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SORPTION OF TUNGSTEN(VI) AND RHENIUM(VII) ON VARIOUS ION-EXCHANGE MATERIALS

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ABSTRACT

The comparative distribution coefficients of W and Re on Al_2O_3, H-ZrO_2, Silica-gel, Charcoal, HAP, Lead, H-MnO_2, H-CeO_2, H-TiO_2, H-SnO_2, organic anion, and cation exchangers were determined at different pH values and acid concentrations, in order to choose the most suitable exchanger for construction of a$^{188}W \rightarrow {}^{188}Re$ generator. The experimental results clearly select Al_2O_3 as the best adsorbent. Other adsorbents may find application as tandem a column matrix to reduce the ^{188}W breakthrough in the final $^{188}ReO_4^-$ eluate.

Key Words: Tungsten(VI); Rhenium(VII); Ion-exchangers; Distribution coefficients; Separation factor

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INTRODUCTION

Currently there is noticeable interest in rhenium-188 for various medical applications. Tumor therapy with ^{188}Re labeled-antibodies (1–3) is the major application of this radioisotope. Treatment of medullary thyroid carcinoma and treatment of bone metastases with ^{188}Re-DMSA (dimercaptosuccinic acid) and phosphonate complexes of ^{188}Re have been reported (4,5). Irradiation of natural tungsten with thermal or epithermal neutrons in a reactor gives several radioisotopes of tungsten and rhenium. The principal activities are due to ^{187}W, ^{185}W, and ^{188}W, whereas ^{186}Re and ^{188}Re are the products of secondary reactions. An important characteristic is availability of ^{188}Re from decay of reactor-produced parent ^{188}W in generator system.

For the isolation of rhenium isotopes from irradiated tungsten, Grosse-Ruyken and Dodge (6) applied a solvent extraction procedure with pyridine. Lewis and Eldridge (7) separated rhenium isotopes from irradiated tungsten by sorbing both nuclides on hydrous zirconium oxide ion-exchanger in the chloride form; the elution of rhenium from the column was effected with a mixture of methyl ethyl ketone and hydrochloric acid. Rhenium-188 is obtained carrier-free as sodium perrhenate or perrhenic acid from either alumina-based chromatographic—type generators (8–11) or as perrhenate from the tungsten-zirconium gel type system (12,13).

The purpose of the present work is to determine the adsorption properties of various ion-exchange materials (commonly used or have potential to be used for $^{188}\text{W} \rightarrow {}^{188}\text{Re}$ generators) for tungsten and rhenium ions by measuring the distribution coefficients of the two ions at different acid concentrations and pH values.

EXPERIMENTAL

The following exchangers were tested:

Aluminium oxide (Al_2O_3) 90 active acidic for column chromatography, 70–230 mesh ASTM (Merck).
Hydrous zirconium oxide (H-ZrO_2) ion exchange crystals, 100–200 mesh (Bio-Rad).
Silica-gel, 70–230 mesh, 60 Angstrom for column chromatography (Aldrich).
Charcoal activated, 0.5–0.8 mm particle size (BDH).
Anion exchange resin, AG 1–X12, analytical grade, 50–100 mesh. Chloride form (Bio-Rad).
Cation exchange resin, AG 50W-X12 analytical grade 200–400 mesh hydrogen form (Bio-Rad).
Hydrous manganese dioxide (H-MnO_2) was prepared (14) by adding a hot solution (∼90°C) of manganese sulfate (71.4 g/l) to a potassium

permanganate solution (21.3 g/l). The resulting manganese dioxide was washed with distilled water, dried at 60°C and sieved. The fraction of 200–400 mesh was used in the experiments.

Hydrated titanium dioxide (H-TiO_2) was prepared by neutralization of titanium (IV) chloride solution with ammonium hydroxide (15). The suspension was aged at room temperature for 50 h under slow stirring and then centrifuged. The solid was suspended in the distilled water and centrifuged. This last procedure was repeated many times until the solid started to peptize. After final washing it was dried at 70–80°C. The resulting glassy lumps were ground to the required mesh size (60–100 mesh).

Hydrated antimony pentoxide (HAP) was prepared (16) by the hydrolysis of $SbCl_5$ with water. The precipitate was filtered off, washed, and dried at 270°C for 5 h. It was then powdered, sieved, and the fraction between 200–400 mesh was collected.

