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SYNTHESIS, CHARACTERIZATION AND APPLICATION OF ZIRCONIUM AND TITANIUM INORGANIC POLYMER SORBENTS FOR THE PREPARATION OF CHROMATOGRAPHIC ^{99m}Tc AND ^{188}Re GENERATORS

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Abstract

The Zirconium polymer compound (PZC) and Titanium polymer compound (PTC) based adsorbents for the preparation of chromatographic ^{99m}Tc and ^{188}Re generators were synthesized. Chemical composition, molecular structure and physicochemical characteristics of these adsorbents were investigated.
The adsorption propertiies of PZC and PTC sorbents in the different Molybdate and Tungstate solutions and the daughter nuclide elution performance were investigated. The Molybdenum adsorption capacities of about 275 mgMo/gPZC and 270 mgMo/gPTC and the ^{99m}Tc elution yield higher than 90% were achieved with both sorbents. The ^{99}Mo breakthrough of 0.015% and Molybdenum element breakthrough lower than 2µg Mo/ml were found in the ^{99m}Tc eluate. The Tungsten adsorption capacities of about 520mgW/gPZC and 515 mgW/gPTC and the ^{188}Re elution yield higher than 80% were also achieved with both PZC and PTC sorbents. The ^{188}W breakthrough of 0.015% and Tungsten element breakthrough lower than 5 µg W /ml were found in the ^{188}Re eluate.The parent nuclide adsorption capacity and the daughter nuclide elution performance of PTC sorbent resembled closely that of PZC one, except that the breakthrough of ^{99}Mo and ^{188}W parent nuclides was higher and PTC column needed smaller saline volume to elute ^{99m}Tc and ^{188}Re daughter nuclides. The^{188}Re eluate concentration process was developed by eluting ^{188}Re from the tandem system of ^{188}W-PTC – Alumina columns with the different concentration saline solutions. The concentration factor higher than 6 was achieved by this concentration technique which offered a potential application for the clinically applicable ^{188}W-^{188}Re generator production using low specific radioactivity ^{188}W produced in rather low power research reactors.

1. INTRODUCTION

At present the supply of ^{99}Mo is based on the research reactor produced ^{99}Mo sources by using the (n,γ) nuclear reaction with natural Mo (^{98}Mo, ~24%), resulting in inexpensive but low specific activity ^{99}Mo or by neutron-induced fission of ^{235}U which gives in expensive but high specific activity of ^{99}Mo. With the "fission method", the technological and infrastructure requirements are more complex and can possibly be sustained by countries with advanced nuclear technology.The technology requirements for the (n,γ) reaction based ^{99}Mo production is rather simple and easily performed in any developing countries operating research reactors.In constrast there is a unique production route for ^{188}W, the parent nuclide of ^{188}Re. The clinically useful amount of ^{188}W can only be produced via the ^{177}W (n, γ) ^{188}W reaction using much higher thermal neutron flux

reactor accessed in a handful of countries in the world. However, the production of ^{188}Re generator can be surely performed in any country based on the overseas supply of ^{188}W solution provided that their generator technplogy was developed.
Alternative technologies for ^{99m}Tc generators using (n, γ) nuclear reaction with natural Molybdenum have been developed and are now under way of development, whereas the ^{188}Re generator production in developing countries is still a concept, the reason of which may be the lack of high performance sorbent for ^{188}W parent nuclide. Although some new technologies have technically been accepted in many countries, there will have to be a substantial economic incentive for large producers of ^{99}Mo or ^{99m}Tc generators to change to a new process because of the existing investment in production infrastructure and in the approval of ^{99}Mo and derived products.
Among these the technologies for ^{99m}Tc generators using Zirconium- or Titanium-Molybdate gel (so called "gel technology") [9, 10] and the Zirconium or Titanium inorganic polymer sorbents based technology [1-8] are considered as new ones. For the reason of compatibility between the fission ^{99}Mo – Alumina sorbent based ^{99m}Tc generator production technology and the (n,γ) ^{99}Mo-PZC or PTC sorbents based one, the latters were to be chosen for further development. This technology option is also a way of development of ^{188}W-^{188}Re radionuclide generator which is nowadays available using Alumina, Zircona or Zirconium- or Titanium-Tungstate gel columns [11-13].
As a contribution, the study on the Zirconium and Titanium inorganic polymer sorbents for the preparation of chromatographic ^{99m}Tc and ^{188}Re generators and the assessment of their adsorption and elution performance for the preparation of a clinicallyavailable ^{99m}Tc and ^{188}Re generator were described in our report.

2. MATERIALS AND METHODS

2.1. Preparation of PZC and PTC sorbents

PZC and PTC sorbents were synthesized from isopropyl alcohol (iPrOH) and the relevant anhydrous metallic chloride under strictly controlled conditions of reaction. The given amount of relevant anhydrous metallic chloride ($ZrCl_4$ for PZC or $TiCl_4$ for PTC) is carefully added to different amounts of iPrOH. The temperature of reaction mixture will immediately reach 97 ^{o}C for the iPrOH-$ZrCl_4$ mixture and 93 ^{o}C for the iPrOH-$TiCl_4$ one. By keeping the temperature of solution at these temperatures, stir this solution gently by magnetic stirrer in open air until this solution become viscous. As the reaction temperature increased, a water-soluble PZC or PTC gel (the intermediate precursors) will be formed at 130 ^{o}C for PZC and at 112 ^{o}C for PTC sorbent. The water-insoluble, solid PZC or PTC materials of particle size of from 0.10 mm to 0.01 mm are splitted out by keeping the reaction temperature at 140 ^{o}C (30 minutes) for PZC and at 125 ^{o}C (45 minutes) for PTC. These were the finished products of PZC and PTC sorbents.The synthesized PZC and PTC samples and their preparation conditions are listed in Tables1 & 2.

TABLE I. CONDITIONS FOR THE CHEMICAL SYNTHESIS OF DIFFERENT PZC SAMPLES

Sample	$ZrCl_4$ weight (g)	Volume of isopropyl alcohol (ml)	Reaction temperature at final stage (^oC)
PZC_1	50	40	140
PZC_2	50	80	140
PZC_3	50	100	140

TABLE II. CONDITIONS FOR THE CHEMICAL SYNTHESIS OF DIFFERENT PTC SAMPLES

Sample	$TiCl_4$ weight (g)	Volume of isopropyl alcohol (ml)	Reaction temperature at final stage (^oC)
PTC_1	40.7	40	125
PTC_2	40.7	80	125
PTC_3	40.7	100	125

2.2. Investigation on the chemical composition, structure and physicochemical properties of the PZC and PTC sorbents

Zr and Ti contents of the sorbents were analyzed with gravimetric method by ignition of the sorbent samples at 1200^{o}C for two hours. ZrO_2 and TiO_2 weight was measured and Zr and Ti content calculated.

Carbon, hydrogen and oxygen element content of PZC and PTC samples were determined by thermal decomposition of the sorbents on Perkinelmer 2400 II instrument.

Chlorine content of sorbent was analyzed by thermal decomposition of sorbent samples. The decomposed product, HCl was trapped in an alkaline solution and Cl^- content was determined by ion chromatography.

