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## Solid Phase Sorption of Phenols on Metals Acetylacetonates

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### Abstract

The solid phase extraction properties of surface layers of Eu(III), Al(III), Fe(III), Cr(III) acetylacetonates are compared for sorption some phenols and chlorophenols. The effects of the energies of adsorption and complexation on the retention of various sorbates were calculated. GC methods with preconcentration are proposed to evaluate phenols by means of solid-phase extraction on a sorbent with a surface layer of Eu acetylacetonate with extraction effectiveness of 85 %.

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### 1. Introduction

The determination of phenols and chlorophenols is necessary because of their toxicity and their widespread use in industry. Nowadays, the most widely used GC needs in pretreatment before separation of phenols. To avoid this disadvantage, phenols are derivatized to give less polar compounds<sup>1</sup>. The synthesis of new sorption materials is difficult, if not impossible, to accomplish without a detailed study of the physicochemical processes on their surface<sup>2,3</sup>. For sorbents modified with metal containing compounds, the complexation between metal ions and organic sorbates plays a special role<sup>4,5</sup>. The selectivity of separation and polarity with respect to organic compounds of various classes is largely determined by the contribution of chemisorption to the retention of sorbates. To predict the properties of sorbents for solid phase extraction and to purposefully modify their characteristics, it is necessary

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to examine how the natures of the metal and ligands affect the contribution from complexation. In the present work, we aimed at the use of the sorbents containing Eu(III), Al(III), Fe(III) and Cr(III) acetylacetonates complexes for solid phase extraction of phenols from waters.

## 2. Experimental

A layer of mesoporous silica was synthesized on the surface of a Chromatone N\_AW diatomite support (0.20–0.25 mm). Synthesis was performed at room temperature via the reaction of hydrolysis of TES in a mixed water–ethanol solvent with polyethylene glycol (PEG 115) used as a template. SASEs were dissolved in ethanol; water and solutions of TES and HCl were then added in various quantities to the obtained homogenous solution<sup>6,7</sup>. The reaction mixture was applied to the Chromatone N\_AW and dried using a rotary evaporator at 60°C. It was then calcinated in a muffle furnace at temperatures of 25°C to 600°C for 6 h with a heating rate 1.5 K/min. The sorbents obtained in this fashion were further modified by applying acetylacetonates of metals Me(acac)<sub>n</sub> from solution with the gradual evaporation of the volatile solvent (CHCl<sub>3</sub>) at room temperature, ensuring a sufficiently homogeneous coating of the sorbent's surface<sup>8</sup>.

The morphology of the surface was studied using Carl Zeiss NVision 40 and JSM-6460 scanning electron microscope (Table 1). Our chromatographic investigations were performed using a Angilent 6490N gas chromatograph equipped with a flame ionization detector. IR spectra of sorbents dried at 60°C were obtained with Nicolet 6700 FTIR spectrometer in a range of 500 – 4000 cm<sup>-1</sup> and with IRS-29 spectrophotometer in a range of 400 – 2000 cm<sup>-1</sup>. UV-vis spectra in the range 220–340 nm were recorded using SP-20 spectrophotometer.

Table 1. Properties of sorbent surface modified by metal chelates

Property	Initial Chromatone	Eu(acac) <sub>3</sub>	Al(acac) <sub>3</sub>	Fe(acac) <sub>3</sub>	Cr(acac) <sub>3</sub>
Average pore volume, cm <sup>3</sup> /g	1.0±0.1	1.2±0.1	0.8±0.1	0.9±0.1	0.8±0.1
Average pore diameter, nm	16±2	15±2	9±1	11±2	10±2
Metal ions, % weight	0	1.6±0.1	2.0±0.2	1.8±0.1	1.7±0.1

Derivatographic method also determined the amount of metal acetylacetonates formed after chemical bonding<sup>9</sup>. There was high thermal stability of the complex bonded noticed, i.e. destruction begins at temperatures higher than 180 °C (Figure 1). Concentrating was carried out on 70 mm length and 4 mm in diameter steel for-column containing 0.7 g of Chromatone N AW sorbent with chelate complex adsorption layer or equivalent amount of 0.8 g