Hydrous tin (IV) oxide (H-SnO_2) was prepared (17) by the reaction of high purity tin foil with hot 35% W/W HNO_3. The precipitate obtained was insoluble in dilute solutions of H_2SO_4 and HCl, a property typical of the material called β-stannic acid. This precipitate was filtered and washed thoroughly with distilled water until the pH of the washings was about 5–6. The product was then air dried at 30°C to constant weight.

Hydrous cerium oxide (H-CeO_2) was prepared (18) by the addition of 1 M of sodium hydroxide to a solution of cerium sulfate; an amber crystalline material was obtained.

Lead fine granular (E, Merck) particle size about 0.1–0.3 mm.

The radiotracer ^{187}W was prepared by neutron activation of WO_3 in the Pakistan Research Reactor–I. The irradiated material was dissolved in conc NH_4OH, evaporated to dryness, and finally taken in distilled water (pH ~7). Carrier free ^{188}Re as Na $^{188}ReO_4$ was eluted with 0.9% saline from an alumina-based $^{188}W \rightarrow {}^{188}Re$ generator system supplied by MAP Finland.

Distribution coefficients [K_d] were measured by means of a batch method using ^{187}W and ^{188}Re as radiotracers at room temperature. A 0.1 g exchanger was added to 6 ml solution containing the tracers. In all experiments, the initial W(VI)concentrations were 0.264 mg/ml, whereas the $^{188}Re(VII)$ concentrations were kept ~70 μci/ml in 0.004 M NaCl. The pH of the solutions was adjusted to the desired value by adding hydrochloric acid or sodium hydroxide.

After 1 h of continuous agitation, the solutions were centrifuged and separated. The activities were measured by means of a well-type counter. The distribution coefficients were calculated by using the following expression.

$$K_d = \frac{I_o - I_e}{I_e} \times \frac{V}{W}$$

where:

I_o = net counting rate of the initial solution
I_e = net counting rate of the solution after 1 h equilibration
V = volume of the solution [ml]
W = weight of exchanger [g]

Separation factor (α) was calculated by the expression $\frac{K_d,W}{K_d,\mathrm{Re}}$.

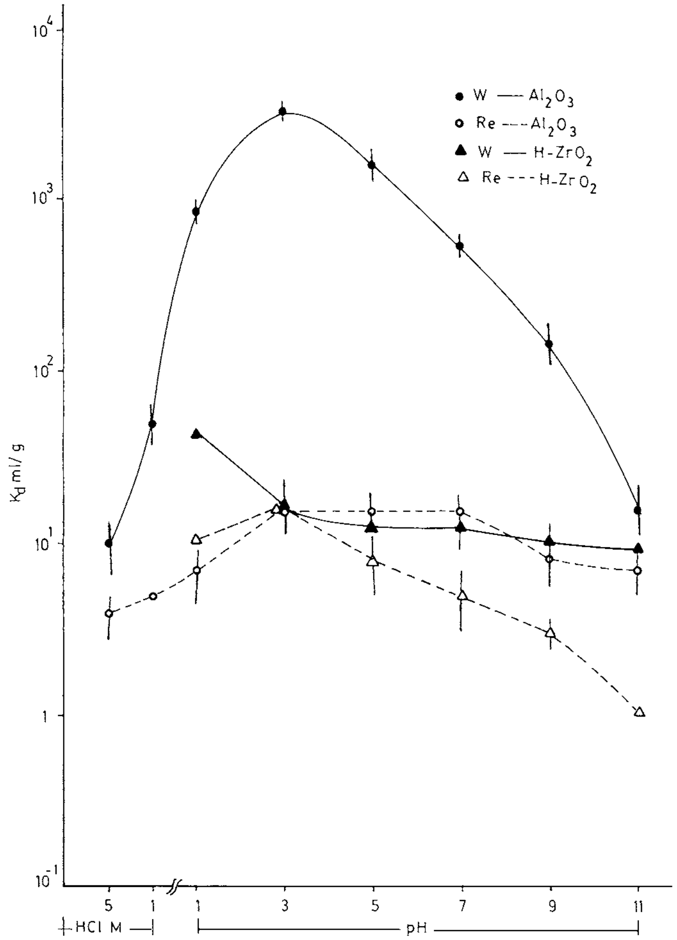


Figure 1. Sorption of W and Re on Al_2O_3 and hydrous ZrO_2 (HZO) (all values represent the average of four measurements ± SD whose range is displaced by error bars where applicable).