Thermal analysis of sorbent samples was carried out on MB-7H derivatographer instrument with N_2 gas flow rate of 50 cc/min and heating rate of 10^{o}C/min.

Potentiometric titration of PZC and PTC samples was carried out with 0.1 g weight PZC and/or PTC sorbent samples in 60 ml 0.1 M NaCl solution. Titration solution was 0.1 M NaOH solution.

Infra-red spectrum of sorbent samples was recorded on Brucker-IFS 48 * Carlo Erba-GC 6130 instrument.

X-ray diffraction pattern of sorbent samples was recorded on Rigaku Miniflex diffractometer with CuKα ray and CuNi filter at 40KV/20 mA.

2.3. Investigation on the mother nuclide adsorption and daughter nuclide elution

2.3.1. ^{99}Mo-^{99m}Tc nuclide generator system

15 ml radioactive ^{99}Mo solution of concentration of 13.35 mg Mo / ml, pH=7 were added to the PTC or PZC sorbent samples of 0.75 g weight which were then gently shaken in water bath at 50^{o}C overnight. After shaking the samples were let to stand and a portion

of clear supernatant solution was taken out to measure ^{99}Mo radioactivity for the Molybdenum adsorption capacity calculation and then the remained solution was decanted to get the solid sorbent part. This solid PZC or PTC sample was packed in the 8ml glass column and washed with 50 ml water followed by passing column with 10 ml saline. Then the first ^{99m}Tc elution was started after 24 hours of equilibration time and an elution was daily conducted.

All experiments were carried out with the PZC or PTC columns of ^{99}Mo radioactivity of 10 – 30 mCi. Each column was eluted for five to seven days (one elution a day). Elution yield, ^{99}Mo break-through (by Capintec Dose Calibrator), Mo elemental content (by photospectrometric method) were determined for each elution.

Different conditions for adsorption and post-adsorption treatment were applied. These conditions are as follows:

- Normal adsorption in aqueous solution of Molybdate;
- Normal adsorption in the NaOCl (0.05% NaOCl) added aqueous Molybdate solution.
- Adsorption in the Acetate buffer solution of Molybdate (Acetate buffer solution of 0.2M acetic acid, pH=5)
- Adsorption in the NaOCl added Acetate solution of Molybdate (Acetate buffer solution of 0.2M acetic acid, containing 0.05% NaOCl , pH=5)
- The ^{99m}Tc elution performance of the ^{99}Mo adsorbed PZC and/or PTC column post stream- sterilization was also investigated. For this purpose a normal adsorption in NaOCl (0.05% NaOCl) added aqueous solution of Molybdate was followed by sterilization in autoclave.

Investigation on the effect of the Mo-content of adsorption solution on the Mo-adsorption capacity of the sorbents and on the ^{99m}Tc elution yield and Mo-breakthrough of ^{99m}Tc eluate: The variable volumes (as specified in Tab.7 below) of the radioactive ^{99}Mo solution of concentration of 13.35 mg Mo / ml, pH=7 were added to PZC and PTC samples of 0.2 g weight, then these samples were gently shaken in water bath at 50 ^{o}C overnight. After shaking the samples were let to stand and a portion of clear supernatant solution was taken out to measure ^{99}Mo radioactivity for Molybdenum adsorption capacity calculation and then the remained solution was decanted to get the solid sorbent part which was then packed on a small column. These solid PZC and PTC columns were washed with 10 ml water followed by passing columns with 10 ml saline. After this step the first ^{99m}Tc elution was started after 24 hours of equilibration time and an elution was daily conducted.

2.3.2. ^{188}W -^{188}Re nuclide generator system

A similar procedure as above was applied for investigation on the ^{188}W adsorption and ^{188}Re elution using PZC and PTC sorbents. The radioactive ^{188}W solution of concentration of 25.6 mg W/ ml (pH=7) was used instead of molybdate solution. The 5-10 mCi ^{188}W radioactivities were used in all column experiments.

Investigation on the effect of the W-content of adsorption solution on the W-adsorption capacity of the sorbents and on the ^{188}Re elution yield and W-breakthrough of ^{188}Re eluate: A similar procedure as above was applied to the investigation on the effect of the W-content of adsorption solution on the W-adsorption capacity of PZC and PTC sorbents and on the ^{188}Re elution yield and W-breakthrough of ^{188}Re eluate. The variable volumes (as specified in Tab.9 below) of the radioactive ^{188}W solution of concentration of 25.6 mg

W / ml, pH=7 was used instead of molybdate solution. The 5-10 mCi ^{188}W radioactivities were used in all column experiments.

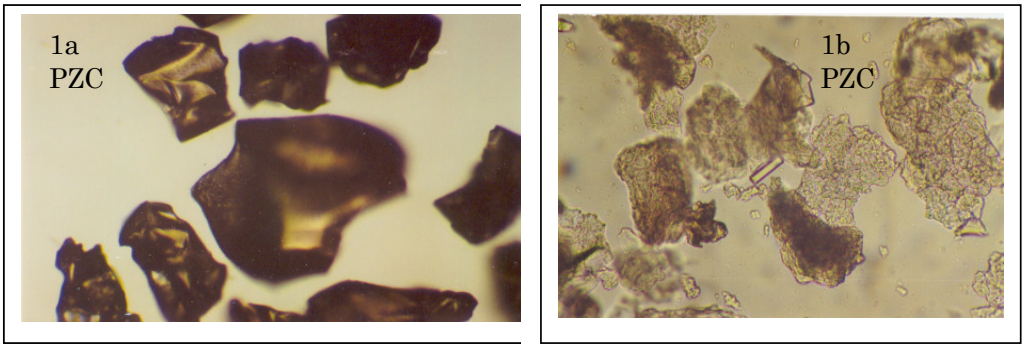
2.4. The PTC or PZC sorbent based ^{188}Re elution-concentration systems

The investigation on the ^{188}Re concentration process was carried out by eluting ^{188}Re from the ^{188}W-PTC column with dilute saline solution and then this eluate was passed through a small alumina column where all $^{188}ReO_4^-$ was retained, then $^{188}ReO_4^-$ was eluted with a small volume of physiological saline.

3. RESULTS AND DISCUSSION

3.1. Synthesis and specification of PZC and PTC sorbents

Both PTC and PZC sorbents are light brown in colour. Their appearance changed into white color when being soaked in water. They swell well in water and were hydrolyzed to give an acidic solution while the solid matrix of sorbents remains unsoluble. The volume of swollen PZC and PTC beds is 1.25 and 1.35 times, respectively, as large as the dry ones. The results of characterization of the PTC and PZC sorbents were presented in Fig.1 and in Tabs.3& 4.
About synthesis conditions, the adsorption capacity of both PZC and PTC sorbents decrease with the increase of reaction temperature, whereas the increase in molar ratio of reactants (isopropyl/$MeCl_4$) brought about a higher degree of swelling of sorbent particle in aqueous solution. This favored the diffusion of the Molybdate and/or Tungstate ions into solid matrix of the sorbents during adsorption process. But the swelling of particles will give in the decrease in the mechanical stability of the sorbent particles. This issue can be experienced in the microscopic pictures of PZC and PTC sorbents before and after being hydrolyzed in aqueous sodium-molybdate solutions (Fig. 1).For further investigations the PZC2 and PTC2 sorbent samples were used due to of their favorable stability.



