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INORGANIC SYNTHESIS AND INDUSTRIAL  
INORGANIC CHEMISTRY

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## Use of Silochrome with Grafted Layers of Transition Metal Acetonates for Sorption Concentration of Volatile Organic Substances from Aqueous Media

E. A. Pakhnutova, Yu. G. Slizhov, and A. I. Makarycheva

National Research Tomsk State University, pr. Lenina 36, Tomsk, 634050 Russia

e-mail: pakhnutovae@mail.ru

Received March 29, 2016

**Abstract**—Sorbents based on silica of Silochrome S-120 brand with covalently attached layers of transition metal acetylacetonates were synthesized. The sorption properties of the resulting chelate-containing materials were studied and the analytical potential of their application for rapid sorption concentration of volatile organic compounds from water bodies was evaluated.

**DOI:** 10.1134/S1070427216050086

Development of high-efficiency methods for concentration of environment contaminants is a topical task for modern ecological and analytical chemistry [1]. The determination of most of volatile organic compounds (VOCs) is based on the gas-chromatographic method distinguished by simple equipment, low detection limits, and high selectivity. The maximum permissible concentrations (MPCs) of some VOCs may constitute several micrograms per liter (ppb), and, therefore, it becomes necessary to use additional concentration.

A variant of the dynamic sorption, the sorption concentration combined with a static gas extraction [2, 3] or with a dynamic and continuous extraction [4, 5], and the purge-and-trap method in which the dynamic sorption and the gas extraction are combined are attributed to widely used methods for concentration of volatile organic substances from water bodies. The last method has an advantage of making possible the VOC extraction in the continuous on-line mode [6, 7].

Despite the wide variety of materials used in concentration, development of new sorbents with prescribed properties for effective and selective extraction of various substances and toxicants from rather diverse objects and a search for new approaches to their correct determination with preliminary application of sorption

concentration and physicochemical methods are an important topical task.

Microcomponents are most frequently concentrated with synthetic polymers [8], carbon sorbents [9], and chemically modified silicas (CMSs). As a rule, the maximum sorption capacity for VOCs is exhibited by carbon sorbents. However, the fact that microimpurities are firmly retained in these sorbents makes the desorption difficult and restricts their application [9]. The problem of the thermal desorption of analytes is solved by using surface-layered sorbents modified with inorganic salts [10, 11].

The common disadvantage of polymeric adsorbents is their low sorption capacity for polar organic substances, which gives no way of reaching high concentration coefficients. Amorphous porous silicas are versatile sorbents because their structural characteristics (specific surface area, pore diameter and volume, particle size, and strength) can be varied in the course of synthesis [12].

In our opinion, of particular interest in this regard are CMS-based sorption materials and, in particular, silica gels with grafted layers of chelate complexes. A characteristic feature of these sorbents is that the sorption process occurs in a thin surface layer of the modifier,

which provides a high mass-transfer rate, and the use of SiO<sub>2</sub> with a developed specific surface area and a substantial porosity ensures the high permeability of the sorption layer.

The chemical modification of silicas with  $\beta$ -diketonates of transition metals makes it possible to obtain materials in which the sorption properties of the surface depend on the nature of a ligand and a central metal ion, as well as on the electron density distribution in the structure of the grafted complex. The simultaneous existence of several active centers in a complex compound enables various specific interactions of these sorbents with sorbates of various kinds, which makes it possible to raise the efficiency of the dynamic sorption concentration of VOCs on chelate-containing sorbents [13, 14].

The goal of our study was to assess the practical application potential of sorbents based on Silochrome S-120 with grafted layers of nickel, cobalt, and copper acetylacetonates for rapid sorption concentration of volatile organic compounds from water bodies.

## EXPERIMENTAL

Sorption materials were produced from silica of Silochrome S-120, which has high thermal, mechanical, and chemical stability, by sequential assembly via the SiO<sub>2</sub> chlorination stage and subsequent synthesis on its surface of nickel, cobalt, and copper acetylacetonates by the procedure reported in [4]. The structure of the chelates and the surface morphology were examined by IR and Raman spectroscopy and scanning electron microscopy (SEM) [15].

