IAEA'S CO-ORDINATED RESEARCH PROJECT

2nd Research Co-nation Meeting
on
"DEVELOPMENT OF GENERATOR TECHNOLOGIES FOR THERAPEUTIC RADIONUCLIDES"
3-7 April 2006, European Institute of Oncology, Milan, Italy

CHEMICAL SYNTHESIS AND APPLICATION OF ZIRCONIUM AND TITANIUM POLYMER COMPOUNDS FOR THE PREPARATION OF Tc-99m AND Re-188 CHROMATOGRAPHIC GENERATORS

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Abstract

PZC adsorbent for the preparation of PZC based chromatographic Tc-99m and / or Re-188 generators was successfully synthesized and its chemical composition, molecular structure was determined. ^{99}Mo and/or ^{188}W -adsorption on PZC in different solutions and ^{99m}Tc and/or ^{188}Re elution from PZC columns were investigated. Mo- adsorption capacity of about 285 mgMo/gPZC and Tc-99m elution yield of higher than 90% were achieved with PZC adsorbent. Mo-99 breakthrough of 0.015% and Molybdenum element breakthrough of lower than 5µg Mo/ml were found in Tc-99m eluate.
W- adsorption capacity of about 520 mgW/gPZC and Re-188 elution yield of higher than 80% were also achieved with PZC adsorbent. W-188 breakthrough of 0.015% and Tungsten element breakthrough of lower than 5 µg W /ml were found in Tc-99m eluate.
A good relationship between the W- or Mo-content of adsorption solution and the adsorption capacity, adsorption percentage, chemical breakthrough and relevant radionuclide elution yield was found.

INTRODUCTION

At present nearly the entire supply of Mo-99 is based on the research reactor produced Mo-99 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 leads to expensive but high specific activity of ^{99}Mo. In 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 processing ^{99}Mo from (n, γ) "activation method" is rather simple, and is within the reach of most developing countries operating research reactors.

Alternative technologies for ^{99m}Tc generators using (n, γ) nuclear reaction with natural Mo have been developed and are now under way of development . Although some new technologies have technically been accepted in many countries, there will have to be a substantial economic incentive for large producers of Mo-99 or Tc-99m 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 $^{99}Tc^{m}$ generators using Zirconium- or Titanium-Molybdate gel, so called "gel technology" (9,10..) and polymer Zirconium- or Titanium compound (PZC, PTC) based technology are considered as new ones. For the reason of compatibility between the fission ^{99}Mo and Alumina based Tc-99m generator production technology and the PZC or PTC adsorbent and (n,γ) ^{99}Mo 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(11,12,13).

As a contribution , the chemical synthesis of polymer compound of Zirconium adsorbent (PZC) for the preparation of PZC based chromatographic Tc-99m and Re-188 generators and the assessment of the performance of PZC adsorbent for the preparation of a clinically-available Tc-99m and Re-188 generator were described in our report.

EXPERIMENTAL

Synthesis of PZC

PZC adsorbent was synthesized from isopropyl alcohol (iPrOH) and $ZrCl_4$ under strictly controlled conditions of reaction . 50 gram $ZrCl_4$ are carefully added to different amounts of iPrOH . The temperature of reaction mixture will immediately reach 97 ^oC . By keeping the temperature of solution at 97 ^oC, stir this solution gently by magnetic stirrer in open air until this solution become viscous. As the reaction temperature is increased, a water-soluble gel PZC (an intermediate precursor) will be formed at 130 ^oC . The water-insoluble, solid PZC of particle size of from 0.10 mm to 0.01 mm are splitted out by keeping the reaction temperature at 140 ^oC for 30 minutes. This is the finished product of PZC adsorbent.The synthesized PZC samples and their chemical synthesis conditions are listed in Table 1.

Table 1: 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)
A_1	50	40	140
A_2	50	80	140
A_3	50	100	140

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

Zirconium content of PZC was analyzed by gravimetric method by ignition of PZC at 1200^oC for two hours. ZrO_2 was measured and Zirconium content calculated.

Carbon , Hydrogen and oxygen element content of PZC were determined by thermal decomposition of PZC sample on Perkinelmer 2400 II instrument .