RESULTS AND DISCUSSION

The distribution coefficients of *W* and Re as a function of 5 and 1 molar HCl/HNO$_3$ concentrations and of pH on various ion exchangers are given in Figures 1 through 6. Tungsten is known to exist as various species in aqueous solutions. The ratio of species depends on the pH and *W*. In basic solutions, normal tungstates predominate. As the pH is lowered, cationic species WO$_2^{+2}$, WO$_2$OH$^+$,

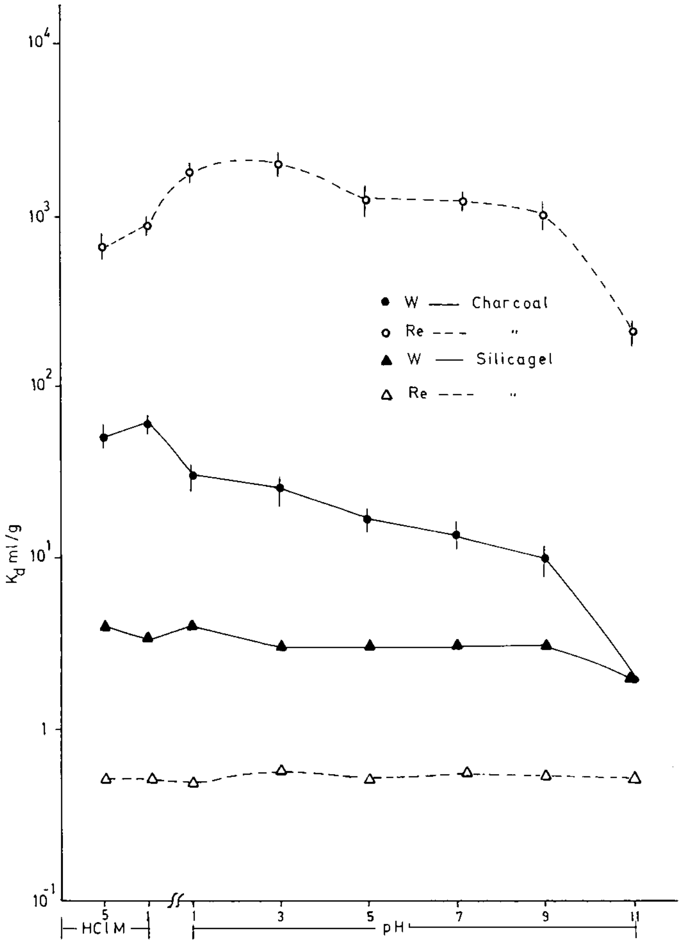
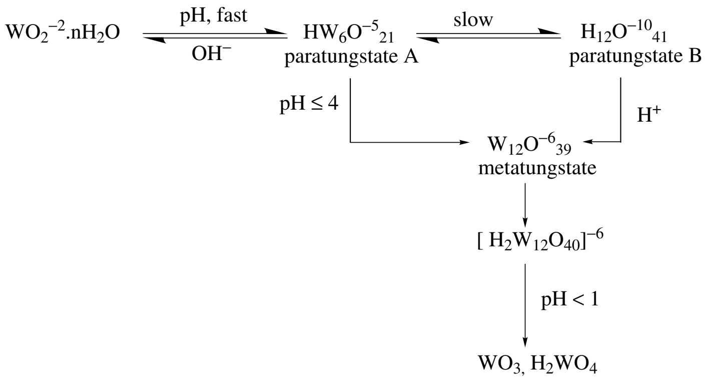


Figure 2. Sorption of *W* and Re on charcoal and silica-gel (all values represent the average of four measurements ± SD whose range is displaced by error bars where applicable).

and so forth appear in dilute solutions. Polyanion form as *W* is increased (18).