Parameters of the specific surface area and the porosity of the sorbents were evaluated with a TriStar II automated gas-adsorption analyzer by using the volumetric variant of the sorption method. The specific surface area was calculated by the BET method in the automatic mode upon avacuum treatment at 200°C for 2 h from the isotherm of low-temperature sorption of the nitrogen vapor.

The thermal stability of the chromatographic sorbents was determined by thermal analysis on a Netzsch STA 449 instrument in air in the temperature range 25–600°C at a heating rate of 10 deg min<sup>-1</sup>.

To assess the analytical potential of the chelate-containing sorbents, we passed model gas mixtures of VOCs with constant concentration through sorption columns packed with these sorbents at a prescribed rate.

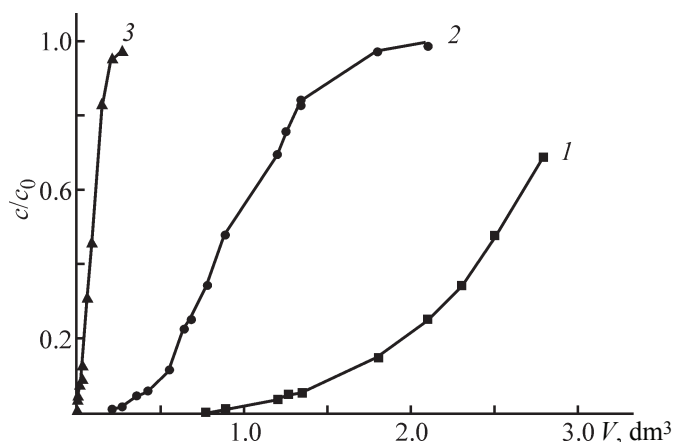
To prepare the model gas mixtures, a flow of helium was passed at a constant rate through aqueous solutions of organic substances of various classes: toluene, hexane, methanol, and acetone. Then the gas and liquid phases were sampled at the column outlet, with the concentrations of the substances being sorbed subsequently determined. The extraction time was varied within the range 1–60 min. The optimal conditions of the dynamic gas extraction were determined by varying the flow rate of the extracting gas from 10 to 45 cm<sup>3</sup> min<sup>-1</sup>, and the concentration of the analytes in the model solution, from 20 to 50 mg dm<sup>-3</sup>.

To determine the breakthrough volumes  $V_B$  and the retention volumes  $V_R$  of the test compounds, we measured in chromatograms the heights  $h$  of the analyte peaks and related these heights to the heights  $h_0$  of peaks obtained on introducing into the chromatograph the model mixture delivered into the sorption column [11]. Within the range in which the detector signal linearly depends on the analyte concentration, the value of  $h/h_0$  is equal to  $c/c_0$ , where  $c$  and  $c_0$  are the analyte concentrations at the outlet and inlet of the sorption column, respectively. The output curves of retention of the test compounds were plotted as dependences of  $c/c_0$  on  $V$ , where  $V$  is the gas volume passed through the column. As  $V_B$  was taken the volume  $V$  of a gas passed through the column, which corresponds to the 95% extraction of an analyte from a sample. As  $V_R$  was taken the volume of the gas passed through the column, for which the condition  $c/c_0 = 0.5$  is satisfied. As the parameter describing the mass-exchange efficiency served the height equivalent to a theoretical plate (HETP), with consideration for the length of the sorption column packed with the sorbent under study and for the number  $N$  of plates, found by the formula [16]:

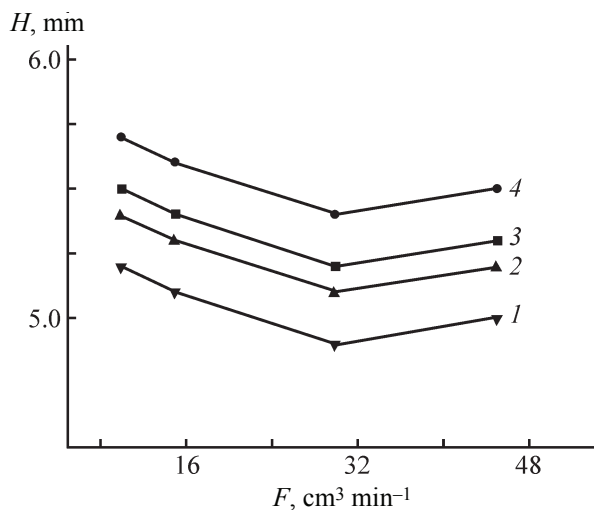
$$N = V_R^2 (V_R - V_{0.16})^{-2},$$

where,  $V_R$  is the retention volume and  $V_{0.16}$  is the sample volume for which the condition  $c/c_0$  is satisfied.

The organic substances concentrated in the sorption column upon dynamic sorption were desorbed by liquid extraction with organic solvents (dichloromethane, dimethylformamide, ethyl acetate) and by the thermal desorption method. To perform the thermal desorption, the concentrator was placed directly in the evaporator of the gas chromatograph at a temperature of 180–250°C, which was the starting procedure of the gas-chromatographic analysis. The study was carried out with a Chrom-5 gas chromatograph with flame-ionization detector and column packed with Chromaton-N-AW-DMCS + 15%



**Fig. 1.** Output curves of methanol retention on Silochrome S-120 with a layer of nickel acetylacetonate. ( $c/c_0$ ) Ratio between the analyte concentrations at the outlet and inlet of the sorption column, respectively, and ( $V$ ) volume of the extracting gas; the same for Fig. 4. Flow rate of the extracting gas (helium) ( $\text{cm}^3 \text{min}^{-1}$ ): (1) 15, (2) 30, (3) 45.



**Fig. 2.** Dependence of HETP  $H$  for (1, 3) methanol and (2, 4) acetone on the flow rate  $F$  of the extracting gas for sorbents (3, 4) Silochrome S-120 and (1, 2) Silochrome S-120 with a layer of nickel acetylacetonate. (1) Hexane, (2) toluene, (3) methanol, (4) acetone on Silochrome S-120 with a layer of nickel acetylacetonate.

Carbowax (column length 1.2 m and inner diameter 3 mm) in the isothermal mode at a temperature of  $150^\circ\text{C}$ .

The sorbents synthesized in the study were used for gas-extractive concentration of volatile organic compounds from samples of river (Ushaika River, Tomsk) and industrial water (Tomskneftekhimi OOO, Tomsk), with the subsequent thermal and liquid-extractive desorption of the concentrated impurities. Helium was passed as an extractive gas through a 120- $\text{cm}^3$  water sample at a

rate of  $30 \text{ cm}^3 \text{min}^{-1}$  in the course of 30 min. The VOCs were extracted by the thermal desorption method, with the subsequent analysis on Agilent 6890N gas chromatograph equipped with a flame-ionization detector (DIP) and NR-5 capillary column ( $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ ): input with 1 : 4 split ratio; linear velocity of the carrier gas,  $1.2 \text{ cm}^3 \text{min}^{-1}$ ; evaporator and detector temperatures  $250^\circ\text{C}$ ; and temperature programmed in the following mode: 5 min at  $50^\circ\text{C}$  and heating to  $230^\circ\text{C}$  at a rate of  $10 \text{ deg min}^{-1}$ .

Prior to performing the liquid desorption, we preliminarily dried the concentration column with the sorbent and eluted VOCs with 3  $\text{cm}^3$  of dichloromethane. The chromatomass-spectrometric analysis was made with an Agilent Technologies 7890A instrument. Wastewater components were identified by the retention times of standard compounds, Kovach indices with the use of the NIST database, and mass spectra. The concentration of effluents in a sample was found from the area of chromatographic peaks by using the absolute calibration method.

## RESULTS AND DISCUSSION

The texture characteristics of the samples under study (Table 1) indicate that both the starting and modified Silochrome S-120 belong to mesoporous sorbents (average pore diameter 33–36 nm). As a result of deposition of metal acetylacetonates onto the surface of  $\text{SiO}_2$ , the specific surface area decreases (from 112 to  $89 \text{ m}^2 \text{g}^{-1}$ ) and so does the porosity because of the filling of fine pores with the chelate. According to the thermal analysis data (Table 1), the materials synthesized in the study can be used for gas-chromatographic studies at rather high temperatures ( $290\text{--}300^\circ\text{C}$ ) without disintegration of the modifying complex.

