

# Synthesis of Silokhrom S-120 Grafted with Transition-Metal Acetylacetonate Layers and Its Acid–Base and Chromatographic Properties

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**Abstract**—We have synthesized sorbents based on Silokhrom S-120 silica gel grafted with Ni<sup>2+</sup>, Co<sup>2+</sup>, and Cu<sup>2+</sup> acetylacetonate layers. Using pH measurements and a Hammett indicator method, we have studied the acid–base properties and composition of donor–acceptor centers on silica gel surfaces before and after modification. We have determined chromatographic retention parameters for test compounds and evaluated the polarity and selectivity of the sorbents. Modification with acetylacetonate chelates has been shown to increase the surface acidity of Silokhrom S-120, leading to changes in various types of intermolecular interaction.

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## INTRODUCTION

At present, a new direction in the research of chelate-containing chromatographic materials is the study of sorbents chemically grafted with surface layers. Since there is the possibility of varying the composition of complexes grafted onto the surface and controlling the nature of sorbate–sorbent interactions, such chelate layers are suitable for preconcentrating and analytically separating a wide range of substances, including those exhibiting selectivity not only to a particular class of compounds but also to a particular substance [1, 2]. In connection with this, there is currently great interest in the synthesis and characterization of chelate-containing materials.

The ability to predict physicochemical and analytical properties of sorbents depends crucially on knowledge of quantitative correlations based on data characterizing the properties of materials of interest [3]. One important step in studies of fundamental physicochemical relationships is to assess acid–base properties, which are of paramount importance in characterizing any compound grafted onto a surface and the associated ion-exchange and complexation processes [4].

According to current views, the surface of adsorbents is a set of Lewis and Brønsted centers of both the acidic and basic types [5]. Their strength and concentration depend on modifiers, synthesis conditions, impurity content, and other factors, and determine the reactivity and sorption capacity of the surface and the chromatographic retention and separation mechanisms.

The objectives of this work were to synthesize chelate-containing sorbents, analyze the effect of transi-

tion-metal chelates (copper, nickel, and cobalt acetylacetonates) on the distribution of donor–acceptor centers over the surface of Silokhrom S-120 using pH measurements and Hammett indicator adsorption, and examine the relationship between the acid–base state of the surface and chromatographic retention characteristics.

## EXPERIMENTAL

Chelate-containing gas-chromatographic materials were prepared using Silokhrom S-120 silica gel, which offers good mechanical, thermal, and chemical stability. The sorbents were produced by a sequential assembly method via the chlorination of the silica gel with thionyl chloride in a methylene chloride solution at room temperature. The modifier ligand used was acetylacetonate (aac). To run the chemical reaction on the sorbent surface, we synthesized its sodium salt. To attach the ligand, the salt was dissolved in dimethylformamide and applied to the surface of the chlorinated silica gel through gradual solvent evaporation. In the final step, the modified silica gel was treated with an ethanolic solution of copper, nickel, and cobalt chlorides [6]. To confirm the structure of the chelates and examine the surface morphology, we used IR spectroscopy and scanning electron microscopy [7].

The specific surface area and porosity of the sorbents were evaluated using a TriStar II automatic gas adsorption analyzer and a volumetric sorption method. The specific surface area was calculated by the BET method in automatic mode after evacuation at 200°C for 2 h, using a low-temperature nitrogen vapor sorption isotherm.

The acid–base properties of the surface of the sorbents were studied using pH measurements, which allow one to estimate the integral surface acidity, and Hammett indicator adsorption, which is utilized to assess and differentiate the acid–base properties of surfaces. The pH of an adsorbent suspension in double-distilled water was monitored from the instant of formation until electrochemical equilibrium was reached, using a Mul'titest IPL-11 pH meter with an ESK-10601 combination glass electrode. The parameters used to characterize the acid–base state of the surface were the suspension pH values after the sample had been in contact with water for 5, 10, and 15 s. From these data, we assessed the strength of Lewis basic and acidic centers on the surface. The content of donor–acceptor centers before and after Silokhrom S-120 modification was determined by an indicator method using Hammett acid–base indicators and spectrophotometrically in the visible range. The indicators used and their characteristics are listed in Table 1.