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

Thermal analysis of PZC sample was carried out on MB-7H derivatographer instrument with N_2 gas flow rate of 50 cc/min and heating rate of 10^oC/min.

Potentiometric titration of PZC sample was carried out with 0.1 g weight sample of PZC in 60 ml 0.1 M NaCl solution . Titration solution was 0.1 M NaOH solution.

Infra-red spectrum of PZC sample was recorded on Brucker-IFS 48 * Carlo Erba-GC 6130 instrument with PZC sample mixed KBr pellet.

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

Investigation on Molybdenum adsorption and Tc-99m elution using PZC adsorbent.

15 ml radioactive Mo-99 solution of concentration of 13.35 mg Mo / ml, pH=7 were added to PZC samples of 0.75 g weight, then these samples were gently shaken in water bath of 50^oC overnight. After shaking the samples were let to stand and a portion of clear supernatant solution was taken out to measure Mo-99 radioactivity for Mo–adsorption capacity calculation and then the remained solution was decanted to get the solid PZC part. This solid PZC sample was packed in 8ml glass column and washed with 50 ml water followed by passing column with 10 ml saline. After this step the first Tc-99m elution was started after 24 hours of equilibration time and an elution was daily conducted.

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

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

a- Normal adsorption in aqueous solution of Molybdate;

b- Normal adsorption in NaOCl (0.05% NaOCl) added aqueous solution of Molybdate .

c- Adsorption in Acetate buffer solution of Molybdate (Acetate buffer solution of 0.2M acetic acid, pH=5)

d- Adsorption in NaOCl added Acetate solution of Molybdate (Acetate buffer solution of 0.2M acetic acid, containing 0.05% NaOCl , pH=5)

e- The Tc-99m elution performance of Mo-99 adsorbed PZC column post stream-sterilization was also investigated.For this purpose a normal adsorption in NaOCl (0.05% NaOCl) added aqueous solution of Molybdate wasfollowed by sterilization in autoclave.

Investigation on Tungsten adsorption and Re-188 elution using PZC adsorbent.

The similar procedure as above was applied for investigation on Tungsten adsorption and

Re-188 elution using PZC adsorbent. The radioactive W-188 solution of concentration of 25.6 mg W/ ml (pH=7) was used instead of molybdate solution. The 5-10 mCi W-188 radioactivity was used in all the column experiments.

Investigation on the effect of the Mo-content of adsorption solution on the Mo-adsorption capacity of PZC and on the Tc-99m elution yield and Mo-breakthrough of Tc-99m eluate.

The variable volumes (as specified in Table 8 below) of the radioactive Mo-99 solution of concentration of 13.35 mg Mo / ml , pH=7 were added to PZC samples of 0.2 g weight, then these samples were gently shaken in water bath of 50 ^{o}C overnight. After shaking the samples were let to stand and a portion of clear supernatant solution was taken out to measure Mo-99 radioactivity for Mo–adsorption capacity calculation and then the remained solution was decanted to get the solid PZC part which was then packed on a small column. This solid PZC column was washed with 10 ml water followed by passing column with 10 ml saline. After this step the first Tc-99m elution was started after 24 hours of equilibration time and an elution was daily conducted.

Investigation on the effect of the W-content of adsorption solution on the W-adsorption capacity of PZC and on the Re-188 elution yield and W-breakthrough of Re-188 eluate.

The similar procedure as above was applied in the investigation on the effect of the W-content of adsorption solution on the W-adsorption capacity of PZC and on the Re-188 elution yield and W-breakthrough of Re-188 eluate. The variable volumes (as specified in Table 11 below) of the radioactive W-188 solution of concentration of 25.6 mg Mo / ml , pH=7 was used instead of molybdate solution. The 5-10 mCi W-188 radioactivity was used in all the column experiments.