A study of the influence exerted by the flow rate of the extracting gas on the sorption characteristics of the materials demonstrated that raising the flow rate of helium to  $45 \text{ cm}^3 \text{min}^{-1}$  results in a substantial decrease in the retention volumes of the sorbates (Fig. 1). This is due to the smaller penetration depth of analyte molecules into pores of silica. At the same time, lowering the flow rate to  $15 \text{ cm}^3 \text{min}^{-1}$  leads to a longer gas extraction process and to a considerable expenditure of the extracting gas. The optimal flow rate for the rapid sorption concentration of VOCs from aqueous solutions for the sorption materials under study is  $30 \text{ cm}^3 \text{min}^{-1}$ .

Figure 2 compares the dependences of the HETP of methanol and acetone on the flow rate of the extracting

**Table 1.** Specific surface area  $S_{sp}$ , porosity, and thermal stability of the sorbents under study

Sorbent	$S_{sp}$ , $m^2 g^{-1}$	Total pore volume, $cm^3 g^{-1}$	Average pore size, nm	$T_{max}$ , $^{\circ}C$
Silochrome S-120	112	1.08	38	–
Silochrome S-120 + nickel acetylacetonate	98	0.98	36	300
Silochrome S-120 + cobalt acetylacetonate	89	0.92	33	290
Silochrome S-120 + copper acetylacetonate	99	0.81	33	290

**Table 2.** Analyte retention volumes  $V$  in sorption concentration on the sorbents under study, based on Silochrome S-120  $c_0 = 20 mg dm^{-3}$ ,  $F(He) = 30 cm^3 min^{-1}$ ,  $t_{exp} = 1-60 min$ 

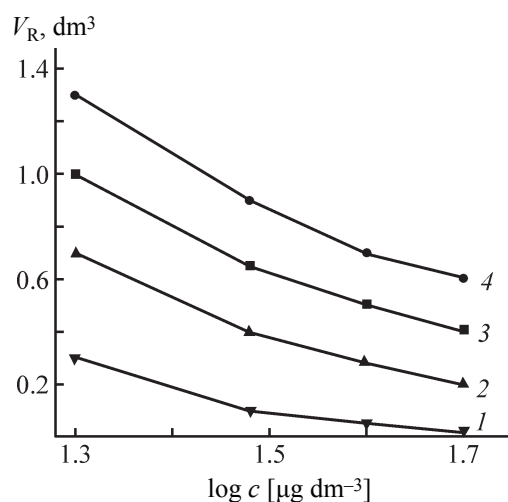
Sorbent	Retention volume $V$ , $dm^3$			
	hexane	toluene	methanol	acetone
Silochrome S-120	$0.06 \pm 0.01$	$1.2 \pm 0.1$	$1.6 \pm 0.1$	$1.9 \pm 0.1$
Silochrome S-120 + nickel acetylacetonate	$0.04 \pm 0.01$	$0.5 \pm 0.1$	$0.8 \pm 0.1$	$1.0 \pm 0.1$
Silochrome S-120 + cobalt acetylacetonate	$0.05 \pm 0.01$	$0.8 \pm 0.1$	$1.3 \pm 0.1$	$1.4 \pm 0.1$
Silochrome S-120 + copper acetylacetonate	$0.06 \pm 0.01$	$1.0 \pm 0.1$	$1.4 \pm 0.1$	$1.7 \pm 0.1$

gas through sorption columns packed with the starting and modified Silochrome S-120 and a bed formed by nickel acetylacetonate of a single granulometric composition (particle size 0.20–0.35 mm. According to these dependences, the mass-exchange efficiency decreases (HETP grows) at a helium flow rate of  $15 cm^3 min^{-1}$  and at the flow rate of helium through the sorbent raised to  $45 cm^3 min^{-1}$ . Thus, the sorption efficiency grows when the extracting gas is passed at a rate of  $30 cm^3 min^{-1}$ .