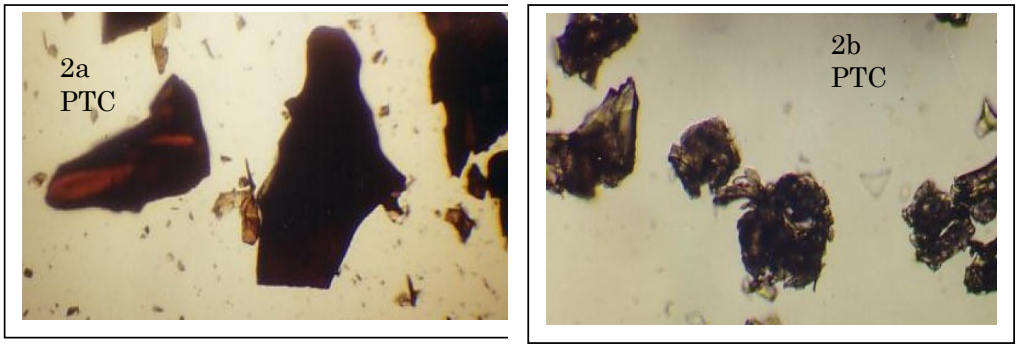


FIG. 1. Microscopic pictures of original PZC2 and PTC2 sorbents before (1a and 2a) and after Molybdenum adsorption in a sodium molybdate solution of pH=4.5 (1b and 2b).

3.2. Chemical composition and molecular formula of PZC and PTC sorbents

The results of chemical and thermal analysis were listed in Tables 3 &4 and Fig.2. Based on the obtained results the molecular structure of PZC and PTC sorbents were described as below.

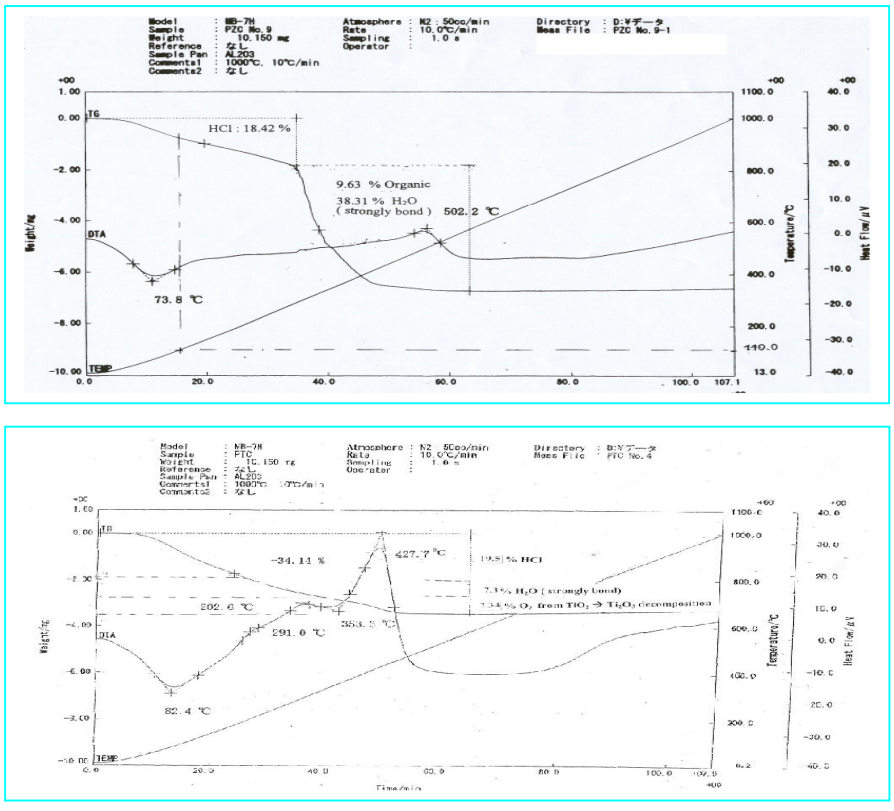


FIG. 2. Thermal analysis of PZC (a) and PTC (b) sorbents

TABLE III. THE CHEMICAL COMPOSITION OF THE PZC SORBENT

Element	Cl	H	Zr	O	H_2O	(H + O + C) Organic
Content (% weight)	17,90	0,505	24,92	8,74	38,31	9,63
Atom ratio	1,87	1,87	1	2	7,83	x

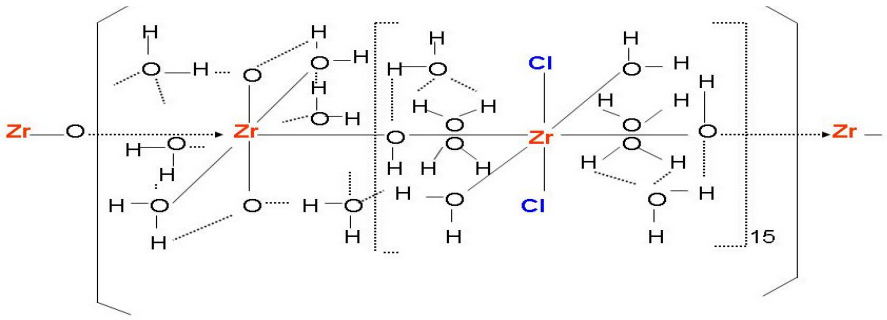
TABLE IV. THE CHEMICAL COMPOSITION OF THE PTC SORBENT

Element	Cl	H	Ti	O	H_2O
Content (% weight))	18.965	0.535	43.870	29.33	7.300
Atomic ratio	0.584	0.584	1.0	2.001	0.443

Molecular formula of PZC sorbent: Actual molecular weight (organic residue included): M= 5901.3 (X organic molecules in one PZC molecule was equivalent to 9.63% of PZC molecular weight as seen at thermal analysis). Because the organic substance in this formula was attributed to a residual organic by-product of chemical synthesis reaction and was completely being released from polymer matrix in aqueous solution, the segment unit of real polymer compound is of the following formula:

$$Zr_{15}(OH)_{30}Cl_{30}(ZrO_2).\ 126\ H_2O$$

The steric arrangement of atoms in this molecule is shown as follows:



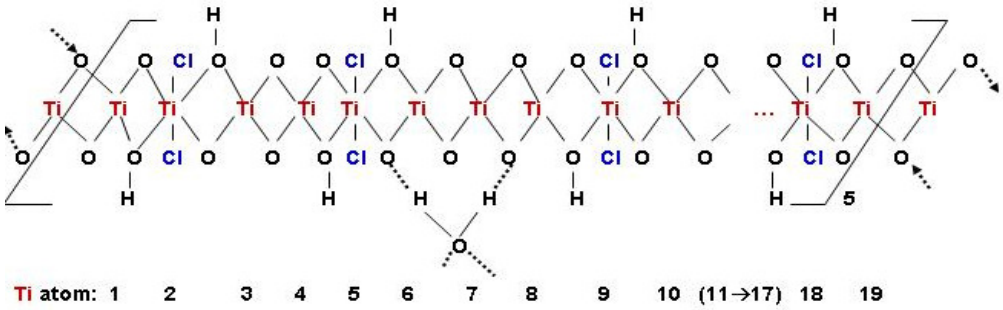
Real molecular weight (organic residue excluded): M= 5333.02; Chlorine ion content: 5.63 millimol Cl /g PZC sorbent ; Ion exchange capacity: 5.63 meq /g PZC sorbent

The ion exchange capacity derived from the above chemical formula offers an adsorption capacity of 270.0 mg Mo / g PZC or 517.1 mg W / g PZC by assuming molybdate or tungstate ions adsorbed on PZC in the form of MoO_4^{2-} or WO_4^{2-}, respectively, and one molarity of MoO_4^{2-} or WO_4^{2-} ion consuming 2 equivalences of ion-exchange capacity of

PZC and PTC sorbents (one equivalence of MoO_4^{2-} ion is 48 g Molybdenum and one equivalence of WO_4^{2-} ion is 91.925 g). This type of strong adsorption gives in a covalent bond between molybdate or tungstate ions and Zirconium metal atom.