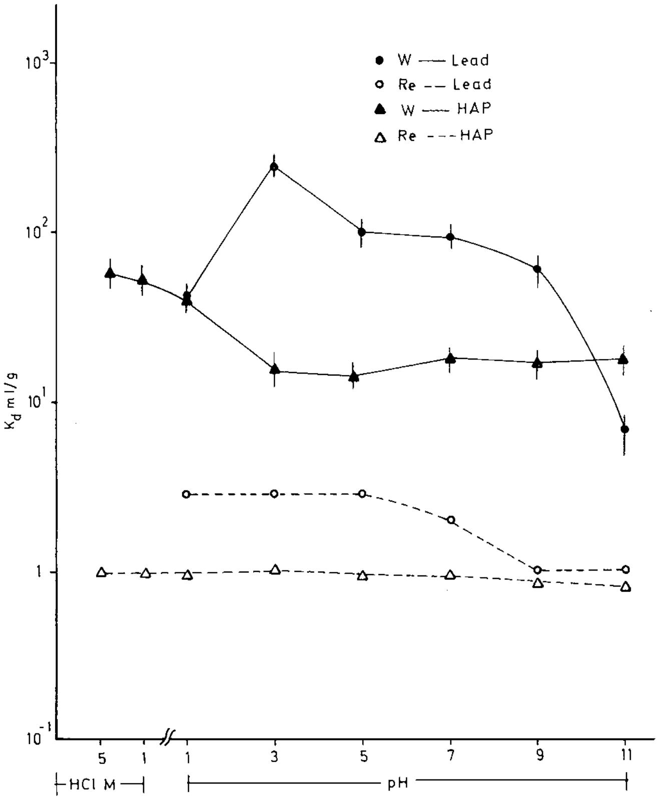


Figure 3. Sorption of *W* and Re on lead (Pb) and hydrated antimony pentoxide (HAP) (all values represent the average of four measurements ± SD whose range is displaced by error bars where applicable).

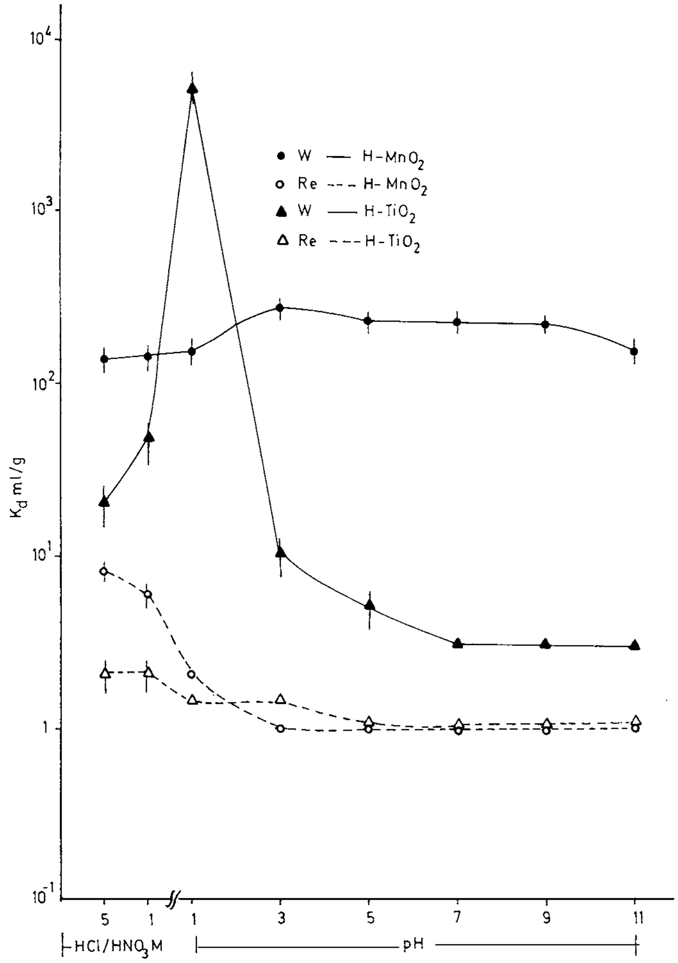


Figure 4. Sorption of *W* and Re on hydrous MnO$_2$ and hydrous TiO$_2$ (all values represent the average of four measurements ± SD whose range is displaced by error bars where applicable).

