

# Management of Sorbent Selectivity Based on Modified Tin (IV) Phosphate

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## Article Info

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## Abstract:

The ion-exchange properties of tin (IV) phosphate during sorption of alkali metal cations are studied. It was shown that the selectivity series has the form  $Cs \gg Rb \gg K \gg Na$  and, with an increase in the tin (IV) content during synthesis, the distribution coefficients slightly increase, which is associated with an increase in the amorphous state of the ion exchanger. When using citric and sulfosalicylic acids as modifiers, the selectivity series for transition elements is as follows:  $Fe^{3+} \gg Co^{2+} \gg Zn^{2+} \geq Cu^{2+} \gg Ni^{2+}$ . For acetic, boric and formic acids:  $Cu^{2+} \gg Fe^{3+} \gg Zn^{2+} \gg Co^{2+} \gg Ni^{2+}$ . A feature of inorganic ion exchangers is their selectivity. These include sorbents based on salts of tetravalent metals (zirconium, titanium, germanium, lead, hafnium, tin), a large number of works are devoted to the synthesis of which. Recently, attention has been paid to their modification [1-7]. The least studied inorganic ion exchanger is tin (IV) phosphate, whose properties can be changed by introducing various modifiers.

**Keywords:** *selectivity, modified phosphates, crystalline phosphates, cations, phosphate sorption, ion-exchange mechanism, ion-exchangers.*

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## I. Introduction

Group IV metal phosphates are promising inorganic sorbents. However, the use of these ion exchangers is hindered by such disadvantages as poor reproducibility of properties from synthesis to synthesis. To improve the reproducibility of ion-exchange properties and to increase the exchange capacity and selectivity of inorganic ion exchangers, modifying and applying syntheses are widely used.

The structure and ion-exchange properties of inorganic sorbents, including tin (IV) phosphate, largely depend on the methodological subtleties of their synthesis and modifier.

To control the ion-exchange properties of sorbents, application and modification with additives of inorganic ion exchangers are used. Cations, anions, complex compounds, as well as other classes of inorganic and organic compounds, are used as modifiers and applicators.

The authors of [9,10,28] studied the modification of inorganic ion exchangers based on metal (IV) phosphates by metal cations, including in the form of complex compounds, which is performed by mixing the starting materials during gel structuring, upon contact of metal (IV) phosphate with salt solution. In this case, the introduction of metal cations is aimed at expanding the cavities in order to subsequently facilitate the entry of sorbed metals into the structure of the sorbent, especially those whose dimensions are larger than the cavity size of the unmodified sorbent.

Modification and application can take place by means of interlayer inclusion. During interlayer inclusion, neutral polar molecules are inserted between sheets of a layered insoluble compound, which include ion exchangers based on Group IV metal phosphates of the Periodic system.

## II. Research

In order to control the selectivity of inorganic ion exchangers, tin (IV) phosphate

samples modified with various classes of compounds were synthesized and studied. The synthesis was carried out by direct precipitation and high temperature boiling. In the synthesis of tin phosphate by high-temperature boiling, phosphoric acid of a concentration of 12 mol/L and a molar ratio of phosphorus: tin of 10 were used. Some deviation in the value of the molar ratio P: Sn in the initial mixture, in particular within the range of P: Sn = (8 ÷ 10):1, does not significantly affect the structure and ion exchange properties of the resulting ion exchanger.

A feature of the synthesis is the creation of conditions for the maturation of the sorbent structure. Due to the fact that the ion exchanger is supposed to be used for deep purification of elements with similar properties and for obtaining salts of high purity, only bidistilled water was used to achieve the required acidity when its structure was ripened. The required amount of starting components, the volume of phosphoric acid and the volume of bidistilled water) for the synthesis was calculated based on the fact that the mass of the resulting SnHPO<sub>4</sub> should be 20g.