RESULTS AND DISCUSSION

Synthesis and specification of PZC

This finished product of PZC adsorbent is light brown in colour. It swells in water to become white in colour and the volume of swollen PZC bed is 1.25 times as large as the dry one. The adsorption capacity of synthesized PZC adsorbent for Molybdenum at pH=5 varies from 100 to 290 mg Mo/ g PZC depending on the temperature and duration of solid polymer PZC product formation. About synthesis conditions ,the Molybdenum adsorption capacity of PZC decreased with the increase of reaction temperature, whereas the increase in molar ratio of reactants (isopropyl/$ZrCl_4$) brought about a higher degree of swelling of PZC particle in aqueous solution. This favored the diffusion of Molybdate ions into PZC matrix during adsorption process. But the swelling of particles will give in the decrease in mechanical stability of PZC.

Chemical composition and molecular formula of PZC.

The results of chemical and thermal analysis were listed in tables 2.

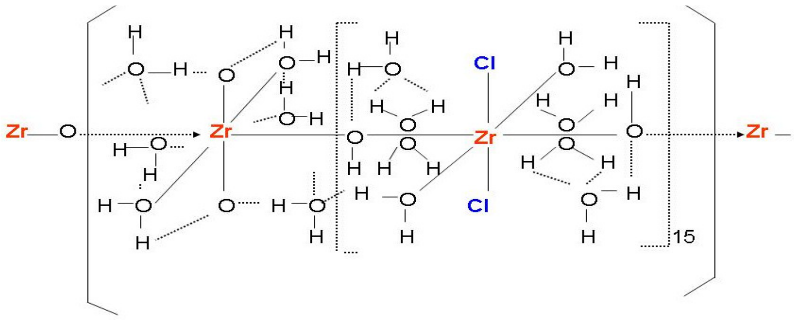
Table 2: The chemical analysis results of the synthesized PZC adsorbent

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

As shown in themoanalysis diagram 18.42% weight loss at 110 ^oC is attributed to HCl decomposed from PZC . This amount of HCl is equivalent to 17,9% chlorine content in PZC sample, which can be explained basing on the 110^{o}C boiling point of an azeotrop solution of HCl gas at 760 mm Hg .
Based on the obtained results the molecular structure of PZC is described as below .

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

The steric arrangement of atoms are shown as follows:



Real molecular weight (organic residue excluded): M= 5333.02
Chlorine ion content : 5.63 millimol Cl- / gram PZC adsorbent.
Ion exchange capacity : 5.63 meqv./g PZC adsorbent

This capacity offers an adsorption capacity of 270.0 mg Mo / g PTC 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 adsorbent(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 give in an covalent bond between molybdate or tungstate ions and Zirconium metal atom.
The theoretical values of adsorption capacity calculated from the above molecular formula gave a good agreement with the practical values achieved at the potential titration and at the Mo and/or W adsorption experiments (see fig.5 and tables 4,5).

In Table 3 the infrared analysis results of PZC sample are shown .

Table 3: Infrared absorption of PZC

Wave number ,cm^{-1}	Intensity	Chemical bond characteristics	
3353,9	Very strong (broad)	ν (OH)	OH in Zr-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 $ZrO_2.XH_2O$ sample a good agreement was found . The organic trace amount retained in the PZC detected at 2900 cm-1 is assigned to organic by-product of chemical synthesis reaction, but not to the reactant iso-propyl alcohol.

Behaviours of PZC in the aqueous solution.

The potentiometric titration of PZC adsorbent gave a value of 5,65 meqv H^+/g PZC at pH=11 . This amount is equivalent to 5,65 meqv.Cl^-/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 adsorbent 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 bonds together, so being hydrolized in water . The hydrolysis reaction can be described as follows :

$$—O—\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{Zr}}—O— + 2H_2O \rightleftharpoons —O—\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{Zr}}—O— \quad + \quad 2HCl$$

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 particle of PZC. This acidity will destroy $–ZrO-(ZrO)_n-ZrO-$ bonds and make PZC become soluble in water , if PZC is left to stand in open air for three weeks.

PZC adsorbent contains a minor quantity of unidentified organic compound (2.53 % Carbon , 1.96 % Hydrogen , 5.14 % Oxygen) . This organic substance will be released when PZC adsorbent is hydrolized in aqueous solution.

Molybdenum adsorption and Tc-99m elution performance of PZC adsorbent .