In aqueous solutions, Re occurs as the perrhenate ion ReO_4^-. Like pertechnetate, perrhenate (VII) is very stable in aqueous solution and are only a weak oxidant. Hexavalent tungsten exists, in weakly acidic or neutral solutions, predominantly in the anionic form, hence negligible adsorption was achieved on organic cation exchanger AG 50W-X12. Similar behavior was also noted for Re on organic cation exchanger (Fig. 6). Figure 6 also shows sorption of Re and *W* on an

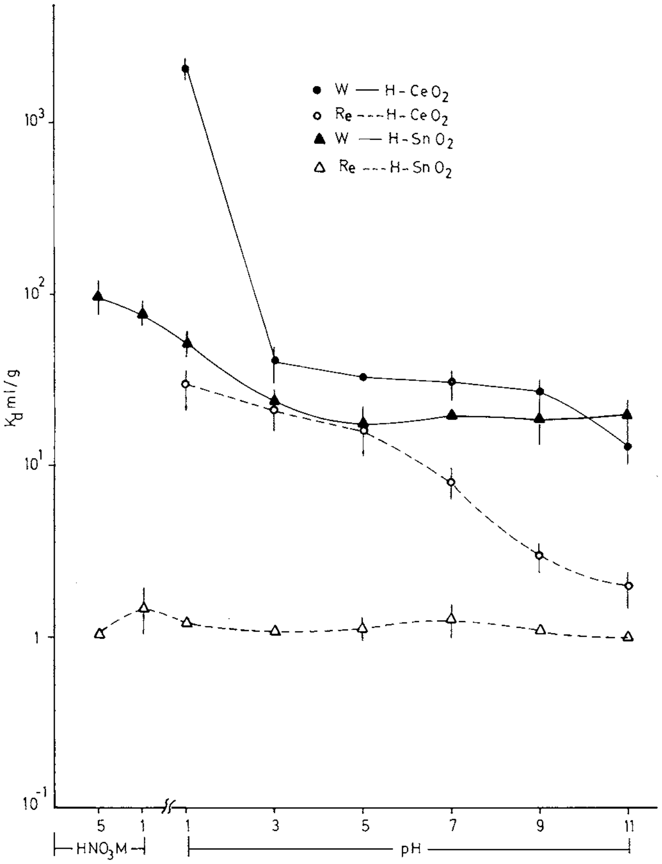


Figure 5. Sorption of *W* and Re on hydrated CeO_2 and SnO_2 (all values represent the average of four measurements ± SD whose range is displaced by error bars where applicable).

organic anion exchanger AG 1-X10. Re is more strongly adsorbed than the *W* on anion exchanger. Therefore, separation of Re and W was possible (19). However, this separation procedure could not be valuable for development of $^{188}W \rightarrow {}^{188}Re$ generator system, because W is first eluted, whereas for a column chromatographic generator system ^{188}W (parent) must stay on ion-exchange material, and repeated elution of ^{188}Re is mandatory. Various inorganic ion-exchange materials studied showed better adsorption for W, whereas Re was poorly adsorbed, except in the case of activated charcoal, where pattern of W and Re adsorption was found similar to anion exchanger (Fig. 2). Important distribution coefficients (K_d) values and W/Re separation factor for various ion-exchange materials are listed in Table 1.

In most of the cases ReO_4^- is poorly adsorbed, but W shows significant adsorption. The optimum pH range for W adsorption is between pH 1 and 3. Hydrated SnO_2 and hydrated CeO_2 (Fig. 5), hydrated MnO_2 and hydrated TiO_2 (Fig. 4), lead metal powder and HAP (Fig. 3), charcoal and silica gel (Fig. 2), and Al_2O_3 and hydrous ZrO_2 (Fig. 1) show very little affinity for ReO_4^-. Separation of Re from W on Al_2O_3, SnO_2, ZrO_2, HAP, silica gel, and lead metal may be achieved, and