Table 1. Synthesis conditions and characterization of modified tin (IV) phosphate

Sample N	Modifier	Synthesis time, h	Correlation P:Sn		Correlation Sn: modifier	
			Start.	In sorb.	Start.	In sorb.
1	-	48	10	1,7	-	-
2	-	6	3	1,5	-	-
3	Sodiumhexanitrocobaltate	24	10	1,8	1:0,5	1:0,19
4	Sodiumhexanitrocobaltate	48	10	1,8	1:0,5	1:0,27
5	Sodiumhexanitrocobaltate	72	10	2,4	1:1	1: 0,72
6	Sodiumhexanitrocobaltate	72	10	1,2	1:0,5	1:0,32
7	Sodiumhexanitrocobaltate	72	10	1,3	1:0,25	1:0,15
8	Cu <sup>2+</sup>	24	10	1,5	1:10	1:0,84
9	Cu <sup>2+</sup>	48	10	1,9	1:10	1:1,02

10	Cr <sup>2+</sup>	48	10	2,1	1:10	1:0,80
11	Cr <sup>3+</sup>	48	10	2,2	1:10	1:1,58

The structural features of unmodified and modified tin (IV) phosphate samples were studied by X-ray diffraction, infrared spectroscopy, thermogravimetry, X-ray fluorescence analysis, and electron microscopy.

X-ray phase analysis of the synthesized sorbents was performed on a Dron-3 device using the powder method using CoK $\alpha$  radiation. Interplanar distances were determined from the values of angles  $\theta$ , corresponding to the maxima of diffraction peaks in the diffraction pattern. IR spectra were recorded on a Perkm-Elmer spectrometer and on an IFS25 spectrometer in the region of 4000-400 cm. Samples were prepared by grinding in liquid paraffin. Derivatograms of the samples were obtained on a Q 1500D derivatograph system F. Paulik - I. Paulik - L. Erdey, firm "MOM" (Hungary).

It was established that the samples obtained by the direct deposition method

(synthesis time is 6 hours) are X-ray amorphous, and the samples obtained by high-temperature boiling are crystalline.

A comparison of the IR spectra of unmodified (sample 1) tin (IV) phosphate and tin (IV) phosphate modified with sodium hexanitrocobaltate (sample 3) is shown in Fig. 1, and for samples 4,5,7 in Fig. 2. In the IR spectra of unmodified tin phosphate Sn (HPO<sub>4</sub>)<sub>2</sub> · H<sub>2</sub>O (sample 1), bands of 510 and 615 cm<sup>-1</sup> are observed, related to the deformation vibrations of the distorted tetrahedron of the [O<sub>3</sub>PO<sup>-</sup>] 3- anion, as well as bands caused by symmetric (950, 965 cm<sup>-1</sup>) and antisymmetric (1030, 1080.1100 cm<sup>-1</sup>) stretching vibrations of the distorted tetrahedron of the [O<sub>3</sub>PO<sup>-</sup>] 3- anion. The splitting of the bands is caused by the violation of the symmetry of the ideal tetrahedron of the [PO<sub>4</sub>] 3- anion in the crystal under the influence of the surrounding cations.