The optical density of the starting indicator solutions ( $D_0$ ) was measured on a PE-5400 VIS/UV spectrophotometer. Next, sorbent suspensions in the solutions were prepared and their optical density ( $D_1$ ) was determined after adsorption equilibrium had been reached and the precipitate was separated from the solution by decantation. To take into account the influence of the pH of the medium and sample dissolution on the optical density when the sample was in contact with solution, a sorbent suspension in distilled water was prepared, an indicator solution was added to the decantate 120 min later, and the optical density ( $D_2$ ) was measured. The concentration of centers of a given acid strength ( $q$ , mmol/g), equivalent to the amount of the adsorbed indicator,  $q_{pK_a}$ , was calculated as

$$q_{pK_a} = \frac{C_{\text{Ind}} V_{\text{Ind}}}{D_0} \left[ \frac{|D_0 - D_1|}{\alpha_1} \pm \frac{|D_0 - D_2|}{\alpha_2} \right],$$

where  $C_{\text{Ind}}$  and  $V_{\text{Ind}}$  are the indicator concentration and volume, and  $\alpha_1$  and  $\alpha_2$  are the sample weights in the  $D_1$  and  $D_2$  measurements. The minus sign corresponds to similar variations in  $D_1$  and  $D_2$  relative to  $D_0$ , and the plus sign corresponds to opposite variations [8].

Acid strength distribution curves of adsorption centers on sample surfaces (acid–base spectra) were plotted as  $q_{pK_a}$  against  $pK_a$ . The acidity function of sorbent surfaces was calculated as

$$H_0 = \frac{\sum pK_a q_{pK_a}}{\sum q_{pK_a}}$$

The relative standard deviation in parallel optical density measurements for a given sample was estimated at  $\Delta q_{pK_a} = \pm 0.40\%$  [9].

The chromatographic behavior of the sorbents was studied isothermally on a Chrom 5 gas chromatograph

**Table 1.** Characteristics of the acid–base indicators used

Indicator	$pK_a$	$\lambda_{\text{max}}$ , nm
<i>o</i> -Nitroaniline	−0.29	410
Crystal violet	+0.80	580
Brilliant green	+1.30	610
<i>m</i> -Nitroaniline	+2.50	340
Methyl orange	+3.46	460
Bromophenol blue	+4.10	590
Methyl red	+5.00	430
Chrysoidine	+5.50	448
Bromocresol purple	+6.40	540
<i>p</i> -Nitrophenol	+7.15	360
Bromothymol blue	+7.30	430
Phenol red	+8.00	430
Thymol blue	+8.80	430
Pyrocatechol	+9.45	274
Nile blue	+10.5	640
Tropaeolin O	+12.0	440
Indigo carmine	+12.8	610
<i>m</i> -Dinitrobenzene	+16.8	315

equipped with a plasma ionization detector. We used glass columns 1.2 m in length and 3 mm in inner diameter. The carrier gas (helium) flow rate was 30 cm<sup>3</sup>/min.

## RESULTS AND DISCUSSION

Our results demonstrate that the surface modification of Silokhrom S-120 with metal chelates leads to a decrease in specific surface area and porosity, which is caused by the retention of the complexes by the edges of large pores and the closure of small pores because of the filling with the chelate (Table 2).

Figure 1 shows the time dependences of the pH of aqueous suspensions for Silokhrom S-120 before and after the modification with nickel, cobalt, and copper acetylacetonates. The arrangement of the curves demonstrates that the surfaces of the samples differ in acid–base state. The surface of Silokhrom S-120, which consists predominantly of SiO<sub>2</sub>, is a set of Lewis and Brønsted centers of both the acidic and basic types. A Lewis acidic center is a vacant level of a Si atom, capable of accepting an electron pair. Lewis basic centers each are formed by two-electron orbitals

**Table 2.** Structural characteristics of the sorbents (relative uncertainty  $\Delta \pm 10\%$ )

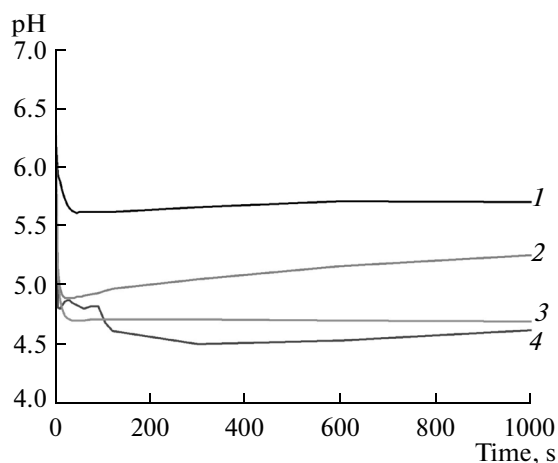
Sorbent	Specific surface area, m <sup>2</sup> /g	Total pore volume, cm <sup>3</sup> /g	Average pore size, nm
Silokhrom S-120	112	1	37
Silokhrom S-120 + Ni(acac)	93	1	33
Silokhrom S-120 + Co(acac)	84	0.96	32
Silokhrom S-120 + Cu(acac)	83	0.86	34