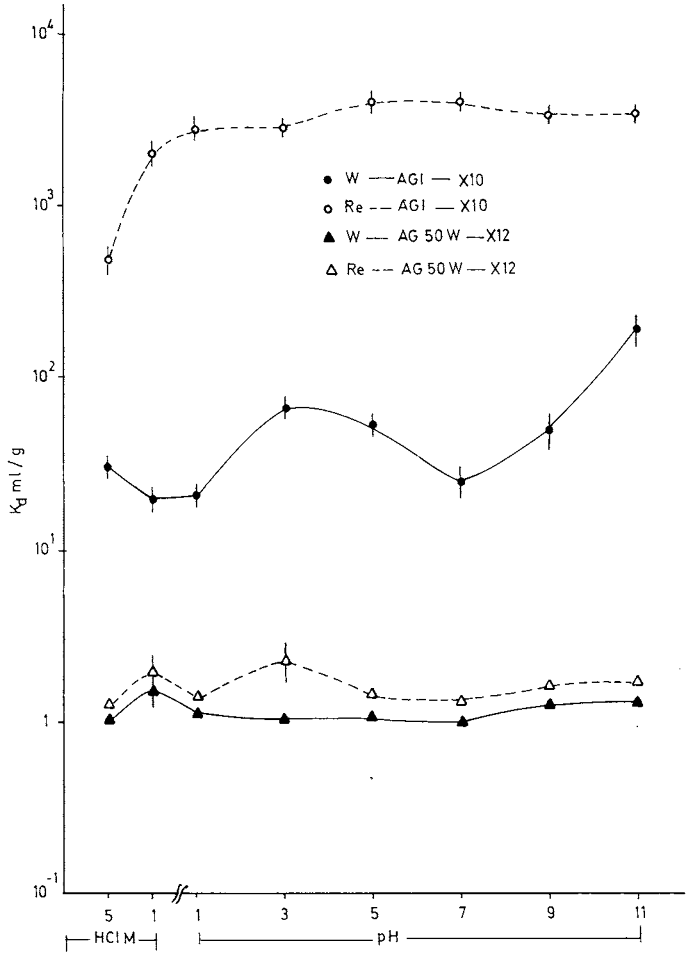


Figure 6. Sorption of *W* and Re on anion and cation exchangers (all values represent the average of four measurements ± SD whose range is displaced by error bars where applicable).

Table 1. Distribution Coefficients and W/Re Separation Factor (α) for Various Ion-Exchangers

Ion-Exchanger	pH	K_d W	K_d Re	$\alpha = \frac{K_d, W}{K_d, \mathrm{Re}}$
Al_2O_3	3	3414	15	227
Silica-gel	1	4	1	4
H-ZrO_2	1	43	10	43
Charcoal	3	26	2162	0.012
Lead (Pb)	3	241	3	80
HAP	1	40	1	40
H-MnO_2	3	280	1	280
H-TiO_2	1	5000	1.5	3333
H-CeO_2	1	2190	30	73
H-SnO_2	1	52	1	52
AG 1-X10	3	64	2700	0.0237
AG 50W-X12	1	1	1	1

these adsorbents can be successfully utilized as column matrix for construction of ^{188}W–^{188}Re generator system. It is obvious from the distribution coefficient (K_d) values that the capacity of W increases in the order silica-gel < charcoal < HAP <H-ZrO_2 < H-SnO_2 < AG I-X10 < Pb < H-MnO_2 < H-CeO_2 < Al_2O_3 < H-TiO_2. The highest distribution coefficient obtained on H-TiO_2 for W may be due to precipitation of WO_3. Hydrous titanium oxide used had an amphoteric and monofunctional character. At pH 1 K_d value reaches a maximum, whereas from 3 pH to 11 pH K_d values were not significant. As oxoanions are easy to hydrolyze at this pH, formation of pseudocolloids cannot be ruled out. Complexation of titanium ions on the surface with some polymeric variety of WO_3, is also possible. The experimental data demonstrated that Al_2O_3 has the best sorption properties for W. This oxide is known as an amphoteric ion exchanger with properties that change as a function of pH. The adsorption of tungstate ions onto alumina is strongly affected by pH due to changes in the chemical structure of the tungstate ion as described in the beginning of this section. The surface electrical charge of alumina is also strongly affected by pH changes. It is well known that alumina is positively charged in an acidic medium and can adsorb the negative charged tungstate ion. However in the region of neutral to basic pH, the surface electrical charge is neutral or negative, and therefore the K_d values are low in these regions.

Gel generators based on Zr, Zn, Ti, Ni, Mn, Co, and Pb tungstates (13,20) are prepared as potential supports for the development of ^{188}Re radiopharmaceuticals. However, the ^{188}W breakthrough is rather high (0.01%). Tandem columns with adsorbents like Al_2O_3, H-ZrO_2, H-CeO_2, Pb powder, H-MnO_2, and H-SnO_2 may play an important role in the reduction of the ^{188}W breakthrough in the final eluate (ReO_4^-).

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