

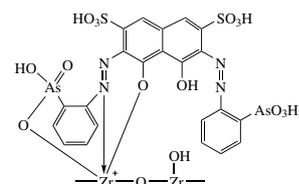
Surface modification of zirconia by Arsenazo III

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A sorbent of zirconia with covalently immobilized Arsenazo III has been obtained by the sorption of the organic reagent from aqueous solutions, and its properties have been defined.



Mechanically and hydrolytically stable modified sorbents based on metal oxides are a potential alternative to organic polymer and silica sorbents, which are widely used for the separation and preconcentration of inorganic substances.

The modification of oxide surfaces with silanes, carboxylic and phosphonic acids and their derivatives in organic solvents was described; the resulting sorbents were unstable in aqueous media and thus useless in inorganic analysis.¹ It was suggested that the oxide surface can be modified by the complexation of Lewis acid sites (partially coordinated metal ions) with the functional analytical groups of organic reagents.² The surface modification of alumina with organic analytical reagents by the formation of a surface complex similarly to complexation in solution was reported.^{3–5}

Earlier, we studied the modification of an alumina surface by the sorption of organic reagents capable of complexation with aluminum ions in aqueous solutions.⁶ The resulting sorbent of alumina with non-covalently immobilized Tyrone was successfully used for the extraction of transition metal ions from solutions.⁷

Probably, a Lewis acid center adsorbs water molecules to be converted into a weak Brønsted acid center. A ligand-exchange model was suggested to describe the sorption of acidic organic modifiers on the surface of alumina.^{8,9} The protonated groups AlOH_2^+ exist at the alumina surface in acidic media, and the organic reagent has to form a stable complex with aluminum. Unfortunately, the complexes of aluminum with organic reagents occur in a range of pH 5–7.

Since it is well known that stable zirconium complexes with Arsenazo group reagents (especially, Arsenazo III) are formed in strongly acidic media,¹⁰ we studied the modification of zirconia with analytical grade Arsenazo III (Reakhim, Russia).

Zirconia (Merck) with a particle size of 10 μm , a specific surface area of 190 $\text{m}^2 \text{g}^{-1}$ and an average pore diameter of 9 nm was used. The sorption of the reagent was carried out in the batch mode, and the sorbent was filtered and dried in air; then, the diffuse reflection spectrum was measured. The reagent distribution was controlled by measuring the optical density of an aqueous phase. The reagent sorption was maximal in 0.1–2 M HCl.

The diffuse reflection spectrum of sorbent treated at pH 6 has three absorption bands due to the reagent itself in solution (540 nm), the complex of zirconium with Arsenazo III in neutral media (570 nm) and the same complex in acidic media (670 nm). The spectrum of the sorbent produced in 0.3 M HCl was the same

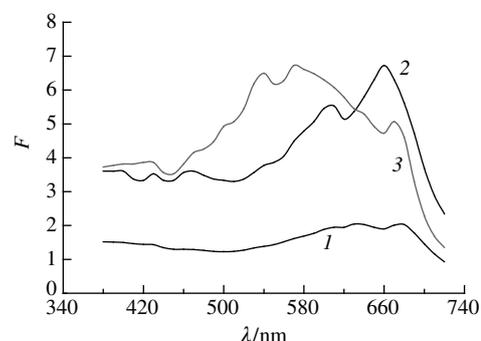


Figure 1 Diffuse reflection spectrum of zirconia treated by Arsenazo III in (1) 6 M HCl, (2) 0.3 M HCl and (3) at pH 6.

as that for a complex of zirconium with Arsenazo III in acidic solution (maxima at 610 and 665 nm). The spectrum of the sorbent obtained from 6 M HCl has similar absorption bands (610 and 670 nm) but of lower intensity since the decrease in the reagent sorption was observed under these conditions (Figure 1).