Molecular formula of PTC sorbent: $Ti_{40}\,Cl_{80}\,(OH)_{80}\,(TiO_2)_{97}.60H_2O$

The molecular structure of PTC is depicted as below:



Real molecular weight (organic residue excluded): M= 14939.56.
Chlorine ion content: 5.35 millimol Cl / g PTC sorbent.
Ion exchange capacity: 5.35 meq / g PTC sorbent

The Chlorine content of PTC sorbent is 5.35 millimol / gram PTC sorbent (18.965 % of Chlorine element in one gram PTC). This is equivalent to the ion exchange capacity of 5.35 meq /g PTC sorbent and consequently offers an adsorption capacity of 257.0 mg Mo / g PTC or 491.8 mg W / g PTC by assuming molybdate or tungstate ions adsorbed on PTC in the form of MoO_4^{2-} or WO_4^{2-} ,respectively and one molarity of MoO_4^{2-} or WO_4^{2-} ion consuming 2 equivalences of ion-exchange capacity of PTC sorbent. This type of strong adsorption gives in a covalent bond between molybdate or tungstate ions and Titanium metal atom. The theoretical values of adsorption capacity calculated from the molecular formula of PZC and PTC compounds detailed above gives good agreement with the practical values achieved at the potential titration and at the Mo and/or W adsorption experiments (see Fig.4 and Tables 6&8).

The adsorption capacity of both sorbents was variable depending on the temperature, reaction time and gel aging process before forming solid polymer PZC and PTC products. The actual Molybdenum adsorption of PZC and PTC sorbents to some extent higher than the above mentioned values counted for the non-covalently adsorbed molybdate ions and/or for adsorption of small amount of poly-molybdate ions at the beginning stage of adsorption in the strongly acidic solution due to hydrolysis of –Zr-Cl (or -Ti-Cl) groups of the back-bone of PZC or PTC molecules.

These types of weak adsorption is considered as the reason of higher Molybdate or Tungstate break-through of PZC or PTC columns of higher Molybdate or Tungstate loading as commonly experienced in our work, respectively.

In Fig. 3 and Table 5 the infrared spectrum and related data of PZC and PTC sorbents are shown.

TABLE V. INFRARED ABSORPTION OF PZC AND PTC SORBENTS

Wave number ,cm^{-1}	Intensity	Chemical bond characteristics	Specified group
3353,9	Very strong (broad)	ν (OH)	OH in Zr-OH , Ti-OH and in $-CH_2-CH(OH)-CH_3$
3300	Very strong	ν (OH_3^+)	
2900	Very strong	ν (CH)	$-CH_2-CH_2-$
2900	Weak	ν (H_3O^+)	
1619,7	medium	δ (H_2O)	
666,0	medium	ν (Zr-O)	

By comparing the obtained results to infrared absorption data of $ZrO_2.XH_2O$ and $TiO_2.XH_2O$ samples a good agreement was found . The organic trace amount retained in the PZCand PTC detected at 2900 cm-1 is assigned to organic by-product of chemical synthesis reaction, but not to the reactant iso-propyl alcohol.
X-ray diffraction analysis result showed an amorphous structure of the PZC and PTC sorbents.

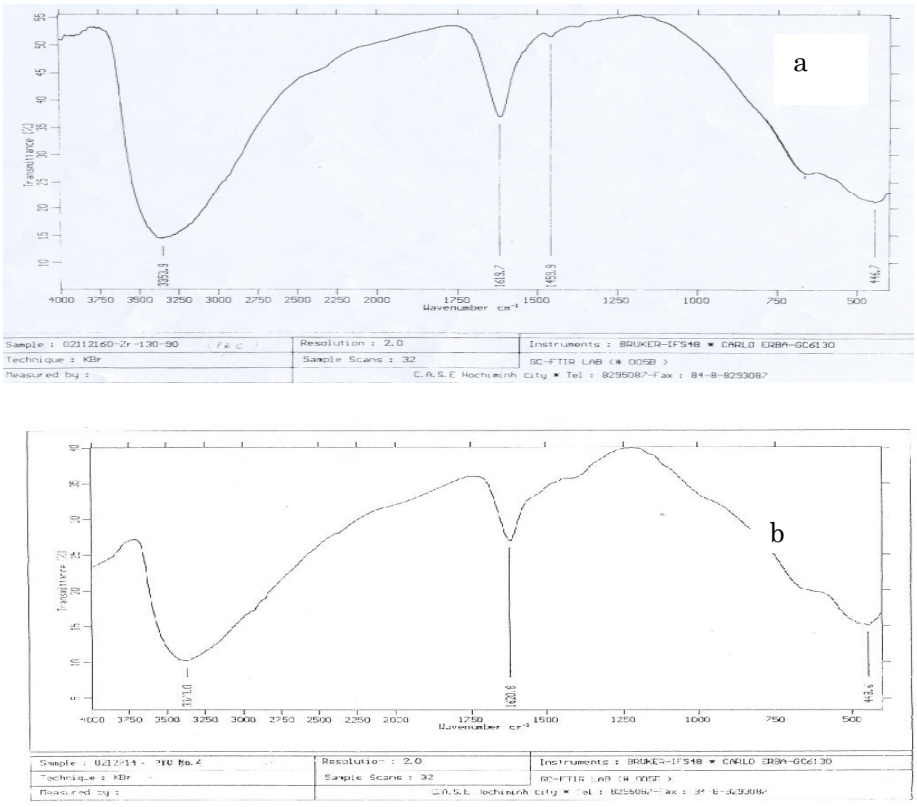
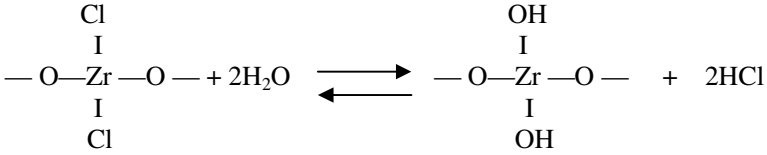


