

Inorganic anion exchanger based on silica with grafted polyhexamethyleneguanidine hydrochloride

E.S.Yanovska, A.D.Dadashev, V.A.Tertykh**

Chemistry Department, T.Shevchenko Kyiv National University,
64 Volodymyrska St., 01033 Kyiv, Ukraine

*O.Chuiko Institute of Surface Chemistry, National Academy of Sciences
of Ukraine, 17 General Naumov St., 03164 Kyiv, Ukraine

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Polyhexamethyleneguanidine hydrochloride has been chemically anchored on the surface of amino-containing silica gel preliminarily activated with cyanuric chloride. The possibility of application of the modified adsorbent for extraction and preconcentration V(V), Mo(VI), W(VI) and Cr(VI) anionic forms in acidic media has been demonstrated. Methods of sorption-X-ray fluorescence and sorption-photometric determination of microquantities of these metal-containing anions have been elaborated.

Проведено химическое закрепление гидрохлорида полигексаметиленгуанидина на поверхности аминоксодержащего силикагеля, предварительно активированного хлористым циануром. Показана возможность использования модифицированного адсорбента для удаления и предконцентрирования анионных форм V(V), Mo(VI), W(VI) и Cr(VI) в кислой среде, что позволило разработать методику сорбционно-рентгенофлуоресцентного и сорбционно-фотометрического анализа микроколичеств металлосодержащих анионов.

Polyhexamethyleneguanidine hydrochloride (PHMG-Cl) belongs to high-molecular cationic polyelectrolytes having properties of polyamines and quaternary ammonium compounds as a result of the guanidine groups presence in polymeric chain containing substituted and protonated amino groups [1].

PHMG is known to be a weak basic anion-exchange polymer with biocidal properties and it can be used for simultaneous disinfection and purification of water from anionic impurities, such as CrO_4^{2-} , AsO_3^{3-} [2, 3]. PHMG shows also high complexing ability with respect to ions of lead, zinc, cadmium and some other cations of toxic metals [4–6]. Activated carbon and zeolites with PHMG adsorbed on surface were applied as adsorbents with antiseptic and fungicidal activities [3, 6, 9]. Complexing

properties of silica with adsorbed PHMG towards minor quantities of V(V), Mo(VI) and W(VI) cationic forms in neutral medium have been studied in [7, 8]. Adsorbents with chemically immobilized polymer are the most suitable for preconcentration and water purification applications. However, investigations in this direction are practically absent. There are only works concerning cross-linking of PHMG adsorbed on the surface of a natural zeolite (tuff-containing clinoptilolite) with epichlorohydrin [10, 11]. The adsorbent obtained has a high desalinating ability and antibacterial action in the water purification processes.

The aim of this work is to elaborate a method for covalent anchorage of PHMG-Cl on the silica surface, study of adsorption properties of modified silica towards metal-containing anions of elements of V and VI

groups of the Periodic Table. The usage possibilities of the synthesized adsorbent for solid-phase extraction and concentration of these anions from diluted multicomponent aqueous solutions followed by photometric and X-ray-fluorescence detection are also studied.

The starting solutions were prepared by dissolving precise sample weights of the Analar grade $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$, NH_4VO_3 , Na_3AsO_4 and $\text{K}_2\text{HPO}_4\cdot 3\text{H}_2\text{O}$ salts using the method described in [12]. The working solutions were prepared from the starting one immediately before experiments. Silica gel (Merck) with 256 m²/g specific surface area, 12 nm pore size and 0.10–0.20 mm particle diameter was used as the support. Extraction and concentration of Mo(VI), W(VI), Cr(VI), V(V), As(V) and P(V) anionic forms were carried out in the static mode by contacting 0.1–0.2 g of modified silica with 25–50 ml of solution. The working solution pH was maintained by adding buffer solutions prepared from standard titrimetric substances or ammonia acetate mixtures and was controlled by an I-130.2M.1 ionometer. The equilibrium concentrations of anions were studied photometrically using an SF-46 spectrophotometer (Russia) with square cells of 1 cm thickness at the following wavelengths: $\lambda = 470$ nm for Mo(VI), $\lambda = 610$ nm for W(VI), $\lambda = 540$ nm for Cr(VI), $\lambda = 490$ nm for V(V), $\lambda = 740$ nm for As(V), $\lambda = 700$ nm for P(V) using methods described in [13, 14].