The results obtained in a study of the sorption properties of Silochrome S-120 modified with nickel, cobalt, and copper acetylacetonates suggest that, as the concentration of sorbates in an aqueous solution is lowered in the course of a gas-extraction concentration, their retention parameters become larger. Figure 3 shows how the retention volumes of hexane, toluene, methanol, and acetone depend on their content in the aqueous solutions. This run of the dependences of the retention volumes on the VOC concentration plays a positive role when the dynamic gas extraction method is used as a preliminary concentration stage because the lower content of sorbates in water provides larger coefficients of their concentration.

According to the retention data for the substances being analyzed, use of unmodified  $SiO_2$  is inappropriate

in the case of the gas extraction because the degree of extraction of concentrated components does not exceed 70%, this being due to the developed specific surface area ( $112 m^2 g^{-1}$ ) and hindered desorption from fine pores. Modification of the surface of Silochrome S-120 with metal acetylacetonates diminishes the specific surface area and the porosity, which favors a faster elution of

**Fig. 3.** Dependence of the retention volume  $V_R$  on the VOC concentration  $\log c$  in an aqueous solution.

**Table 3.** Evaluation of the significance of the systematic error of the procedure for gas-chromatographic determination of VOCs in water bodies via sorption concentration on Silochrome S-120 with a grafted layer of copper acetylacetonate<sup>a</sup>

Analyte	Introduced $c_0$ , mg dm <sup>-3</sup>	Found $\bar{c}$ , mg dm <sup>-3</sup>	$S_x$	$t_{\text{exp}}$	$t_{\text{tab}}$
Toluene	10	9.2 ± 1.3	0.57	4.1	4.3
	20	19.3 ± 1.6	0.49	2.8	4.3
Hexane	10	9.4 ± 1.1	0.42	4.1	4.3
	20	19.1 ± 1.7	0.64	2.9	4.3
Methanol	10	9.3 ± 1.4	0.49	4.2	4.3
	20	19.2 ± 1.7	0.57	3.8	4.3
Acetone	10	9.1 ± 1.2	0.64	4.0	4.3
	20	19.4 ± 1.1	0.42	2.6	4.3

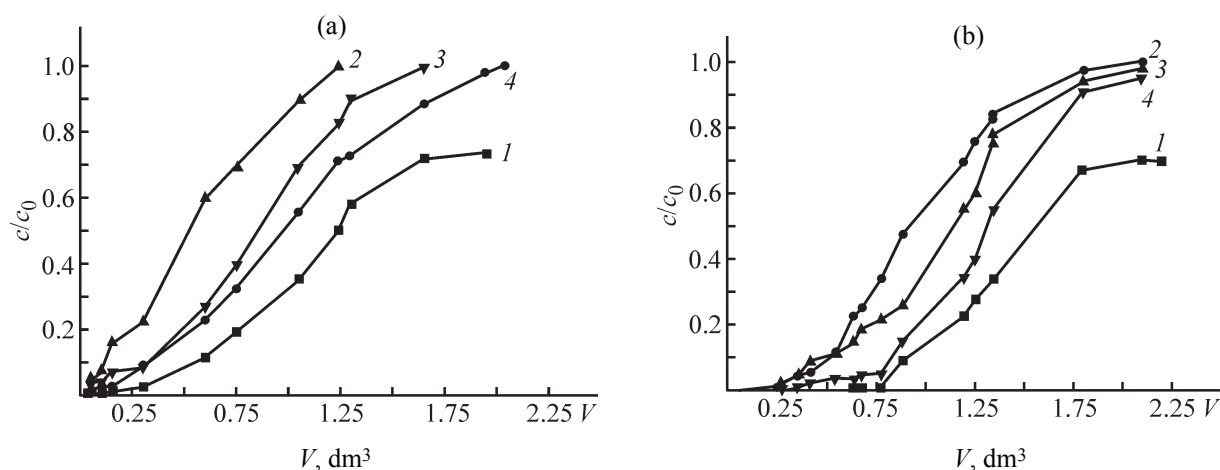
<sup>a</sup>  $S_x$  is the standard deviation;  $t_{\text{tab}}$ , tabulated value of the Student's coefficient ( $P=0.95$ ,  $n=3$ ); and  $t_{\text{exp}}$ , experimental values of the  $t$ -criterion [20].

the sorbates and an increase in the degree of their elution to 100%.