FIG. 3. Infrared spectra of PZC (a) and PTC (b) sorbents

3.3. Behaviours of PZC and PTC sorbents in the aqueous solution

The results of potentiometric titration of PZC and PTC sorbents were shown in Fig.4. A value of 5.65 meq H^+/g PZC was found at pH=11. This amount is equivalent to 5.65 meqCl^-/g PZC and agrees with chlorine content of PZC found in the thermal analysis mentioned above. By comparing this titration results with ion-exchange capacity values calculated for a molecular formula as established above, a good agreement was achieved.
Behaviours of PZC in the aqueous solution can be summarized as follows: PZC sorbent is hydrolized, but not dissolved, in aqueous solution and gives an acidic solution (pH=1.6) in water.This PZC product mainly composed of (-ZrO-) and (-ZrO^+Cl^--) groups bond together, so being hydrolized in water . The hydrolysis reaction can be described as follows:



The HCl formed during hydrolysis will make water acidic. In open air PZC adsorbs water molecules from humid environment and very strong acidic medium will be formed in the PZC particles. This acidity will destroy –ZrO-$(ZrO)_n$-ZrO- bonds and make PZC sorbent soluble in water , if PZC is left to stand in open air for three weeks. PZC sorbent contains a minor quantity of unidentified organic compound (2.53 % Carbon, 1.96 % Hydrogen and 5.14 % Oxygen). This organic substance will be released when PZC adsorbent is hydrolized in aqueous solution.
The same potentiometric titration of PTC sorbent was found. But the 5.35 meq H^+/g PTC capacity was found for PTC sorbent at pH=11. The hydrolysis property of the PTC sorbent is similar to that of PZC sorbent.

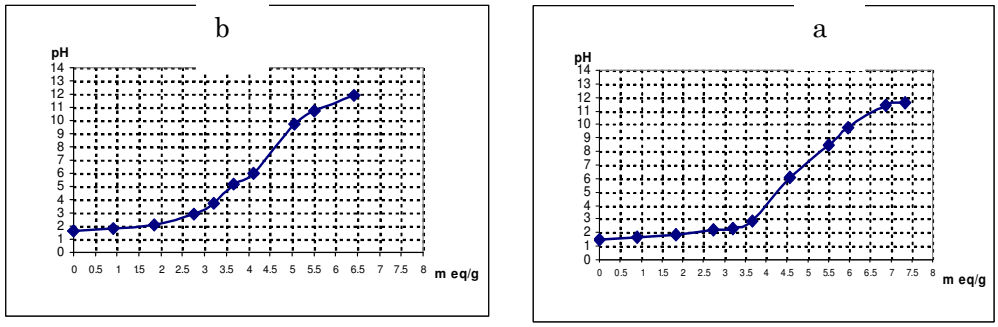


FIG. 4. Potentiometric titration curve of PZC (a) and PTC (b) sorbents

3.4. Molybdenum adsorption and ^{99m}Tc elution performance of PZC and PTC sorbents

Mo adsorption capacity and other characteristics of PZC and PTC samples vs. adsorption time shown in Table 6 and ^{99m}Tc elution profiles in Figs. 5 &6 fulfilled the requirements to be used for the chromatographic ^{99}Mo-^{99m}Tc generator preparation.

TABLE 6. MOLYBDENUM ADSORPTION CHARACTERISTICS OF THE PZC2 AND PTC2 SORBENTS

Sorbent sample	Molybdenum adsorption capacity (mgMo/g sorbent) (*)	Particle size of sorbent (mm)	Swelling in H_2O (% volume)	Reaction time (min.)	^{99m}Tc elution yield (%)
PZC2-1	255.1	0.1 – 0.001	23.5	30	92.5
PZC2-2	275.2	0.1 – 0.001	25.4	45	91.3
PZC2-3	290.3	0.1 – 0.001	28.3	50	88.5
PTC2-1	250.0	0.1 - 0.001	24.5	35	88.3
PTC2-2	270.3	0.1 – 0.001	26.2	45	90.8
PTC2-3	293.0	0.1 – 0.001	29.5	55	91.9

(*) The Mo adsorption capacity of PZC2 and PTC2 sorbents (see Table 1) in Molybdate solution of concentration of 13,35mgMo/ml and pH = 7 (pH of post adsorption solution was pH = 5). Normal conditions of ^{99}Mo adsorption in Molybdate aqueous solution was applied (see Experimental Section).

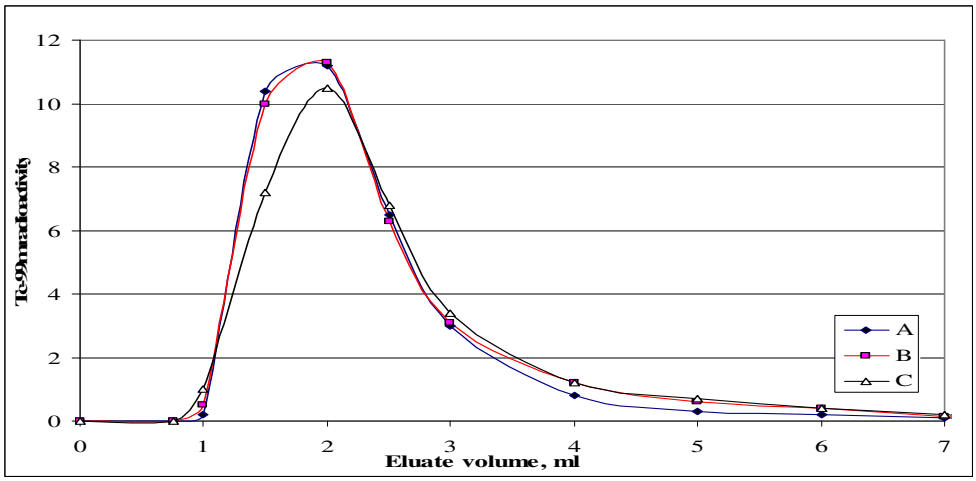


FIG. 5. ^{99m}Tc elution characteristics of different ^{99}Mo-PTC columns

A, B, C: The ^{99m}Tc elution profiles of ^{99}Mo-PTC columns loaded with 1.0 gram of sorbent samples PTC2-1, PTC2-2 and PTC2-3 (presented in Tab.6, respectively) The normal conditions of ^{99}Mo adsorption in Molybdate aqueous solution were applied (see Experimental Section).
The elution is performed with 0.9% saline (Arbitrary ^{99m}Tc radioactivity scale).