The complexes of Mo(VI), W(VI), Cr(VI), V(V), As(V) and P(V) with bromopyrogallol red (BPR) on the silica surface with chemically bound PHMG were obtained as follows. The equal weights (0.10–0.25 g) with different quantities of anions adsorbed on modified silica surface were put into 50 ml glasses and 10 ml of water-alcohol (1:1) solution of BPR with concentration of

$1\cdot 10^{-4}$ mole/L was added to each sample. The obtained mixtures were stayed for 1 h with stirring using a glass rod. Then the formed colored complexes were placed on paper filters (yellow and red strip) and washed from excess dye by 10 ml water-alcohol mixture few times. The so obtained samples of colored complexes were dried at room temperature for 1 day. Electron diffuse reflection spectra were registered using a Specord-40 spectrophotometer (Germany). The X-ray-fluorescence was measured using an ElvaX multi-channel X-ray fluorescence spectrometer (Ukraine).

Chemical binding of PHMG-Cl was realized in three stages. At the first stage, amino-containing silica gel was obtained by surface chemical modification with solution of 3-aminopropyltriethoxysilane in toluene. At the second stage, the aminosilica surface was activated with cyanuric chloride (2,4,6-trichloro-*symm*-triazine) [15]. The goal of the third stage consisted in chemical binding of PHMG-Cl to the modified silica surface via interaction of immobilized cyanuric chloride with the polymeric macromolecules: To confirm the chemical immobilization of PHMG on the silica surface, IR-spectra of starting polymer, aminopropyl silica and synthesized adsorbent were compared. The concentration of bound PHMG was determined using thermogravimetric (TG) data and spectrophotometric analysis of intensity of colored complexes with bromophenol blue at $\lambda = 600$ nm. It follows from TG-data that the synthesized samples of chemically modified silica contain 44–65 mg of polymer per 1 g of support. The spectrophotometric analysis has shown the concentration of grafted PHMG on silica surface 44–67 mg/g. Thus, results of analysis made by different methods are in good agreement.

The dependence of extraction extent of Mo(VI), W(VI), Cr(VI), V(V), As(V) and P(V)

Table 1. Dependence of adsorption extent on the solution pH for anions of V and VI groups elements at silica with covalently bound polyhexamethyleneguanidine hydrochloride

pH	Adsorption, %						
	WO_4^{2-}	MoO_4^{2-}	$\text{K}_2\text{Cr}_2\text{O}_7$	$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	VO_3^-	PO_4^{3-}	AsO_4^{3-}
1.00	20	49	70	77	10	72	88.5
1.68	99.99	80	96	98.6	30	–	–
4.00	20	95	40	48.5	90	62	81.5
6.86	–	56	8	14	99.99	–	–
7.00	15	99.6	97.5	98	60	60	99.99
8.04	30	65	45	51.5	20	62	81.5

anions on silica with chemically bound PHMG on the medium acidity in the static adsorption mode is shown in Table 1. The maximum adsorption of Cr(VI) anions on modified silica in the form of dichromate ions ($\text{Cr}_2\text{O}_7^{2-}$) is attained in acidic solution ($\text{pH} = 1.7\text{--}2$) and in the form of chromate (CrO_4^{2-}) or hydrochromate ions (HCrO_4^-), in neutral medium. Adsorption of Cr(VI) anions occurs better in the presence of ammonium ions than in potassium ions presence. This fact can be explained by additional exchange processes of ammonium nitrogen atoms with quaternary nitrogen atoms of PHMG bound on silica surface.

Quantitative adsorption of Mo(VI) anions (Table 1) is observed in neutral medium in the form of molybdate ions. However, the high adsorption activity of obtained modified silica towards Mo(VI) anions was also detected at $\text{pH} = 4.0$ (adsorption degree about 95 %). It must be taken into consideration that at this pH value, there is equilibrium mixture of molybdate (MoO_4^{2-}), hexamolybdate ($[\text{Mo}_6\text{O}_{21}]^{6-}$) and heptamolybdate ions ($[\text{Mo}_7\text{O}_{24}]^{6-}$) in solution [16]. W(VI) anions are quantitatively adsorbed on silica with chemically bound PHMG at $\text{pH} \sim 2$. In these conditions, tungsten exists in form of dodecatungstate ions ($[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$) [14, 16].

For phosphate ions, the adsorption degree is essentially independent of the medium acidity and amounts 60–70 % in pH range from 1 up to 8 (Table 1). Unlike phosphorus, the quantitative adsorption of As(V) and V(V) anions was observed only in neutral medium. At other pH values, the adsorption degree of arsenate (AsO_4^{3-}) and vanadate ions (VO_3^-) was decreased to 80–90 %.