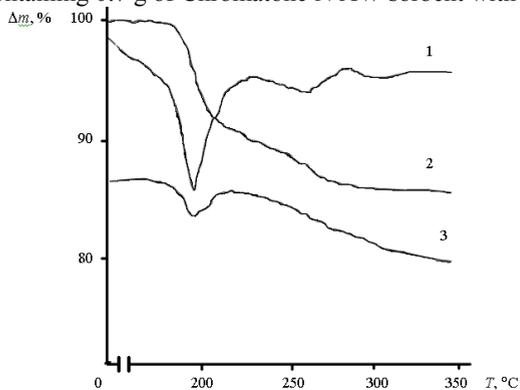


Fig. 1. Thermodestruction of Eu(acac)<sub>3</sub>: 1 – DTG; 2 – TG ; 3 - DTA

Tenax sorbent. Polymeric sorbent Tenax is divinylbenzene copolymer and at the same time has hydrophilic and hydrophobic properties, combined inversed-phase and anion-exchange functions for solid phase extraction from water solution. Sorption was carried out in dynamic mode by pumping water solution through for-column, phenols concentration of 1–50 µg/l at the speed of 1 ml/min. Micropump Gilson Minipuls-2 (USA) was used to create sample stream through sorbent. Concentrator reverse air steam was done for 5 minutes after concentration to remove excessive water for desorption by 3 ml methanol, acquired solution was evaporated to dryness and dissolved in 50-µl chlorophorm.

## 3. Results and discussion

The sorption of sorbates at chelate modified surface in solid phase extraction (Figure 2, 3) is largely associated with the adsorption on the surface and the intermolecular interactions of sorbate molecules with the coordination sphere of the metal atom<sup>10–12</sup>. To compare the relative contributions from these two mechanisms, we calculated the molecular energies of retention for test organic compounds. To estimate the ability of the sorbent to participate selective interactions, we calculated the effective heat of sorption ΔH, a parameter that characterizes the retention of

sorbates, and the pure heat of sorption  $\Delta H_s$ , which characterizes the interaction of the sorbate with the chelate. The difference between these quantities is the heat of sorption at the selective interface of the sorption system (Table 2). Cr acetylacetonates sorbs phenols less effectively compared to other acetylacetonates, which is due to partial destruction of a bond with the complex surface during methanol sorption. In eluting mix through sorbent containing Cr acetylacetonate, the latter shatters, and the longer the process, the less it is possible to model analysis results.

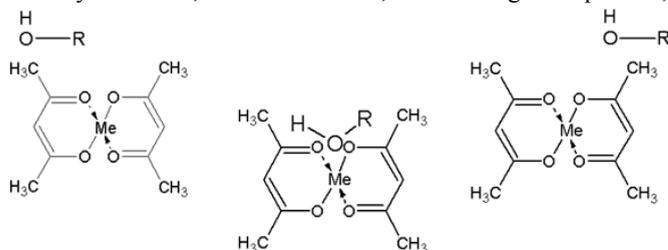


Fig. 2. Mechanism of intermolecular interactions of sorbate molecule with the coordination sphere of the metal atom

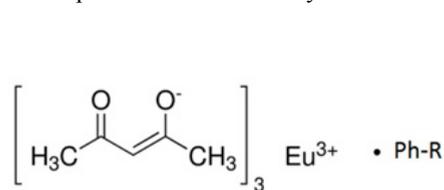


Fig. 3. Scheme of intermolecular complex

Table 2. The sorption heats for test organic compounds for 1 -  $\text{Eu}(\text{acac})_3$ ; 2 -  $\text{Al}(\text{acac})_3$ ; 3 -  $\text{Fe}(\text{acac})_3$

Substances	1		2		3	
	$\Delta H$	$\Delta H_s$	$\Delta H$	$\Delta H_s$	$\Delta H$	$\Delta H_s$
Methanol	11.39	10.2	12.41	7.3	18.87	10.1
Ethanol	13.60	12.0	14.11	8.5	24.99	12.5
Propanol	16.15	13.4	18.02	9.6	26.86	11.1
Butanol	18.53	14.4	21.08	11.7	30.77	8.5
Hexene-1	16.66	17.7	18.53	14.9	18.53	14.0
Heptene-1	28.05	12.1	32.13	9.5	32.81	11.4
Octene-1	29.92	14.0	34.34	10.8	34.68	13.2
Benzene	12.58	11.8	14.11	9.2	13.77	10.7
Methylbenzene	14.45	13.4	15.81	11.1	15.64	12.0
Acetone	7.14	8.9	7.48	8.1	11.90	7.8
Ethanal	7.99	9.2	13.26	11.1	10.54	12.2
Propanal	10.03	10.7	15.3	13.3	13.60	15.3
Butanal	12.41	13.9	20.74	17.3	15.47	18.5
Nitropropane	32.47	16.1	36.55	12.4	37.23	15.1
Pyridine	34.19	16.6	37.91	13.9	39.14	16.1