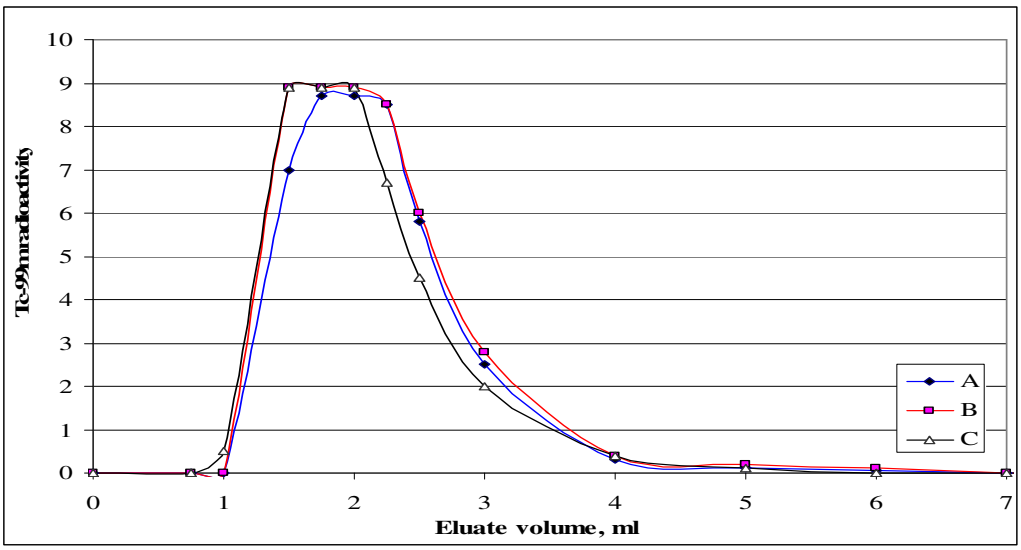


FIG. 6. ^{99m}Tc elution characteristics of different ^{99}Mo-PZC columns
A, B, C: The ^{99m}Tc elution profiles of ^{99}Mo-PZC columns loaded with 1.0 gram of sorbent samples PZC2-3, PZC2-2 and PZC2-1 (presented in Tab.6, respectively) The normal conditions of ^{99}Mo adsorption in Molybdate aqueous solution was applied (see Experimental Section).
The elution is performed with 0.9% saline (Arbitrary ^{99m}Tc radioactivity scale).

Effect of the solution Mo-content on the Mo-adsorption capacity of PZC and PTC sorbent and on the ^{99m}Tc elution yield and Mo-breakthrough of ^{99m}Tc eluate

The experimental results presented in Table 7 revealed the fact that the Mo-adsorption capacity of PZC and PTC sorbent and Mo-breakthrough of ^{99}Mo-PZC and ^{99}Mo-PTC column decreased with the increasing Mo-content of adsorption solution. This is attributed to the excess of weakly bound Molybdate ion on the surface of sorbent particles. This excess of Molybdate ion may block the pathway of ^{99m}Tc pertechnetate ion out- diffusion and cause the lower ^{99m}Tc elution yield. The lower Mo-content in the adsorption solution has caused the adsorption unsaturated and left to some extent free active groups of high anion-affinity on the sorbent particle surface. The action of these groups may contribute a retention power to reduce ^{99m}Tc elution yield and Mo-breakthrough in ^{99m}Tc eluate.
In our experiment the adsorption percentage of around 90% was chosen as an optimal value for Mo-adsorption to give a ^{99}Mo- PZC and ^{99}Mo- PZC column of highest performance.

TABLE 7. EFFECT OF THE SOLUTION Mo-CONTENT ON THE Mo-ADSORPTION CAPACITY OF SORBENTS AND ON THE ELUTION YIELD AND Mo-BREAKTHROUGH OF ^{99m}Tc ELUATE

Sample **	PZC2-1	PZC2-2	PZC2-3	PZC2-4	PTC2-1	PTC2-2	PTC2-3	PTC2-4
Weight of sorbent , (g)	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Volume of Mo solution , (ml)	3.75	4.50	5.25	6.00	3.75	4.50	5.25	6.00
Mo-content of adsorption solution , (mgMo /g sorbent)	249.6	299.6	349.5	399.4	249.6	299.6	349.5	399.4
Mo-adsorption capacity , (mg Mo / g sorbent)	236.5	275.1	287.8	307.2	221.5	270.2	281.3	297.5
Adsorption percentage, (%) *	94.70	91.80	82.33	76.90	88.7	92.8	80.5	74.5
^{99m}Tc elution yield, (%)	74.50	92.80	83.00	80.00	80.1	85.3	82.1	75.1
Mo -Breakthrough in first elution ,(µgMo/ml)	84.0	133.0	221.0	245.0	101.0	155.1	240.0	266.3
Mo -Breakthrough in second-to-fifth elution ,(µgMo/ml)	1.8 ± 0.6	21.1 ± 0.7	42.5 ± 0.9	47.2 ± 0.6	2.1 ± 0.5	18.5 ± 0.3	46.1 ± 0.7	52.5 ± 0.3

(**) PZC2 and PTC2 samples are found in Table 1. Applied elution volume: 5 ml 0.9% NaCl

(*) Adsorption percentage (%) = 100 x(Mo adsorption capacity / Mo content of solution)

The solution composition effects on the molybdenum adsorption and ^{99m}Tc elution performance of PZC and PTC sorbents.

Studies on the adsorption and ^{99m}Tc elution performance of ^{99}Mo- PZC and ^{99}Mo- PTC column in different solutions were performed. It is found that the NaOCl oxidizing agent added to Mo-solution has increased the Mo-adsorption capacity and ^{99m}Tc elution performance of ^{99}Mo- PZC and ^{99}Mo- PTC columns. The maximal Mo adsorption capacity of around 275.0mgMo/g PZC and 270.0 mgMo/g PTC was achieved.The capacity also varied depending on the applied adsorption conditions.The adsorption in the acetate buffer solution of Molybdate showed a better integrity of sorbent particles (amount of fine particles is smaller) compared with sorbent particles adsorbing Mo in pure water solution of Molybdate.

The sterilizing ^{99}Mo- PZC and ^{99}Mo- PTC columns in the autoclave reduced the elution yield of ^{99m}Tc to some extent, but did not affect the Mo-breakthrough of column.

3.5. Tungsten adsorption and ^{188}Re elution performance of PZC and PTCsorbents

Tungsten adsorption capacity and other characteristics of PZC and PTC samples vs. adsorption time shown in Table 8 and ^{188}Re elution profiles in Fig.7&8 fulfilled the requirements to be used for the chromatographic ^{188}W-^{188}Re generator preparation.

TABLE 8. TUNGSTEN ADSORPTION CHARACTERISTICS OF THE PZC2 AND PTC2 SORBENTS

Sorbent sample	Tungsten adsorption capacity (mgW/g sorbent) (*)	Particle size of sorbent (mm)	Swelling in H_2O (% volume)	Reaction time (min.)	^{188}Re elution yield (%)
PZC2-1	515.2	0.1 – 0.001	22.5	30	90.3
PZC2-2	520.1	0.1 – 0.001	24.4	45	91.2
PZC2-3	541.2	0.1 – 0.001	29.3	50	88.3
PTC2-1	492.2	0.1 – 0.001	23.5	35	89.2
PTC2-2	515.1	0.1 – 0.001	26.3	45	90.4
PTC2-3	521.3	0.1 – 0.001	28.5	60	93.4

(*) The W adsorption capacity of PZC and PTC sorbents in Tungstate solution of concentration of 25.6 mg W /ml and pH = 7 (pH of post adsorption solution was pH = 4.5). The normal conditions of ^{188}W adsorption in Tungstate aqueous solution was applied (see Experimental Section).