Mo adsorption capacity and other characteristics of PZC samples vs. reaction (adsorption) time shown in table 4 and Tc-99m elution profiles in fig.6 fulfilled the requirements to be used for the chromatographic ^{99}Mo-^{99m}Tc generator preparation.

Table 4: Molybdenum adsorption characteristics of the synthesized PZC :

PZC sample	Molybdenum adsorption capacity (mgMo/gPZC) (*)	Particle size of PZC (mm)	Swelling in H_2O (% volume)	Reaction time (min.)
A_1	255,1	0,1 - 0,001	23,5	30
A_2	285,2	0,1 - 0,001	25,4	45
A_3	290,3	0,1 - 0,001	28,3	50

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

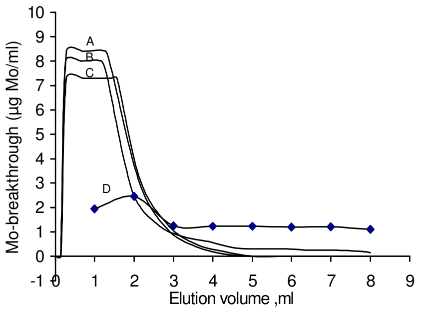


Fig. 1: ^{99m}Tc elution characteristics of different ^{99}Mo-PZC columns

A, B , C : The Tc-99m elution profiles of ^{99}Mo-PZC columns loaded with 1.0 gram of PZC samples A_3, A_2, A_1 (present in table 4) , 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 Tc-99m radioactivity Scale).
D : Mo content in the different eluate fractions of the elution profile A.

Tungsten adsorption and Re-188 elution performance of PZC adsorbent.

W adsorption capacity and other characteristics of PZC samples vs. reaction (adsorption) time shown in table 5 and Re-188 elution profiles in fig.2 fulfilled the requirements to be used for the chromatographic ^{188}W--^{188}Re generator preparation.

Table 5: Tungsten adsorption characteristics of the synthesized PZC :

PZC sample	Molybdenum adsorption capacity (mgW /gPZC) (*)	Particle size of PZC (mm)	Swelling in H_2O (% volume)	Reaction time (Min.)
A_1	515.2	0,1 - 0,001	22,5	30
A_2	525.1	0,1 - 0,001	24,4	45
A_3	541.2	0,1 - 0,001	29,3	50

(*) The W adsorption capacity of PZC 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 W-188 adsorption in Tungstate aqueous solution was applied (see Experimental Section).

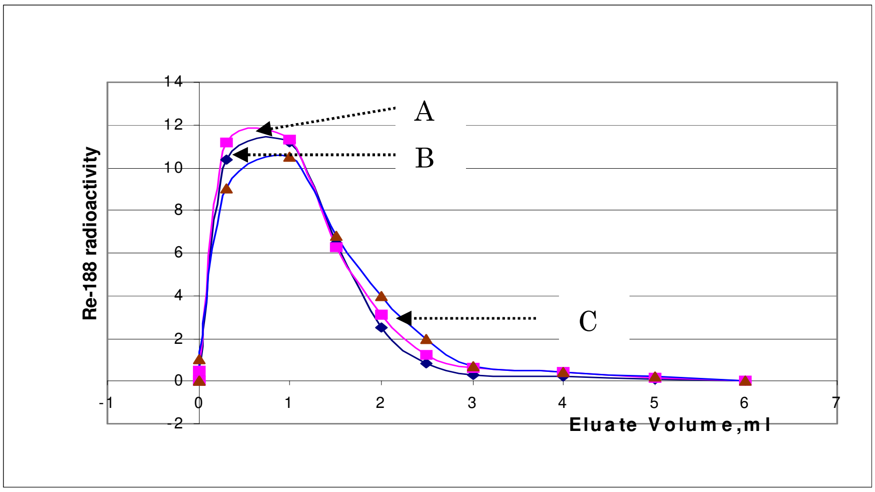


Fig. 2: ^{188}Re elution characteristics of different ^{188}W-PZC columns .