At the same time, the VOC retention parameters and the sorption concentration efficiency are affected by the metal ion in the modifying complex grafted to the surface of the starting Silochrome S-120. In particular, changing the nature of the central metal ion in the chelate structure in the order Ni(II) → Co(II) → Cu(II) leads to an increase in the retention volumes of the analytes (Table 2). The largest sorbate retention parameters are characteristic of silica gels with a grafted layer of copper acetylacetonate (Fig. 4). This is presumably due to the formation of coordination-unsaturated complexes of metal  $\beta$ -diketonates on the SiO<sub>2</sub> surface of varied stoichiometry, predominantly with M : L ratio of 1 : 2 for nickel and cobalt chelates and M : L = 1 : 1 for

copper acetylacetonates, which is confirmed by the data obtained in a study of the acid-base and chromatographic properties of the materials under consideration [16–18]. As the nature of the metal in the grafted complex is varied, the strength and concentration of centers inclined to be involved in donor-acceptor interactions, the chromatographic polarity, and the thermodynamic characteristics of sorption for electron-donor sorbate molecules, all grow in the order Ni(II) < Co(II) < Cu(II).

The final stage of the sorption concentration of volatile organic compounds on chelate-containing sorbents is their thermal desorption or desorption by elution with organic solvents. It was found that the rapid quantitative (>95%) thermal desorption of thermally stable organic substances from the surface of the silicas under study into the carrier-gas flow is possible at 180–250°C.



**Fig. 4.** Output curves of (a) toluene and (b) methanol retention on (1) starting Silochrome S-120 and (2–4) that modified with (2) nickel, (3) cobalt, and (4) copper acetylacetonates from aqueous solutions.  $c_0 = 20$  mg dm<sup>-3</sup>,  $F(\text{He}) = 30$  cm<sup>3</sup> min<sup>-1</sup>,  $t_{\text{extr}} = 1$ –60 min.

In the case of a gas-chromatographic analysis of the concentrate in liquid desorption, it is reasonable to use a solvent whose peak in the chromatogram emerges before or after the peaks associated with the analytes and does not interfere with their determination. Figure 5 shows curves for elution of sorbed toluene and methanol by various solvents. The data obtained indicate that it is preferable to use dichloromethane because smaller eluent volumes are required in this case and the necessary completeness of desorption is reached for the components being determined. In addition, in contrast to dimethylformamide and ethyl acetate, the peak of the low-boiling dichloromethane does not interfere with determination of polar organic compounds and aromatic hydrocarbons with close boiling points.

To assess the significance of the systematic error for the procedure we developed, we analyzed model aqueous solutions with known concentrations of hexane, toluene, methanol, and acetone by using the algorithm that takes into account the error in preparing the solutions [19]. According to the data in Table 3, the experimental values of the *t*-criterion are smaller than the tabulated value of the Student's coefficient, which means that the systematic error of the procedure is nonsignificant on the background of the random inaccuracy, which does not exceed 15% for three parallel measurements and confidence probability  $P = 0.95$ .

Based on the results obtained for the retention of sorbates on the materials under study (Table 2), we used Silochrome S-120 chemically modified with copper acetylacetonate for performing the concentration followed by gas-chromatographic and chromatomass-spectrometric determination of admixtures of volatile organic compounds in real samples of river and industrial water, mostly represented by aliphatic and aromatic hydrocarbons (Table 4).

The results of GC and GC-MS analyses demonstrate that the total content of hydrocarbons in river water is 3.5–3.7 mg dm<sup>-3</sup>. This value exceeds the MPC according to GN (Hygienic Regulation) 2.1.5.1315–03 “Maximum permissible concentrations (MPC) of chemical substances in water of household-drinking and cultural-domestic water bodies” (0.3 mg dm<sup>-3</sup>) and the MPC of noxious substances in water of fishery water basins (0.05 mg dm<sup>-3</sup>) [20].