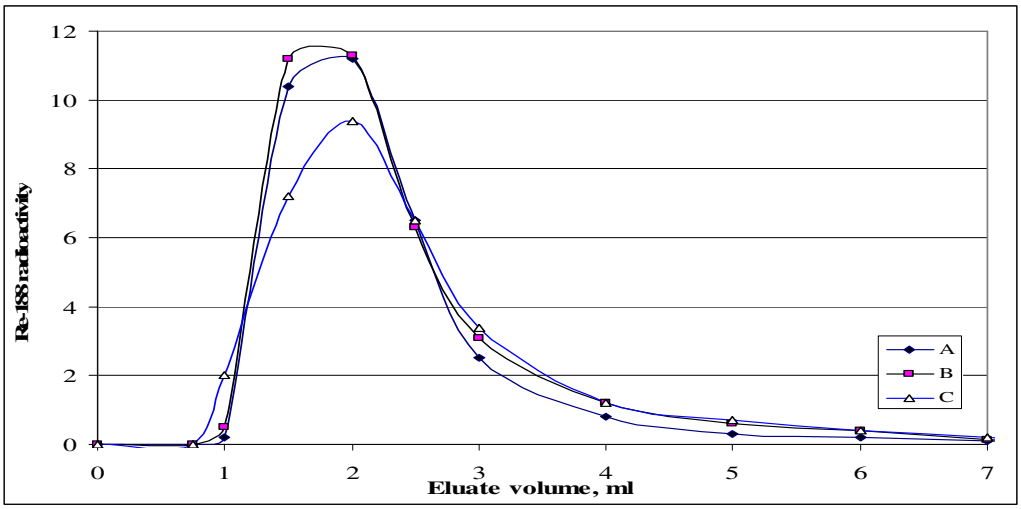


FIG. 7. ^{188}Re elution characteristics of different ^{188}W-PTC columns

A, B , C : The ^{188}Re elution profiles of ^{188}W-PTC columns loaded with 1.0 gram of sorbent samples PTC2-1, PTC2-2 and PTC2-3 (presented in Tab.8, respectively) The normal conditions of ^{188}W adsorption in Tungstate aqueous solution were applied (see Experimental Section).
The elution is performed with 0.9% saline (Arbitrary ^{188}Re radioactivity scale).

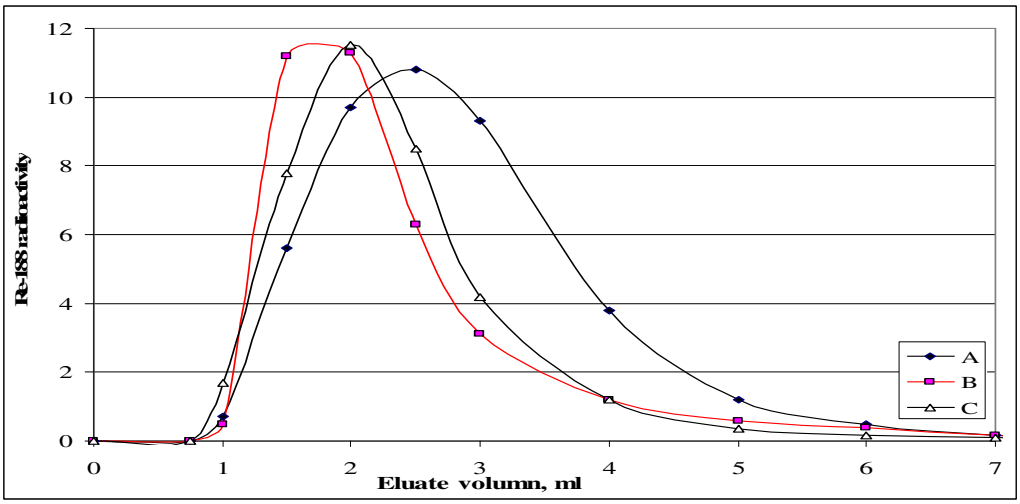


FIG. 8. ^{188}Re elution characteristics of different ^{188}W-PZC columns

A, B , C : The ^{188}Re elution profiles of ^{188}W-PZC columns loaded with 1.0 gram of sorbent samples PZC2-3, PZC2-2 and PZC2-1 (presented in Tab.8, respectively) The normal conditions of ^{188}W adsorption in Tungstate aqueous solution was applied (see Experimental Section).

The elution is performed with 0.9% saline (Arbitrary ^{188}Re radioactivity scale)

Effect of the solution W-content on the W-adsorption capacity and on the ^{188}Re elution yield and W-breakthrough of ^{188}Re eluate

The experimental results presented in Table 9 revealed the fact that the W-adsorption capacity of sorbents and W-breakthrough of ^{188}W-PZC and ^{188}W-PTC columns decreased with the increasing W-content of adsorption solution. This is attributed to the excess of weakly bound Tungstate ion on the sorbent particle surface. This excess of Tungstate ion may block the pathway of ^{188}Re perrhenate ion out- diffusion and cause the lower ^{188}Re elution yield. The solution of lower W-content has caused the adsorption unsaturated and left to some extent free active groups of high anion-affinity on the PZC and PTC sorbent particle surface. The action of these groups may contribute a retention power to reduce ^{188}Re elution yield and W-breakthrough in ^{188}Re eluate. In our experiment the adsorption percentage of around 90% was chosen as an optimal value for W-adsorption to give a ^{188}W- PZC and ^{188}W- PTC columns of highest performance.

TABLE 9. EFFECT OF SOLUTION W-CONTENT ON THE W-ADSORPTION CAPACITY OF SORBENT AND ON THE ELUTION YIELD AND W-BREAKTHROUGH OF ^{188}Re ELUATE.

Sample **	PZC2-1	PZC2-2	PZC2-3	PZC2-4	PTC2-1	PTC2-2	PTC2-3	PTC2-4
Weight of sorbent , (g)	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Volume of W solution , (ml)	3.75	4.50	5.25	6.00	3.75	4.50	5.25	6.00

W-content of adsorption solution , (mgW /g sorbent)	478.6	574.3	670.0	765.7	478.6	574.3	670.0	765.7
W-adsorption capacity , (mg W / g sorbent)	448.0	520.3	544.7	601.8	435.7	515.2	545.1	595.2
Adsorption percentage, (%) *	93.60	90.60	81.3	78.60	91.0	89.9	81.4	77.7
^{188}Re elution yield , (%)	72.50	85.30	81.20	79.00	75.1	86.2	85.6	81.5
W-Breakthrough in first elution ,(µgW/ml)	82.0	125.0	323.0	375.0	98.5	121.5	401.3	405.7
W -Breakthrough in second-to-fifth elution ,(µgW/ml)	10.4 ± 0.4	27.1 ± 0.6	52.4 ± 0.7	60.2 ± 0.5	12.3 ± 0.2	28.2 ± 0.4	58.5 ± 0.5	65.7 ± 0.3

(**) PZC2 and PTC2 sample in Table 1. Applied elution volume: 5 ml 0.9% NaCl

(*) Adsorption percentage (%) = 100 x (W adsorption capacity / W content of solution)

The solution composition effects on the tungsten adsorption and ^{188}Re elution performance of PZC and PTC sorbents

The studies on the W adsorption and ^{188}Re elution performance of ^{188}W- PZC and ^{188}W-PTC sorbents in different solutions were carried out. It is found that the NaOCl oxidizing agent added to W-solution has increased the W-adsorption capacity and ^{188}Re elution performance of ^{188}W- PZC and ^{188}W- PTC columns. Maximum W adsorption capacity of about 520.0 mg W/g PZC and 515.0 mg W/g PTC was achieved.The capacity also varied depending on the applied adsorption conditions.The adsorption in the acetate buffer solution of Molybdate showed a better integrity of PZC and PTC sorbent particles (amount of fine particles is smaller) compared with PZC and PTC particles adsorbing W in pure water solution of Tungstate.