A, B , C : The Re-188 elution profiles of ^{188}W-PZC columns loaded with 1.0 gram of PZC samples A_1, A_2, A_3 (present in table 5) , respectively. The normal conditions of W-188 adsorption in Tungstate aqueous solution was applied (see Experimental Section). The elution is performed with 0.9% saline (Arbitrary Tc-99m radioactivity Scale).

The solution composition effects on the molybdenum adsorption and Tc-99m elution performance of PZC adsorbent . .

In tables 6,7,8 the results of studies on the adsorption and Tc-99m elution performance of ^{99}Mo- PZC in different solutions were presented. It is found that NaOCl oxidizing agent added Mo-solution has increased the Mo-adsorption capacity and Tc-99m elution performance of ^{99}Mo- PZC columns.

Maximum Mo adsorption capacity of about 285.0 mgMo/g PZC was achieved.The capacity also varied depending on the applied adsorption conditions.

The adsorption in Acetate buffer solution of Molybdate showed a better integrity of PZC particles (amount of fine particles is smaller) comparing with PZC particles adsorbing Mo in pure water solution of Molybdate.

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

Table 6 : The Mo adsorption of PZC in different solutions

Sample (***)	pH		Colour of PZC (After adsorption)	Non-adsor-bed Mo-99 radioactivity (%)	Discarded fine PZC powder Mo-99 radio-activity (%)	Generator column Mo-99 radio-activity (%)	Adsorption capacity (mg Mo/g PZC)	Weight of PZC	
	Before Adsorption	After Adsorption						Discarded fine powder (%)	Generator column (%)
I	7	4.6	Light grey-blue	5.2	6.3	88.5	251.5	7.4	92.6
II	7	5.4	Light grey blue	22.0	5.6	72.4	267.5	5.2	94.8
III	7	5.6	Light yellow	21.2	4.6	74.2	284.8	5.5	94.5
IV	7	5.6	Light yellow	24.0	5.7	70.3	285.1	7.6	92.4
V	7	5.4	Light yellow	24.7	5.2	70.1	284.6	7.7	92.3

Table 7: The Tc-99m elution of PZC in different solutions

Sample (***)	First elution			Second to fifth elution (****)		
	Elution Yield of Tc-99m (%)	Mo breakthrough		Elution Yield of Tc-99m (%)	Mo-breakthrough	
		µg Mo (*)	(%) (**)		µg Mo (*)	(%) (**)
I	92.5	42.2	0.031	92.7 ± 0.4	12.0	0.011
II	95.4	41.0	0.032	97.6 ± 0.2	13.3	0.012
III	98.2	36.2	0.025	98.5 ± 0.3	11.5	0.012
IV	98.0	41.0	0.035	98.4 ± 0.1	16.6	0.015
V	95.2	42.0	0.033	96.1 ± 0.2	16.4	0.014

Sample symbol:

(I) With normal condition of Mo-adsorption in aqueous solution of Molybdate and column washing with 50 ml distilled water, eluted with saline.

(II) With normal condition of Mo-adsorption in Acetate buffer solution of Molybdate (pH=5) and column washing with 50 ml distilled water, eluted with saline.

(III) With normal condition of Mo-adsorption in Acetate buffer solution of Molybdate(pH=5) containing 0.05% NaOCl and column washing with 50 ml distilled water, eluted with saline.

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(IV) With normal condition of Mo-adsorption in aqueous solution of Molybdate containing 0.05% NaOCl and column washing with 50 ml distilled water, eluted with saline.

(V) The Tc-99m elution performance of Mo-99 adsorbed PZC column after stream- sterilization (a normal adsorption in NaOCl (0.05% NaOCl) added aqueous solution of Molybdate followed by sterilization in autoclave.)

(*) Total Molybdenum content in 8 ml eluate.

(**) Percentage of Mo-99 radioactivity in the eluate of Tc-99m.

(***) PZC sample A2 in table 4.

(****) ^{99}Mo-PZC column coupled with 1.0 g Alumina clean-up column.

Effect of the solution Mo-content on the Mo-adsorption capacity of PZC and on the Tc-99m elution yield and Mo-breakthrough of Tc-99m eluate.

