 3). As is seen in Table 3 discrepancies between experimentally determined and known (by virtue of Eq. (1)) analytes concentrations are insignificant with respect to the background of random scatter of the analysis results, the relative standard deviation (RSD) never surpassing 6%.

High sample flow rates through the sorption tube are required for express pre-concentration of analytes, while concurrently a pivotal factor, who limits breakthrough volumes, is a mass-transfer flow rate. Our results show that pre-concentration degree of the test organic analytes is several times greater in case of SLSs against the pure BAC. Characteristics of methodologies for gas-chromatographic determination of organic substances vapors using sorption pre-concentration on the devised sorbent are given in Table 4 alongside flame-ionization detection method.

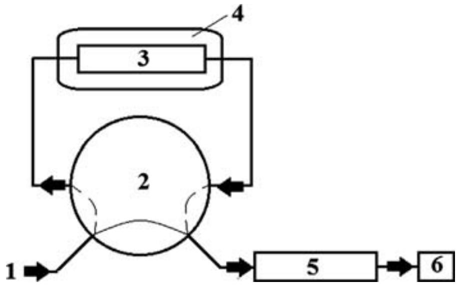

Fig. 5. Flow chart of gas chromatographic analysis with thermal desorption. (1) carrier gas inlet; (2) sampling valve of gas chromatograph; (3) adsorbing tube; (4) electric heater; (5) chromatographic tube; (6) detector.

Table 2
Effect of gaseous phase flow rate through the sorption tube (5 cm × 0.3 cm) upon breakthrough volumes (V_B) of the extracted substances.

Sorbent	V_B, Ml			
	Acetone		Ethanol	
	250 mL/min	750 mL/min	250 mL/min	750 mL/min
BAC 0.45–0.9 mm	2600 ± 200	1400 ± 100	2100 ± 100	800 ± 50
40% coal on PTFE 0.45–0.9 mm	3800 ± 300	2800 ± 200	2900 ± 200	1700 ± 100

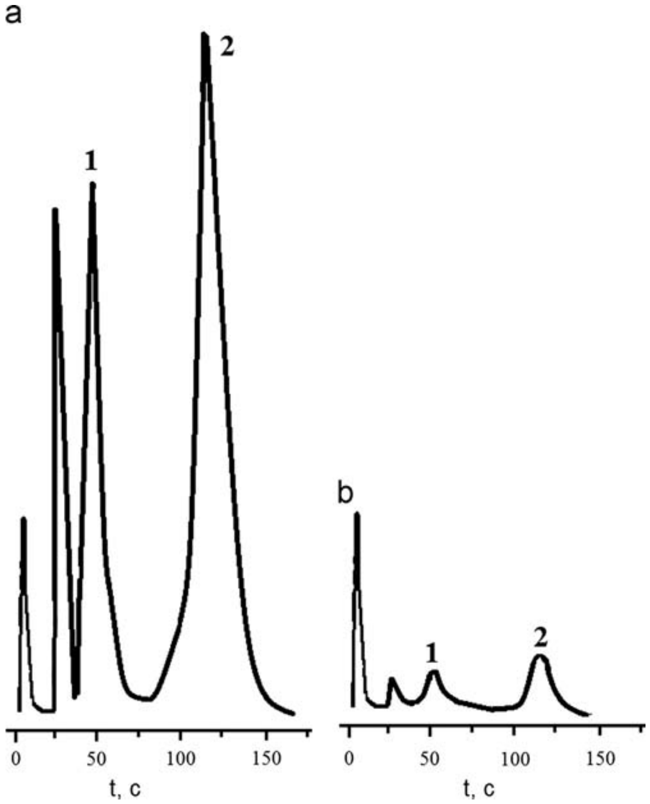

Fig. 6. Chromatograms after a primary (a) and repeat (b) thermal desorption from SLS with BAC content 35%; (1) methanol, (2) ethanol. Concentrations of alcohols in MGM are 160 μg/m^3 and 190 μg/m^3, accordingly.

Table 3
Mean values of recovery of volatile organic compounds from MGM (n=4, confidence probability=0.95) and RSDs, relative standard deviations (repeatability).

Compound	Calculated in accord with Eq. (1) (μg/m^3)	Analytically determined (μg/m^3)	RSD (%)	Recovery (%)
Methanol	162	160 ± 14	5.4	99
	570	580 ± 40	4.8	102
Ethanol	191	187 ± 14	4.6	98
	760	750 ± 50	4.2	98
Acetone	60	63 ± 4	3.8	105
	540	520 ± 30	3.6	96
Methylethyl ketone	82	77 ± 5	3.9	94
	790	760 ± 50	4.1	96
Methyl acetate	54	51 ± 4	4.5	94
	490	460 ± 30	4.3	94
Ethyl acetate	85	81 ± 6	4.8	95
	680	650 ± 40	4.1	96

Table 4
Characteristics of methodologies for determining organic substances vapors in the air by use of sorption pre-concentration and flame-ionization detection. The sorbent—35% BAC on PTEF, tube 5 cm × 0.3 cm. t—pre-concentration duration; V_{sam}=sample volume; $C_{\min}$=detection limit; δ=relative analysis error (confidence probability=95%; n=4) at $C = 5C_{\min}$.

Extracted component	V_{sam}, L	t, min	$C_{\min}$, μg/m^3	δ, %
Methanol	0.5	2	10	12
Ethanol	1	3.0	3	11
Propanol	2.0	4.0	2	15
Acetone	2.0	4.0	2	11
Methylethyl ketone	2.0	4.0	3	12
Methyl acetate	3.0	6.0	1	15
Ethyl acetate	3.0	6.0	2	15
Methyl acrylate	3.0	6.0	1	20
Methyl metacrylate	3.0	6.0	2	20

4. Conclusions

It is established that efficacy of the devised sorbents in terms of dynamic sorption from gaseous media is by far superior with the regard to the efficacy of their bulk-porous analogues in their regular granular form. We established that retention parameters of analytes and efficacy of mass transfer are determined by the SAM content and do not show pronounced dependency upon the method of processing a SLS. We propose a suspension method of preparing non-polar SLS, letting to affix such quantities of SAM, which attain up to 50% of a carrier mass. Express charts of determining low-molecular organic substances (low alcohols, ketones and complex esters) in the air on the level of maximum allowable concentration are worked out, humidity being unnormalized, while pre-concentration being performed on the devised polar and non-polar SLS. Analytes are subsequently thermally desorbed and analyzed by a gas chromatograph.

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