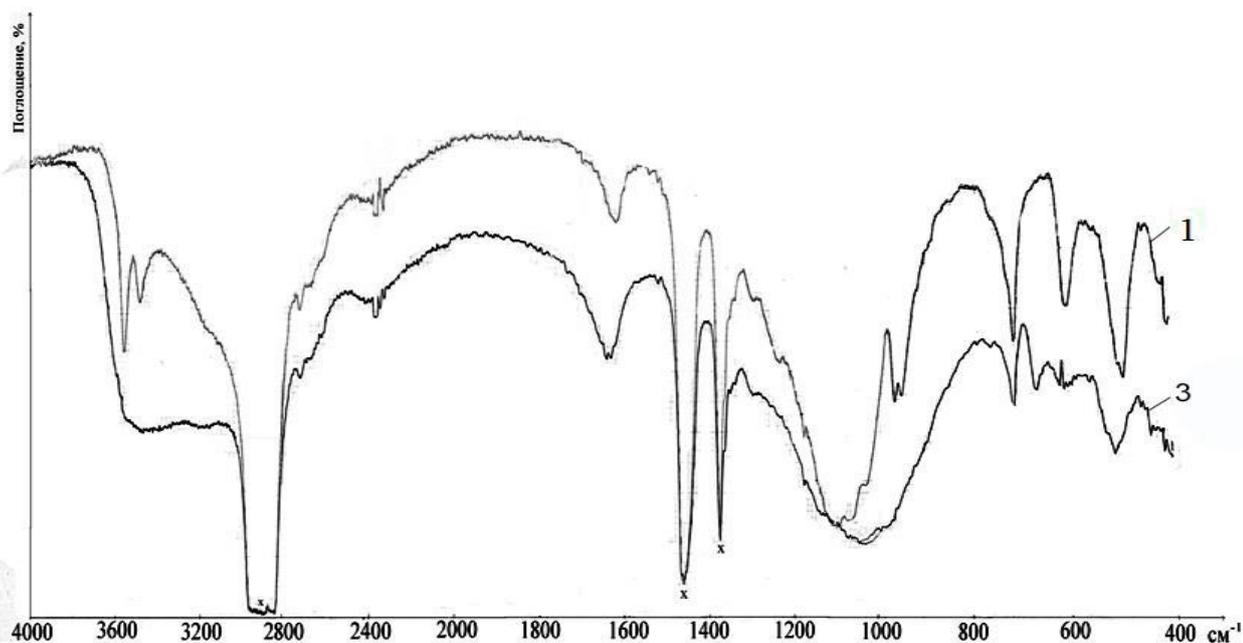


Fig. 1 IR spectra of samples 1.3

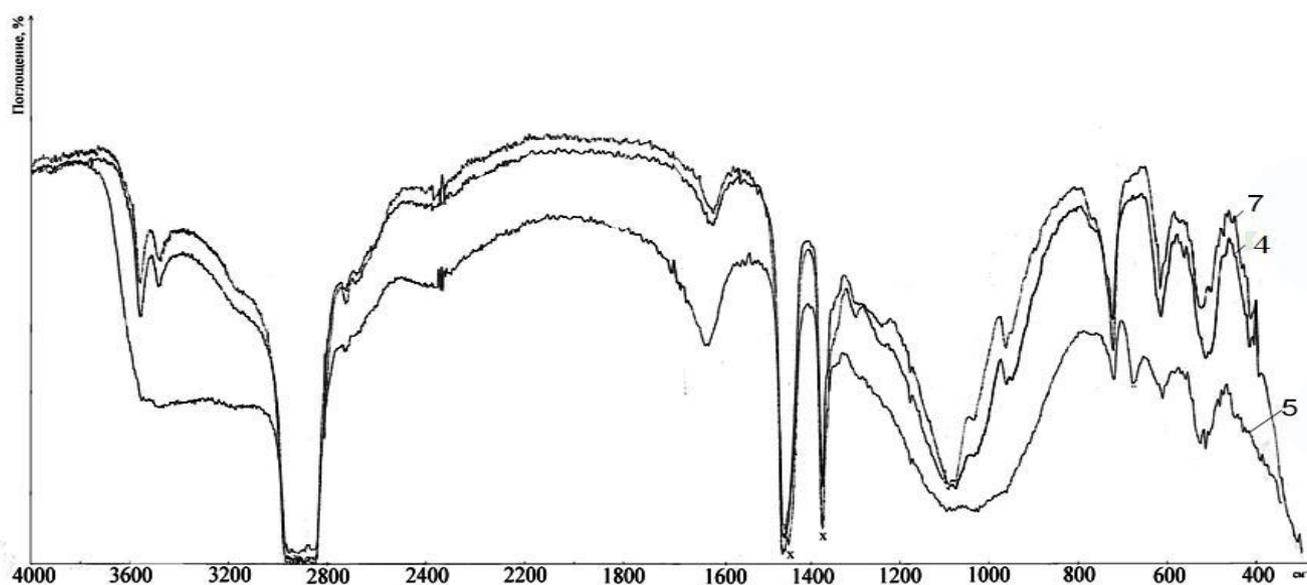


Fig. 2 IR spectra of samples 4, 5, 7

#### X - IR strip of liquid paraffin

The stretching and bending vibrations of the hydroxyl group associated with phosphorus [ $\nu$  (OH) and  $\delta$  (POH)] appear in the spectrum with a wide band in the region of 2500–3300  $\text{cm}^{-1}$  and bands of 1240, 1300  $\text{cm}^{-1}$ , respectively. The bands 3480, 3560  $\text{cm}^{-1}$  belong to the symmetric and antisymmetric vibrations of water molecules, coordinated with respect to the tin cation, and their deformation vibrations lead to the appearance of the band 1625 $^{-1}$ . When sodium hexanitrocobaltate  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ , Cu (II) acetates and chromium (II, III) are introduced into the tin phosphate crystal, a significant violation of the crystal structure occurs, and the environment of the  $[\text{O}_3\text{PO}]^{3-}$  anion changes. This leads to a broadening of the IR bands in the region of 900–1300  $\text{cm}^{-1}$  and they merge into one wide band with a maximum at 1050  $\text{cm}^{-1}$ , and its half-width increases by 1.5 times. The bands related to the stretching vibrations of hydroxyl groups associated with phosphorus and water molecules also merge into one wide band in the region of 2500 - 3700  $\text{cm}^{-1}$ . The IR spectra of the modified crystalline tin (IV) phosphates turn out to be close

to the IR spectra of amorphous tin (IV) phosphate samples.