**Table 3.** Acid–base parameters of the sorbents

Sorbent	pH <sub>0</sub>	pH <sub>10</sub>	pH <sub>60</sub>	pH <sub>120</sub>	pH <sub>i</sub>	H <sub>0</sub>
Silokhrom S-120	6.3	5.9	5.6	5.6	5.7	6.5
Silokhrom S-120 + Ni(acac)	6.7	5.0	4.9	4.9	5.3	9.3
Silokhrom S-120 + Co(acac)	6.4	4.8	4.7	4.7	4.7	8.9
Silokhrom S-120 + Cu(acac)	6.2	4.5	4.8	4.6	4.8	10.6

pH<sub>10</sub>, pH<sub>60</sub>, and pH<sub>120</sub> are the pH values after the sample was in contact with water for 10, 60, and 120 s; pH<sub>i</sub> is the isoionic pH; and H<sub>0</sub> is the Hammett acidity function, evaluated from adsorption center distribution spectra.

of an oxygen atom and are capable of chemical interaction, donating electrons to an energy level of an adsorbed molecule. Brønsted acids and bases on the surface of Silokhrom S-120 are represented by hydroxyl groups, as well as by deprotonated water molecules bonded to Lewis basic or acidic centers by an acidic ( $=\text{Si}^{\delta-}\dots\text{H}-\text{OH}$ ) or basic ( $=\text{Si}^{\delta+}\dots\text{OH}_2$ ) mechanism [10].



**Fig. 1.** Kinetic curves for the variation in the pH of aqueous suspensions: (1) Silokhrom S-120, (2) Silokhrom S-120 + nickel acetylacetonate, (3) Silokhrom S-120 + cobalt acetylacetonate, (4) Silokhrom S-120 + copper acetylacetonate.

At the initial instant, the factor defining the variation in the pH of the medium is the interaction of water molecules with the sample surface and the basic or acidic dissociation of the water. The decrease in the pH of the suspensions during the first few seconds indicates that the surface of the unmodified and modified sorbents has Lewis acidic centers and that water is sorbed on these by an acidic mechanism. The subsequent increase in the pH of the medium until adsorptive–electrochemical equilibrium is reached is due to the predominance of proton donors and acceptors on the surfaces under consideration. In the case of Silokhrom S-120, adsorption–desorption equilibrium is reached in 500 s, and the corresponding steady-state pH value indicates a weakly acidic state of the surface. Chemical surface modification with the metal acetylacetonates leads to a considerable decrease in acidity. The pH values in Table 3, obtained after the samples were in contact with water for 10, 60, and 120 s, demonstrate that the Lewis acidity increases in the order Silokhrom S-120 < Silokhrom S-120 + Ni(acac) < Silokhrom S-120 + Co(acac) < Silokhrom S-120 + Cu(acac). The silica gel grafted with copper acetylacetonate layers has the most pronounced acidic properties: the variation from the unmodified sorbent is 1.4 pH units.

The results of pH measurements were used to assess the integral surface acidity and ascertain the predominance of acidic centers on the surface of our samples. To determine their nature, strength, and concentration, we used Hammett indicator adsorption at  $pK_a$  values in the range  $-0.29$  to  $+16.8$ .

Figure 2 shows adsorption center distributions on the surface of the sorbents in an aqueous medium. It is seen that the distribution of acid–base centers is non-uniform and has discrete, sufficiently well differentiated bands, with maxima of various intensities, corresponding to particular  $pK_a$  values. Under the analytical conditions of this study, the indicators adsorb on both Brønsted and Lewis centers, on which water molecules are adsorbed by the coordination mechanism according to its  $pK_a$  value.

The  $pK_a$  value of 7 corresponds to neutral centers. An increase in  $pK_a$  corresponds to stronger donor properties of atoms on the sorbent surface (acid indicator adsorption), and a decrease corresponds to stronger acceptor properties (base indicator adsorption) [11].