The distinctions observed in the chromatographic properties of the complexes studied are also associated with changes in the ability of the nickel ion to participate in donor-acceptor interactions due to variations in the deficiency of electron density on it.

It was demonstrated [6] that deposited nickel acetylacetonate forms an islet structure in the form of associates with hydrocarbon faces, a factor that contributes to dispersion interactions. Evidence for the existence of such a structure is an enhanced energy of adsorption of the  $\text{CH}_2$  group. Sorbents coated with europium acetylacetonate exhibit a weaker retention of alcohols, a behavior that can be explained by the tetrahedral structure of the immobilized complex. In this case, the complexation with nucleophilic reagents is less pronounced due to the effect of hydrocarbon faces.

The structure of the  $\text{Eu}(\text{acac})_3$  molecule is more accessible to sorbate molecules than that of  $\text{Al}(\text{acac})_3$ . Nevertheless, the rate of elution of the test compounds from  $\text{Fe}(\text{acac})_3$  is high while the chromatographic peaks of the alcohols are more symmetrical, a feature that makes it possible to separate them in the isothermal regime. Like the sorbent coated with  $\text{Al}(\text{acac})_3$ , that coated with  $\text{Fe}(\text{acac})_3$  exhibits no selectivity in the retention of alkenes, aromatics, and ketones in the isothermal regime. We believe that the retention of these classes of compounds is determined by the donor-acceptor complexation with the electron-deficient metal ion rather than by physical adsorption, as can be inferred from the observation that the energy of complexation decreases with increasing temperature. This signifies that the accessibilities of electron-acceptor sites for these complexes are similar. The ability to form unstable complexes decreases with increasing temperature, a behavior typical of external-sphere complexation. The results obtained suggest that the contribution from complexation to the retention correlates with

As can be seen from the above results, the values of retention of alkenes, ketones, aromatics, and alcohols on grafted-to-surface layers of complexes differ from each other, a behavior that can be explained by different contributions from physical adsorption and donor-acceptor interactions to the total energy of sorption. The contribution from physical adsorption decreases with the specific surface area of the sorbent, and, therefore, it becomes smaller after the deposition of the complex-compound layer<sup>13</sup>.

We believe that sorbate molecules can diffuse through the grafted layer and interact immediately with the support surface. This conclusion is supported by the fact that, for alcohols, for which the total energy of adsorption and complexation is 15-35% lower than the predicted total energy of sorption.

the energy of adsorption. The above sorbents coated with europium complexes can be used in the extraction and selective concentration of phenols from complex-composition mixtures.

A general feature of the systems under study is that all the test compounds are retained more weakly on  $\text{Eu}(\text{acac})_3$  compared to the other complexes. At the first stage, the structure of the europium complex forms a flat monolayer attached to the surface by means of donor-acceptor bonds between the oxygen atoms of surface hydroxyl groups with complexing metal ions. This makes it possible for complex molecules to occupy the energetically most favorable positions, i.e., in the plane of the surface, a factor that causes a substantial decrease in the specific surface area and, hence, the ability of sorbate molecules to attach to the surface. The contribution from adsorption increases with the number of carbon atoms in the sorbate molecule (Figure 4).