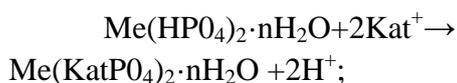
In addition, a band at 675  $\text{cm}^{-1}$  appears in the spectra of modified tin (IV) phosphates caused by deformation vibrations of the  $[\text{NO}_2]$  - anion coordinated to the  $\text{Co}^{3+}$  atom.

According to IR spectroscopy, the largest structural change occurs in samples 3.5, and for samples 4.7 these changes are weak.

The exchange of cations on crystalline phosphates of Group IV metals is due to a complex structure. A feature is that the layers are arranged in such a way that cavities are formed. The holes connecting the cavities allow the spherical cation to enter the cavity. Sorption on amorphous ion exchangers is characterized by good kinetic properties due to the distribution of ion exchange groups throughout the volume of the granules and the presence of zeolite cavities of various sizes. Confirmation of the volumetric nature of sorption is a direct proportionality between the amount of sorbed substance and the mass of the sorbent. The size of the cation has a significant effect on the course of the exchange process.

At the surface of the crystal, the hydrated cation gives up most of its water and diffuses into the cavity either in partially hydrated or fully dehydrated form. With an increase in pH, the exchange of large cations with a radius exceeding the pore diameter is possible, since the layers move apart. Cations located in cavities are able to hydrate again if there is enough space in the cavities to accommodate water or if the hydration energy of cations is large enough to overcome the bonding forces of the layers or even push them to a new interlayer distance. Cations having a diameter exceeding the size of the holes and cavities are not capable of exchange even in a completely dehydrated state.

Sorption on metal phosphates of group IV can proceed by ion-exchange and non-ion-exchange mechanisms. In this case, ion exchange, which is the basis of the sorption process, consists in the replacement of protons of acidic phosphate groups with cations of sorbed elements. The equation for the ion exchange of monovalent cations on metal phosphates can be represented as:



where  $\text{Kat}^+$  — alkali metal cation;  $n\text{H}_2\text{O}$  — the number of water molecules, respectively, before the exchange (H - form) and after the exchange ( $\text{Kat}^+$  - form).

With a change in the ripening pH of the gel structure, the ratio of phosphorus to tin and the sorbent yield change slightly, and the sorption indicators of potassium, rubidium, and cesium ions increase initially, and then decrease and stabilize. The optimum pH of the maturation of the ion exchanger structure corresponds to sample 1 and is equal to 0.8.

This value is slightly higher in acidity compared to the recommended value in a similar method for the synthesis of tin (IV) hydrogen phosphate, due to probably less solubility of the

precipitate during neutralization of divalent tin solutions. At the optimum ratio of phosphorus to tin and the pH of the maturation of the ion exchanger structure, the influence of the duration of the maturation of the structure, the pH of washing the ion exchanger and the concentration of phosphoric acid is studied.

With the introduction of various modifying additives, a different change in the structure of the sorbent occurs, which allows one to control the selectivity and exchange capacity of the sorbents. It is likely that this fact is ensured not only by defects in the structure of the obtained samples, but also by the possible “fixing” of the introduced modifying additive on the surface of the sample and its penetration into the inside of the sorbent. Therefore, the exchange capacity of the modified samples increases due to the possible formation of reaction centers in the form of additional functional groups on the surface of the ion exchanger and the appearance of a surface charge due to the exchange of tin (IV) hydrogen phosphate ions and the modifier. With an increase in the synthesis time of samples by high-temperature boiling, the modifier penetrates the sorbent, disrupting its structure, which becomes similar to amorphous ion exchangers, and also changes pore sizes and interplanar spacings between layers, enabling the possibility of sorption of large cations and separation of elements close in properties.

When considering the ion-exchange mechanism on metal phosphates of a crystalline structure, special attention is paid to the crystal chemical aspects.

The non-ion exchange mechanism can be realized in the form of the formation of a new phase of sparingly soluble compounds, isomorphic substitution of ion exchange resin ions, secondary sorption of coions and other processes of complex physicochemical interactions in sorption systems.