Analysis of the adsorption center distribution spectra indicates that Brønsted acidic ( $pK_a$  1.3 and 6.4) and basic ( $pK_a = 12$ ) centers prevail on the surface of Silokhrom S-120. The modification of the sorbent with the metal acetylacetonates leads to a continuous variation in the surface density of donor–acceptor centers ( $q_{pK_a}$ ). The metal atoms of the acetylacetonate complexes act as Lewis acidic centers, as evidenced by the corresponding bands at  $pK_a = 16.8$  in the adsorption center distribution spectrum, whose intensity increases in the order  $Ni^{2+} - Co^{2+} - Cu^{2+}$ .

The coordination of water molecules by aprotic Lewis centers leads to the formation of secondary Brønsted basic and acidic centers. Applying nickel acetylacetonate to the surface of Silokhrom S-120 reduces the density of Lewis basic adsorption centers and markedly increases that of Brønsted neutral and basic ( $pK_a = 12$ ) centers, which correlates with pH curves. In the case of the sorbent covered with cobalt acetylacetonate layers, the nature of the surface is determined by the presence of proton-acceptor ( $pK_a = 5.5-6.4$ ) and proton-donor  $pK_a = 9.45-12$  Brønsted centers. The silica gel modified with copper acetylacetonate has well-defined acidic properties due to the

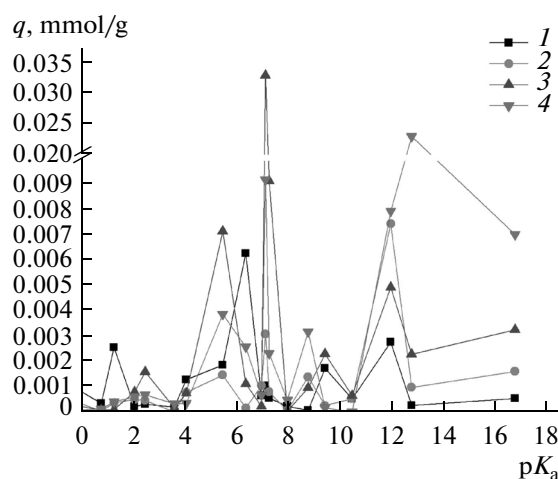


Fig. 2. Distributions of indicator adsorption centers on the surface of the sorbents: (1) Silokhrom S-120, (2) Silokhrom S-120 + nickel acetylacetonate, (3) Silokhrom S-120 + cobalt acetylacetonate, (4) Silokhrom S-120 + copper acetylacetonate.

presence of Lewis adsorption centers in the  $pK_a = 16.8$  region.

In the neutral region, all of the sorbents have a band at  $pK_a \sim 7$ . Characteristically, the adsorption centers in this region have no effect on the polarity of the sorbents with respect to neutral sorbates [12]. With increasing temperature, adsorbate molecules may displace the equilibrium toward proton-donor or proton-acceptor properties of the adsorption centers.

Comparison of the acid–base properties and adsorption center distribution with chromatography data on the retention of test compounds characterizing different types of intermolecular interaction [13] indicates that, in the case of Silokhrom S-120 modified with the acetylacetonates, increasing the acidity increases the retention parameters of aromatic hydrocarbons in the order  $Ni^{2+}, Co^{2+}, Cu^{2+}$  (Table 4). The retention of 2-butanone and nitropropane is due to donor–acceptor complexation. In this case, the sor-

Table 4. Kovach retention indices (RIs) and Rohrschneider polarity factors ( $X$ ,  $Y$ ,  $U$ , and  $Z$ ) of test substances on the sorbents at 150°C

Sorbent	Benzene		2-Butanone		Nitropropane		Ethanol		$\Sigma$
	RI	$X$	RI	$Z$	RI	$U$	RI	$Y$	
Silokhrom S-120	641	0.80	1013	5.37	1118	7.60	862	5.66	19.43
Silokhrom S-120 + Ni(acac)	611	0.50	950	4.74	1123	7.70	836	5.10	18.04
Silokhrom S-120 + Co(acac)	711	1.50	1027	5.51	1144	7.86	906	5.48	20.35
Silokhrom S-120 + Cu(acac)	757	1.96	1117	6.41	1194	8.36	946	5.88	22.61