The experimental results presented in Table 8 revealed the fact that the Mo-adsorption capacity of PZC and Mo-breakthrough of Mo-PZC 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 PZC. This excess of Molybdate ion may block the pathway of Tc-99m pertechnetate ion out- diffusion and cause the lower Tc-99m elution yield . The lower Mo-content of adsorption solution has caused the unsaturated adsorption and left to some extent free active groups of high anion-affinity on PZC surface. The action of these groups may contribute a retention power to reduce Tc-99m elution yield and Mo-breakthrough in Tc-99m 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 column of highest performance.

Table 8 : Effect of the solution Mo-content on the Mo-adsorption capacity of PZC and on the Tc-99m elution yield and Mo-breakthrough of Tc-99m eluate.

(**) PZC sample : A2 sample in table 4.,

- Mo- adsorption capacity: 285 mg Mo / g PZC
- Applied elution volume: 5 ml 0.9% NaCl

(*) Adsorption percentage (%) = 100 x $\frac{\text{Mo adsorption capacity}}{}$

Mo content of solution

Sample **	PZC-A2-1	PZC-A2-2	PZC-A2-3	PZC-A2-4
Weight of PZC , (g)	0.20	0.20	0.20	0.20
Volume of Mo solution , (ml)	3.75	4.50	5.25	6.00
Mo-content of adsorption solution , (mgMo /g PZC)	249.67	299.61	349.54	399.48
Mo-adsorption capacity , (mg Mo / g PZC)	236.5	275.1	287.8	307.2
Adsorption percentage, (%) *	94.70	91.80	82.33	76.90
Tc-99m elution yield , (%)	74.50	92.80	83.00	80.00
Mo -Breakthrough in first elution ,(µgMo/ml)	84.0	133.0	221.0	245.0
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

The solution composition effects on the tungsten adsorption and Re-188 elution performance of PZC adsorbent . .

In tables 9,10,11 the results of studies on W adsorption and Re-188 elution performance of ^{188}W- PZC in different solutions were presented. It is found that NaOCl oxidizing agent added W-solution has increased the W-adsorption capacity and Re-188 elution performance of ^{188}W- PZC columns.

Maximum W adsorption capacity of about 540.0 mg W/g PZC was achieved.The capacity also varied depending on the applied adsorption conditions.

The adsorption in Acetate buffer solution of Molybdate showed a better integrity of PZC particles (amount of fine particles is smaller) comparing with PZC particles adsorbing W in pure water solution of Tungstate.

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

Table 9 : The W adsorption of PZC in different solutions

Sample (***)	pH		Colour of PZC (After adsorp-tion)	Non-adsor-bed W-188 radioac-tivity (%)	Discar-ded fine PZC powder W-188 radio-activity (%)	Genera-tor column W-188 radio-activity (%)	Adsorp-tion capacity (mg W/g PZC)	Weight of PZC	
	Before Adsorp-tion	After Adsorp-tion						Discar-ded fine powder (%)	Genera-tor column (%)
I	7	4.5	Light grey-blue	7.3	7.2	85.5	498.5	7.2	92.8
II	7	5.1	Light grey blue	21.3	3.4	75.3	500.2	4.1	95.9
III	7	5.2	Light yellow	22.4	4.5	73.1	513.8	5.3	94.7
IV	7	5.0	Light yellow	24.8	5.1	70.1	512.1	8.8	91.2
V	7	4.9	Light yellow	25.7	4.3	70.0	525.2	7.2	92.8

<u>Table 10</u>: The Re-188 elution of PZC in different solutions

Sample (***)	First elution			Second to fifth elution (****)		
	Elution Yield of Re-188 (%)	W breakthrough		Elution Yield of Re-188 (%)	W-breakthrough	
		µg W (*)	(%) (**)		µg W (*)	(%) (**)
I	82.5	81.2	0.031	81.5 ± 0.5	11.0	0.012
II	85.4	73.0	0.032	80.3 ± 0.6	12.2	0.010
III	87.2	61.2	0.025	85.6 ± 0.5	11.0	0.015
IV	88.1	75.0	0.032	88.4 ± 0.1	15.6	0.013
V	85.2	81.0	0.043	86.1 ± 0.2	13.4	0.011

Sample symbol:

(I) With normal condition of W-adsorption in aqueous solution of Tungstate and column washing with 50 ml distilled water, eluted with saline.
(II) With normal condition of W-adsorption in Acetate buffer solution of Tungstate (pH=5) and column washing with 50 ml distilled water, eluted with saline.
(III) With normal condition of W-adsorption in Acetate buffer solution of Tungstate (pH=5) containing 0.05% NaOCl and column washing with 50 ml distilled water, eluted with saline.