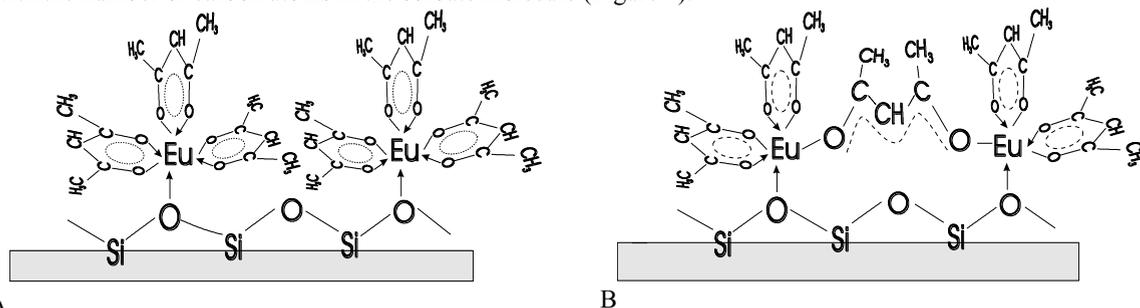


Fig. 4. The structure of the europium complex forms: flat monolayer (A) and energetically most favorable position (B).

The sorption concentrating was carried out with chelate containing sorbents in comparison with standard Tenax polymeric sorbent, which is usually used for similar pretreatment (tables 3, 4).

Table 3. Results of GC determination with varying concentration methods ( $\mu\text{g/l}$ )

Sorbent	Inserted. $\mu\text{g/l}$	Phenol	<i>o</i> - Cresol	<i>m</i> - Cresol	2,4-dimethylphenol	2-chlorophenol	3-chlorophenol
Tenax	1.5	1.5±0.3	1.4±0.7	1.5±0.5	1.7±0.9	1.2±0.3	1.5±0.3
$\text{Eu}(\text{acac})_3$		1.5±0.0	1.5±0.2	1.5±0.7	1.5±0.1	1.5±0.3	1.5±0.3
$\text{Al}(\text{acac})_3$		1.3±0.6	1.5±0.1	1.6±0.1	1.5±0.8	1.5±0.2	1.5±0.2
$\text{Fe}(\text{acac})_3$		1.6±0.8	1.6±0.8	1.6±0.1	1.5±0.2	1.3±0.7	1.5±0.4
Tenax	20.0	18±2	18±2	20±2	21±4	20±2	20±2
$\text{Eu}(\text{acac})_3$		19±1	19±2	19±2	21±1	19±2	20±2
$\text{Al}(\text{acac})_3$		23±4	18±2	21±2	18±2	18±2	20±2
$\text{Fe}(\text{acac})_3$		24±5	16±4	21±2	22±5	16±3	21±2
Tenax	60.0	60±4	60±1	60±0	60±6	60±8	61±3
$\text{Eu}(\text{acac})_3$		60±4	60±4	59±9	59±9	60±4	60±6
$\text{Al}(\text{acac})_3$		58±8	60±9	61±4	60±5	60±8	57±8
$\text{Fe}(\text{acac})_3$		57±5	59±6	58±7	56±7	58±9	58±9

Table 4. Phenols extraction ratio, %

Acids	Tenax	$\text{Eu}(\text{acac})_3$	$\text{Al}(\text{acac})_3$	$\text{Fe}(\text{acac})_3$
Phenol	88±2	85±3	67±3	72±4
3-Chlorophenol	79±2	77±2	64±3	64±4

Europium chelate containing sorbents allow sorbing phenols more effectively than Tenax, because of specific intermolecular interactions of electron-donor oxygen atoms in sorbates functional groups and metal acceptor ions in chelates. Phenols, prone to donor-acceptor interaction as electron pair donor, retain more strongly in chelate complexes than on Tenax electron-donor surface because they form associate with electron-deficient part of metal complex.

Sorbent with Eu acetylacetonate shows selectivity towards phenols, which is due to sorption through selective complexation of electron-deficient chelate parts in adsorbed layer with nucleophilic substances. It is the most efficient variant to use this sorbent for fluorobenzene acids preconcentration from water solutions with following GC determination because it displays stability under water influence. Minimal phenols concentration, which can be determined in model solution at standard concentrating procedure, is 0.5 µg/l. It is possible to use metal acetylacetonates as sorbents during fluorobenzene acids extraction from water solutions. GC methods with preconcentration are proposed to evaluate phenols by means of solid-phase extraction on a sorbent with a surface layer of Eu acetylacetonates with extraction effectiveness of 85 %.

#### 4. Conclusions

New mesoporous chelate containing sorbents for solid phase extraction were synthesized. Modification with chelate containing complexes changes the structure and properties of the initial sorbents. Our investigation of the possibility of using the obtained sorbents allows us to recommend these materials for the solid phase extraction of phenol with 0.5 µg/l concentration level.

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