The kinetic adsorption characteristics of synthesized adsorbent with respect to analyzed anions are summarized in Table 2. The kinetic properties of the obtained ion-exchanger were found to be worse than

those for complexing chemically modified silicas: quantitative extraction of Mo(VI), As(V) and V(V) anions occurs for one day. The exception is tungsten(VI) anions for which adsorption is observed instantly.

To estimate the adsorption capacity of the silica with chemically bound PHMG, the adsorption isotherms for Mo(VI), W(VI), and V(V) anions were studied. The adsorption capacity of the synthesized adsorbent with respect to Mo(VI) anions is 520 mg/g (5.4 mmol/g), for W(VI) anions, more than 640 mg/g (3.5 mmol/g), for V(V) anions, 2.5 mg/g (0.05 mmol/g). The ability of the modified silica to adsorb quantitatively the anions studied in a wide amount range (from some micrograms to hundreds milligrams) indicates a homogeneous distribution of polymer over the support surface. This is a rather valuable characteristic of the obtained adsorbent which can be used for solid-phase extraction of Mo(VI), W(VI), As(V), and V(V) ions. After extraction from solutions, the quantitative analysis of the indicated anions can be carried out in the adsorbent phase by different methods (photometry, neutron activation analysis, X-ray fluorescence spectrometry).

According to [17], elements of V and VI groups of the Periodic Table form colored complexes with bromopyrogallol red in the presence of surfactants (ionic associates). As known from [5, 6], Mo(VI)-BPR and W(VI)-BPR complexes on the silica surface with preliminarily adsorbed PHMG-Cl form colored associates with absorption maximum at 16000 cm^{-1} (625 nm) for molybdenum(VI) and at 17000 cm^{-1} (588 nm) for tungsten(VI). It is to note that Mo(VI)-BPR and W(VI)-BPR complexes have been not adsorbed on unmodified silica surface and no support coloration was observed.

For studied complexes of Mo(VI), W(VI), Cr(VI), V(V), As(V), and P(V) with bromopy-

Table 2. Adsorption kinetics for anions of V and VI groups elements at silica with covalently bound polyhexamethyleneguanidine hydrochloride (static adsorption mode)

Anion	Adsorption, %				
	5 min	20 min	60 min	90 min	24 h
$\text{Cr}_2\text{O}_7^{2-}[\text{HCrO}_4^-]$	92.5	94.0	96.6	96.6	98.6
$\text{MoO}_4^{2-}[\text{Mo}_6\text{O}_{21}]^{6-} [\text{Mo}_7\text{O}_{24}]^{6-}$	86.8	86.1	89.2	89.7	99.6
$[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$	99.99	99.99	99.99	99.99	99.99
PO_4^{3-}	52.8	51.7	54.9	43.8	61.8
AsO_4^{3-}	88.5	88.5	88.5	88.5	99.99
VO_3^-	60.0	50.0	60.0	50.0	99.99

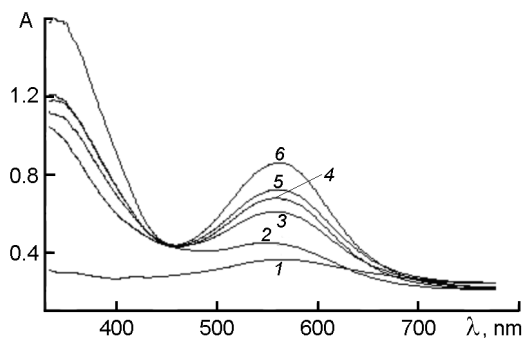


Fig. 1. Diffuse reflection spectra of Bromopyrogallol red (1) and its complexes with Mo(VI) on silicas with immobilized polyhexamethyleneguanidine hydrochloride at the metal amount (mg) 4.0; 7.7; 10.6; 45.8 and 104.0 (2–6, respectively).