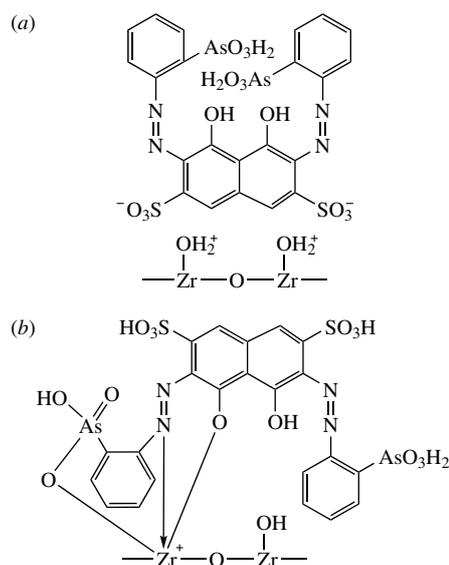


Figure 2 Arsenazo III sorption on zirconia due to (a) electrostatic interactions and (b) chelation.

The sorption of Arsenazo III at pH 6 can probably occur by two mechanisms: first, specific and electrostatic interactions between the reagent and zirconia as in the case of Tyrone on alumina [Figure 2(a)] and, second, chelation, which was confirmed by the absorption bands at 570 and 670 nm.

We assume that the surface modification of zirconia by Arsenazo III is accompanied by complex formation at the sorbent surface. Apparently, in acidic media, the displacement of coordinated water from a Brønsted acid center at the zirconia surface proceeds resulting in the metal ion–reagent coordination as in the case of alumina modification [Figure 2(b)].

According to published data, zirconium in aqueous solution forms a 1 : 1 complex with Arsenazo III. The strong acidic groups of the Arsenazo (two sulfo groups and one arsono group) remain free due to such a structure of the complex [Figure 2(b)]. Assuming a similar chelation scheme on the zirconia surface, we believe that the Arsenazo sorption leads to the formation of a strong-acid cation exchanger.

The sorbent capacity for protons was 0.7 mmol g⁻¹, as determined by the acid-base titration of the sorbent (0.15 g) with a sodium hydroxide solution in 1 M NaCl. Figure 3 shows the isotherm of Arsenazo III sorption on the surface of zirconia in 1 M HCl.

The maximal capacity for Arsenazo III was 0.24 mmol g⁻¹, and the distribution coefficient was 2.4×10⁴ cm³ g⁻¹ within a Henry area.

The obtained sorbent is stable in strongly acidic media (0.05–2 M HCl) and solutions with high ionic strength (up to 1 M NaCl). Therefore, the condition of sorbent formation, the spectral characteristics and properties of the sorbent allow us to assume that the

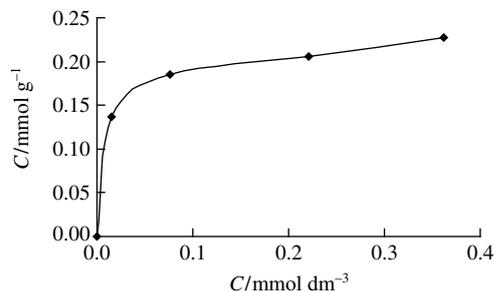


Figure 3 Isotherm of Arsenazo III sorption on zirconia.

Table 1 Chromatographic behavior of alkaline metal cations on the modified zirconia.

Cation	t_R /min	k'	R_S^a	Theoretical plate number per meter
Na ⁺	20.1	4.3	–	1.7×10 ³
K ⁺	30.9	7.1	1.2	1.9×10 ³
Rb ⁺	44.8	10.8	1.0	1.6×10 ³
Cs ⁺	64.1	15.9	1.4	2.5×10 ³

^a $R_S(\text{NH}_4^+/\text{K}) = 0.85$.

prepared zirconia with a covalently immobilized modifier can be used as a cation exchanger for ion chromatography.

Table 1 summarizes the ion-chromatographic properties of the modified sorbent. The average efficiency is 1.9×10³ theoretical plates per meter. The found elution order of the cations Li⁺ ≈ Na⁺ < K⁺ < NH₄⁺ < Rb⁺ < Cs⁺ is consistent with a standard order for cation exchangers (cation concentrations, 0.1 mM; eluent, 0.5 mM HCl; flow rate, 0.45 ml min⁻¹).

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