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(IV) With normal condition of W-adsorption in aqueous solution of Tungstate containing 0.05% NaOCl and column washing with 50 ml distilled water, eluted with saline.
(V) The Re-188 elution performance of W-188 adsorbed PZC column after stream- sterilization (a normal adsorption in NaOCl (0.05% NaOCl) added aqueous solution of Tungstate followed by sterilization in autoclave.)
(*) Total Tungsten content in 8 ml eluate.
(**) Percentage of W-188 radioactivity in the eluate of Re-188.
(***) PZC sample A2 in table 5.
(****) ^{188}W-PZC column coupled with 1.0 g Alumina clean-up column.

Effect of the solution W-content on the W-adsorption capacity of PZC and on the Re-188 elution yield and W-breakthrough of Re-188 eluate.

The experimental results presented in Table 11 revealed the fact that the W-adsorption capacity of PZC and W-breakthrough of W-PZC column decreased with the increasing W-content of adsorption solution. This is attributed to the excess of weakly bound Tungstate ion on the surface of PZC. This excess of Tungstate ion may block the pathway of Re-188 perrhenate ion out- diffusion and cause the lower Re-188 elution yield . The lower W-content of adsorption solution has caused the unsaturated adsorption and left to some extent free active groups of high anion-affinity on PZC surface. The action of these groups may contribute a retention power to reduce Re-188 elution yield and W-breakthrough in Re-188 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 column of highest performance.

<u>Table 11</u> : Effect of the solution W-content on the W-adsorption capacity of PZC and on the Re-188 elution yield and W-breakthrough of Re-188 eluate.
(**) PZC sample : A2 sample in table 5.
- W- adsorption capacity: 520 mg W / g PZC
- Applied elution volume: 5 ml 0.9% NaCl

(*) Adsorption percentage (%) = 100 x $\frac{\text{W adsorption capacity}}{\text{W content of solution}}$

Sample **	PZC-A2-1	PZC-A2-2	PZC-A2-3	PZC-A2-4
Weight of PZC , (g)	0.20	0.20	0.20	0.20
Volume of W solution , (ml)	3.75	4.50	5.25	6.00
W-content of adsorption solution , (mgW /g PZC)	478.6	574.3	670.0	765.7
W-adsorption capacity , (mg W / g PZC)	448.0	520.3	544.7	601.8
Adsorption percentage, (%) *	93.60	90.60	81.3	78.60
Re-188 elution yield , (%)	72.50	85.30	81.20	79.00
W-Breakthrough in first elution ,(µgW/ml)	82.0	125.0	323.0	375.0
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

CONCLUSION

PZC adsorbent for the preparation of PZC based chromatographic Tc-99m and / or Re-188 generators was successfully synthesized and its chemical composition, molecular structure was determined. ^{99}Mo and/or ^{188}W -adsorption on PZC in different solutions and ^{99m}Tc and/or ^{188}Re elution from PZC columns were investigated. Mo- adsorption capacity of about 285 mgMo/gPZC and Tc-99m elution yield of higher than 90% were achieved with PZC adsorbent. Mo-99 breakthrough of 0.015% and Molybdenum element breakthrough of lower than 5µg Mo/ml were found in Tc-99m eluate.
W- adsorption capacity of about 520 mgW/gPZC and Re-188 elution yield of higher than 80% were also achieved with PZC adsorbent. W-188 breakthrough of 0.015% and Tungsten element breakthrough of lower than 5 µg W /ml were found in Tc-99m eluate.
A good relationship between the W- or Mo-content of adsorption solution and the adsorption capacity, adsorption percentage, chemical breakthrough and relevant radionuclide elution yield was found.

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