To ensure the diffusion of cations in  $\alpha$ - $\text{Me}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ , their passage through the face of the coordination polyhedron formed by oxygen atoms with a radius of 1,3Å is necessary. Small cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ) penetrate through it much more easily.

Larger cations - with a radius of 1,3Å (potassium, rubidium and cesium ions for titanium phosphate and rubidium and cesium ions for zirconium phosphate) - need to overcome a significant energy barrier. Therefore, it is necessary to maintain a high pH value of the solution. The low activity of hydrogen ions makes it possible for an additional amount of protons to exit the matrix of ion-exchange material. The latter acquires a negative charge, and an electrostatic potential difference is created between the ion exchanger and the solution, which determines the diffusion of the exchange into the cation exchange resin.

Therefore, on  $\alpha$ - $\text{Me}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ , exchange with lithium and sodium ions occurs in acidic solutions, and cesium only in alkaline. In the case of  $\gamma$ - $\text{Me}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  with a substantially large interplanar spacing, the energy barrier is practically absent and the exchange of all cations easily occurs in acidic solutions. A series of selectivity was determined for amorphous tin (IV) phosphate samples:



The differences between the ion-exchange properties of tin, zirconium, and titanium  $\alpha$ -phosphates are associated mainly with unit cell sizes. The smaller these dimensions, the smaller the size of the holes connecting the cavities, and the higher the steric obstacles for the passage of counterions from one cavity to another. A common method for studying the ion-exchange properties of group IV metal phosphates is their potentiometric titration with solutions of the corresponding bases. The shape of the

potentiometric titration curves is largely determined by the variety of functional groups, the crystallinity of the sorbents and the characteristics of the absorbed ion. For phosphates with a high degree of crystallinity, the plateau has a zero slope, and for low crystalline ones a small positive slope, since they are characterized by less ordering in the arrangement of phosphate groups, which affects the structure of the layers and the heterogeneity of exchange sites.

A decrease in the degree of crystallinity of the sorbent is accompanied by a disordered arrangement of phosphate groups in the crystal lattice, which leads to a change in the lattice parameters and, consequently, to the formation of cavities of various sizes. In ideal crystals, all cavities should be the same. A perfectly crystalline exchanger will not form a solid solution. The exchange process consists in converting the hydrogen form to the salt form. In this case, the slope of the titration curve should be zero.

### III. Conclusions

During the studies, samples of tin (IV) phosphate modified by various classes of compounds were synthesized and studied. The synthesis was performed by direct precipitation and high temperature boiling. In the synthesis of tin phosphate by high-temperature boiling, phosphoric acid with a concentration of 12 mol/L and a molar ratio of phosphorus: tin of 10, were used. Preliminary experiments showed that some deviation in the molar ratio P:Sn in the initial mixture, in particular within the range of P:Sn = (8÷10):1, does not significantly affect the structure and ion-exchange properties of the resulting ion exchanger. However, the recommended synthesis time at boiling point is "several weeks".

This circumstance did not seem to us quite convincing, since it would be more correct to

assume that during the high-temperature processing complex physical and chemical transformations occur that change over time, as a result of which the ion-exchange properties of the synthesized sorbent, namely, its selective properties, will also change. Preliminary experiments have shown the validity of this assumption and studied the effect of time on the properties of the ion exchanger.

In the synthesis of tin phosphate by direct precipitation, orthophosphoric acid with a concentration of 9 mol/L and a molar ratio of phosphorus: tin of 3 was used.

The modifier was introduced in two ways: at the time of synthesis and applying to a previously obtained sample (application). In the modification and application, different classes of compounds were used: salts (sodium acetate  $\text{CH}_3\text{COONa}$ , copper acetate  $(\text{CH}_3\text{COO})_2\text{Cu}$ , chromium acetates  $(\text{CH}_3\text{COO})_2\text{Cr}$  and  $(\text{CH}_3\text{COO})_3\text{Cr}$ , acids (acetic, boric, sulfosalicylic, formic, citric), complex compounds (sodium hexanitrocobaltate (III), potassium hexacyanoferrate (III), sodium tetraphenyl borate), amines (chloraniline). The modifier concentration varied from synthesis to synthesis.

Some modified tin (IV) phosphate samples have very unusual properties, for example, color. For almost all colored samples of modified tin (IV) phosphate, the color will change from white or translucent to a very saturated color, depending on the modifier. But it is important to note that this does not mean that each synthesis of ion exchanger produces colored material.

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