A chromatographic analysis of industrial water (Table 4) demonstrated that the content of benzene and ethylbenzene, toluene and methylbenzene, and methanol does not exceed the MPC specified by the Federal nature

**Table 4.** Results of GC and GC/MS determinations of the content of hydrocarbon impurities in water bodies (1) Industrial water from Tomskneftekhim OOO, Tomsk, and (2) river water from the Ushaika River, Tomsk

Compound	Content, mg dm <sup>-3</sup>	
	1	2
C <sub>4</sub> –C <sub>5</sub> alkanes	4.0 ± 0.1	0.8 ± 0.2
Benzene	2.3 ± 0.1	0.7 ± 0.1
Toluene	2.0 ± 0.1	0.1 ± 0.1
Ethylbenzene	1.7 ± 0.1	–
<i>m</i> -Xylene	2.0 ± 0.1	–
Phenylacetylene	0.6 ± 0.1	–
<i>o,p</i> -Xylenes	6.0 ± 0.2	–
Styrene	1.6 ± 0.1	–
Allylbenzene	1.4 ± 0.1	–
<i>n</i> -Propylbenzene	0.7 ± 0.1	–
1-Ethyl-3-methylbenzene	1.7 ± 0.1	–
1,2,3-Trimethylbenzene	0.8 ± 0.1	–
1-Ethynyl-4-methylbenzene	–	0.5 ± 0.2
5-Methyl-1,6-heptadien-3-ine	–	0.6 ± 0.1
1-Ethyl-4-methylbenzene	0.7 ± 0.1	–
$\alpha$ -Methylstyrene	1.9 ± 0.1	–
2-Methylstyrene	3.1 ± 0.2	–
3-Methylstyrene	2.2 ± 0.1	–
3-Ethylstyrene	4.9 ± 0.2	–
Indan	2.2 ± 0.1	–
Indene	19.1 ± 0.3	0.3 ± 0.1
1,2-Dihydronaphthalene	2.1 ± 0.1	0.4 ± 0.1
Naphthalene	5.5 ± 0.2	0.3 ± 0.1

protection regulatory documents [PND (Environmental Regulatory Document) F 14.1:2:4.57–96 and measurement procedure no. 071–2011 (FR.1.31.2012.11959 Tomskneftekhim OOO)]. The amount of pyrolysis products, such as naphthalene, indene, and xylenes, exceeds the MPC of 5 mg dm<sup>-3</sup> established by regulatory documents [PND F 14.1:2.116–97, PND F 14.1:2:4.5–95 (FR.1.31.2007.03793)]. The industrial water under study (Tomskneftekhim OOO) is subjected to the required additional purification at disposal facilities.

## CONCLUSIONS

(1) Sorbents based on Silochrome S-120 with grafted layers of nickel, cobalt, and copper acetylacetonates were studied. The specific surface area and the porosity of the samples obtained were determined. It was shown that the specific surface area decreases upon modification from 112 to 89 m<sup>2</sup> g<sup>-1</sup>. The results of a thermal analysis were used to assess the thermal stability of the chelates and determine the range of working temperatures of the sorbents synthesized, which can be used up to 290°C without disintegration of the complex.

(2) The chelate-containing sorbents were used to determine the optimal conditions of the dynamic sorption concentration, which provide a high sorption efficiency of volatile organic compounds and a high degree of their extraction.

(3) It was found that, with the metal ion in the grafted chelate varied in order Ni(II) → Co(II) → Cu(II), the largest analyte retention parameters are characteristic of sorbents with a layer of copper acetylacetonate.

(4) The results obtained in the study demonstrate that chemically modified silicas with grafted layers of metal acetylacetonates can be used in rapid preliminary concentration of volatile aliphatic, aromatic, and oxygen-containing substances from aqueous media for their subsequent gas-chromatographic and chromatomass-spectrometric determination.

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