rogallol red on the silica surface with chemically immobilized PHMG, electron diffuse reflection spectra had been registered (Fig. 1). BPR adsorbed on the silica surface with chemically bound PHMG (curve 1) is characterized by a low intensity absorption maximum at $\lambda_{max} = 565$ nm. Beginning from the adsorbed molybdenum mass of 4 mg, Mo(VI) ion associates with BPR on silica surface with immobilized PHMG (Fig. 1) show a wide absorption band at $\lambda_{max} = 550$ – 570 nm, its intensity exceeding that of BPR adsorbed on the sorbent surface. This band intensity was found to increase with increasing amount of molybdenum(VI) adsorbed on the silica surface up to 104 mg. At $\lambda_{max} = 545$ – 555 nm, ionic associates of W(VI) exhibit an absorption band at the substance mass exceeding 0.2 mg. Ionic associates with V(V) mass from 100 μg up to 1 mg with BPR on silica surface with immobilized PHMG are characterized by a wide absorption band at $\lambda_{max} = 580$ nm. The band of As(V) ion associates has an absorption maximum at 570 nm exceeding in intensity other analyzed anions in range 540–580 nm. Unfortunately, the precise quantitative dependence of optical density values for Mo(VI), W(VI), As(V) and V(V) complexes with bromopyrogallol red on silica surface with chemically bound polyhexamethylene guanidine as a function of adsorbed anion mass is not available at present. That is why this method can be applied only for the qualitative detection of these anions. It has been found that presence of phosphate ions and Cr(VI) anions influences adversely the detection.

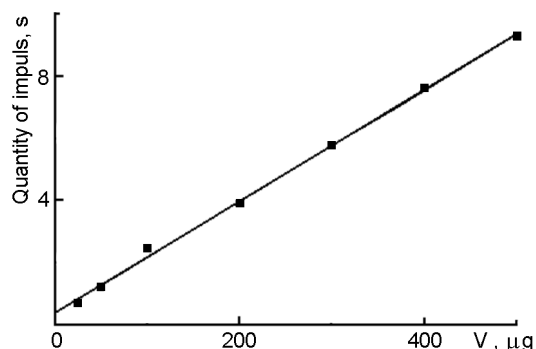


Fig. 2. Intensity of V(V) X-ray fluorescence spectra as a function of the metal content in the adsorbent phase ($r = 0.99901$).

It has been found that optimum measurement conditions for micro amounts of tungsten, molybdenum, and vanadium on the modified silica surface using multichannel X-ray fluorescence spectrometer ElvaX are as follows: current strength $I = 40$ μA , X-ray tube voltage $V = 45$ kV, exposure duration for micro amount detection $t = 250$ s (for milligram amounts, $t = 150$ s). Basing on the data obtained, dependences of characteristic K_{α} -lines intensity for tungsten, vanadium, and molybdenum on the metal mass in the adsorbent phase were plotted. As a rule, air-dried samples of modified silica with metal-containing anion mass adsorbed on surface of 0.2 g were used. These dependences are linear only for milligram (from 0.2 up to 8.0 mg) amounts of tungsten, molybdenum, and for microgram (from 25 up to 500 μg) amounts of vanadium (Fig. 2). This fact provides quantitative determination of these metals in above-mentioned concentration intervals by sorption X-ray fluorescence after the preconcentration on the synthesized adsorbent.

To conclude, the polyhexamethyleneguanidine hydrochloride was covalently bound to the surface of amino-containing silica activated with cyanuric chloride. The synthesized chemically modified silica was found to demonstrate high adsorption activity with respect to anions of elements from V and VI Periodic Table groups in acidic ($\text{pH} = 2$ – 4) and neutral media, where the adsorbent quantitatively extracts V(V), W(VI), Mo(VI), and As(V) anions. Silica with immobilized polyhexamethyleneguanidine hydrochloride has kinetic characteristics typical of polymeric adsorbents. Adsorption equilibrium is reached for one day, the only exception being W(VI) anions which are extracted instantaneously. Possibility of sorp-

tion-photometric determination of Mo(VI), W(VI), V(V) and As(V) minor amounts with bromopyrogallol red has been shown after preconcentration of anions using silica with immobilized polyhexamethyleneguanidine hydrochloride. Method of sorption X-ray fluorescence determination of Mo(VI), W(VI) and V(V) minor amounts has been also proposed.

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Неорганічний аніонообмінник на основі силікагелю з прищепленим полігексаметиленгуанідинхлоридом

Е.С.Яновська, А.Д.Дадашев, В.А.Тьортих

Здійснено хімічне закріплення полігексаметиленгуанідинхлориду на поверхні аміновмісного силікагелю, попередньо активованого хлористим ціануром. Показано можливість використання модифікованого адсорбенту для вилучення та передконцентрування аніонних форм V(V), Mo(VI), W(VI) та Cr(VI) у кислотному середовищі, що дозволило розробити методики сорбційно-рентгенофлуоресцентного та сорбційно-фотометричного методів аналізу мікрокількостей металовмісних аніонів.