The sterilizing ^{188}W- PZC and ^{188}W- PTC columns in the autoclave reduced the elution yield of ^{188}Re to some extent, but did not affect the W-breakthrough of column.

3.6. The PTC or PZC sorbent based ^{188}Re elution-concentration systems

Because the low specific activity ^{188}W was used for the ^{188}W-PTC or ^{188}W-PZC generator column preparation and the eluate of low ^{188}Re concentration was obtained from this column, the ^{188}Re eluate concentration should be carried out to achieve a clinically applicable ^{188}Re solution from the low ^{188}Re concentration eluate of ^{188}W-PTC or ^{188}W-PZC column. The investigation on the ^{188}Re concentration process was carried out by eluting ^{188}Re from the ^{188}W-PTC and/or ^{188}W-PTC columns with a dilute saline solution and then the ^{188}Re eluate achieved was passed through a small alumina column where all $^{188}ReO_4^-$ was retained, after that $^{188}ReO_4^-$ was eluted from Alumina column with a small volume of physiological saline. A typical result of these studies is presented in Table 10 and Fig.9. The concentration factor higher than 6 was achieved with this concentration

technique which offered a potential application for the clinically applicable ^{188}W-^{188}Re generator production using low specific radioactivity ^{188}W produced in rather low power research reactors.

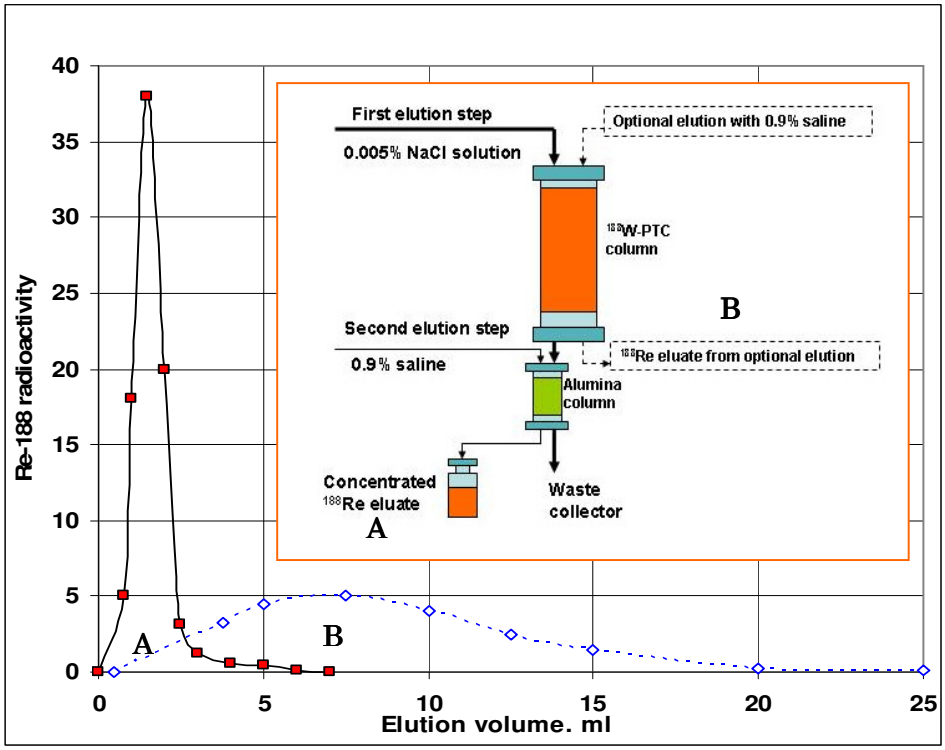


FIG. 9. The daughter nuclide elution-concentration system and the elution profiles
A: Elution profile from Alumina column on second elution step
B: Elution profile from the optional elution mode
PTC sorbent weight: 4 g; Alumina weight; 1.5 g
Tungsten weight loaded onto PTC column: 2.1 g; ^{188}W radioactivity: 6 mCi

TABLE 10. ELUTION PERFORMANCE OF ^{188}W-PTC COLUMN WITH THE ^{188}Re CONCENTRATION SYSTEM

First column (^{188}W-PTC column) elution (0.005 % NaCl eluant)

Eluant volume (ml)	^{188}Re elution yield [%] *	^{188}Re radioactivity retained on Alumina column (mCi)	W- breakthrough in the eluate
20	0	5.5mCi (91.6 % of ^{188}Re radioactivity of ^{188}W-PTC column)	Not detected

Second column (Alumina) elution (0.9% NaCl eluant)

^{188}Re radioactivity &	^{188}Re radioactivity	W-	Eluant	Concentration

^{188}Re elution yield *	remained on Alumina column	breakthrough in the eluate	volume (ml)	factor
5.0 mCi (83.0 % of ^{188}Re radioactivity of ^{188}W-PTC column)	0.5 mCi	Not detected	3	6.7

* This parameter was calculated for whole generator system.
See picture at the right corner of Fig. 9 to identify the elution profiles.^{188}W-PTC column:4.0 g PTC sorbent containing 6 mCi ^{188}W.

FIG.10 . PZC and PTC sorbent synthesis (a), ^{99}Mo column loading process (b) and the PZC and PTC sorbent based ^{99m}Tc generator (c)

4. CONCLUSION

The PZC and PTC sorbents for the preparation of chromatographic ^{99m}Tc and/or ^{188}Re generators were successfully synthesized and their chemical composition and molecular structure determined. The ^{99}Mo and/or ^{188}W -adsorption on the PZC and PTC sorbents in different solutions and the ^{99m}Tc and/or ^{188}Re elution from the parent nuclides adsorpted PZC and PTC columns were investigated. The Molybdenum adsorption capacities of about 275 mgMo/gPZC and 270 mgMo/gPTC and the ^{99m}Tc elution yield higher than 90% were achieved with both sorbents. The ^{99}Mo breakthrough of 0.015% and Molybdenum element breakthrough lower than 2µg Mo/ml were found in ^{99m}Tc eluate. Tungsten adsorption capacities of about 520 mgW/gPZC and 515 mgW/gPTC and ^{188}Re elution yield higher than 80% were also achieved with both PZC and PTC sorbents. The ^{188}W breakthrough of 0.015% and Tungsten element breakthrough lower than 5 µg W /ml were found in ^{188}Re eluate.
A good relationship between the W- and Mo-content of adsorption solution and the adsorption capacity, adsorption percentage, chemical breakthrough and relevant

radionuclide elution yield was found.
The ^{188}Re concentration process was developed by eluting ^{188}Re from the tandem system of ^{188}W-PTC – Alumina columns with the different concentration saline solutions. The concentration factor higher than 6 was achieved by this concentration technique which offered a potential application for the clinically applicable ^{188}W-^{188}Re generator production using low specific radioactivity ^{188}W produced in rather low power research reactors.

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