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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.

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1. Introduction

Concentrations of organic contaminants in the atmosphere are measured to determine background pollution levels and their compliance with maximum permissible 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 latter 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) $^{\circ}\text{C}$ 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 $^{\circ}\text{C}$ (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 $^{\circ}\text{C}$ 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 $^{\circ}\text{C}$) [27]. The said properties of the material ensured that no artifact peaks showed up in the chromatograms below the temperature of 300 $^{\circ}\text{C}$. 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 \times 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:

$$C_G = C_0/K, \quad (1)$$

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:

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

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 $C/C_0=0.16$.

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