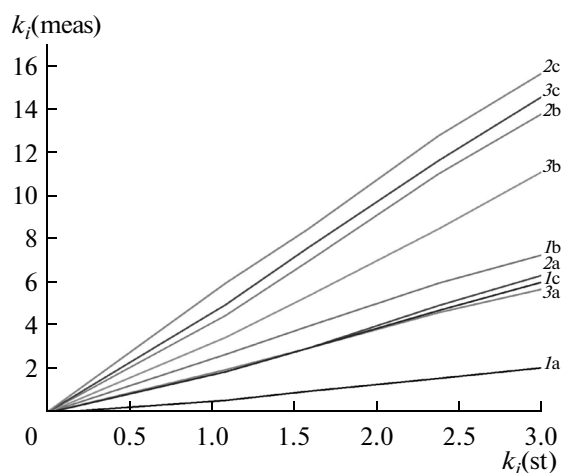


Fig. 3. Capacity coefficients of (a) alkanes, (b) arenes, and (c) alcohols on Silokhrom S-120 modified with (1) nickel, (2) cobalt, and (3) copper acetylacetonates.

bents act as electron acceptors, whereas ketones and nitro compounds act as donors. 2-Butanone and nitropropane adsorption indicates the presence and strength of Lewis acidic centers. In the case of the Silokhrom S-120 with copper acetylacetonate layers, the metal–nitropropane bond strength considerably exceeds that in the other sorbents, as evidenced by the Hammett indicator adsorption and chromatographic analysis data. The lower pH values and higher proton mobility on the modified Silokhrom S-120 lead to considerable ethanol retention, which characterizes the ability of the sorbent to form hydrogen bonds.

A key factor in selecting a sorbent is chromatographic polarity, which was evaluated using Kovach retention indices and Rohrschneider polarity factors with respect to Carboxipack B for standard compounds, each characterizing a particular type of intermolecular interaction in sorbate–sorbent systems. In addition, we used the overall polarity index, defined as the sum of the coefficients  $X$ ,  $Y$ ,  $U$ , and  $Z$ . The presence of acetylacetonate complexes changes the chromatographic polarity to all test substances, but the chemical nature of the complex determines the individual behavior of the sorbent with respect to one compound or another. In particular, in the case of the sorbent grafted with nickel acetylacetonate layer, the contribution of donor interactions ( $Y$ ,  $Z$ ) and  $\pi$ -complexation ( $X$ ) decreases, whereas orientational interactions with nitropropane ( $U$ ) become considerably stronger. The sorbent modified with cobalt acetylacetonate has an increased capability of donor–acceptor ( $U$ ,  $Z$ ) and  $\pi$ – $\pi$  ( $X$ ) interaction and hydrogen bond formation ( $Y$ ). A characteristic feature of all the sorbents is considerable retention of alcohols owing to the formation of hydrogen bonds between the oxygens of the ligand and the hydroxyl groups of the sorbates. It is also worth

noting the highest overall polarity of the Silokhrom S-120 modified with copper acetylacetonate, which has the highest Rohrschneider factor for nitropropane.

We evaluated the selectivity of the chromatographic materials under investigation for the homologous series of  $n$ -alkanes ( $C_5$ – $C_9$ ), aromatic hydrocarbons (benzene, toluene, ethylbenzene,  $m$ -xylene, and mesitylene), and aliphatic alcohols ( $C_1$ – $C_4$ ) at a temperature of  $150^\circ\text{C}$  using the linear relation between the capacity coefficient of the chelate-containing sorbents,  $k_i(\text{meas})$ , and that of unmodified Silokhrom S-120, taken as a standard,  $k_i(\text{st})$  (Fig. 3). The highest selectivity for separation between classes of organic compounds was achieved using columns with the maximum separation between correlation dependences of capacity coefficients, which was supported by regression analysis results [14]. Comparison of their slopes leads us to conclude that the highest separation power for the alcohols and aromatic hydrocarbons is offered by the sorbents with cobalt and copper acetylacetonate layers. All of the sorbents are potentially attractive for separating hydrocarbon mixtures.

## CONCLUSIONS

1. Using pH measurements and a Hammett indicator method, we have studied the acid–base properties and composition of donor–acceptor centers on silica gel surfaces before and after modification. The results demonstrate that the impact of chelates on these characteristics is determined by the nature of the metal and ligand in the structure of the complexes. Whether the sorbent has acidic or basic properties is also influenced by the structural and sorption properties of the support.

2. We have determined retention characteristics for test compounds and evaluated the polarity and selectivity of the sorbents. Modification with  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$  chelates of acetylacetonate increases the surface acidity of Silokhrom S-120, leading to changes in various types of intermolecular interaction.

3. The present results on the nature of the surface of the sorbents extend our understanding of the mechanism of chromatographic retention and separation and offer increased possibilities of targeted selection of sorbents for gas chromatography.

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