Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.yu • www.shd.org.yu/JSCS
*J. Serb. Chem. Soc.* 73 (3) 333–339 (2008) UDC 546.719+66–914:541.183.1:546.33'131:66.049.2
*JSCS–3715* *Original scientific paper*

# Concentration of rhenium from dilute sodium chloride solutions

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(Received 24 May 2007)

*Abstract*: The conditions for the desorption of rhenium from the anion exchange resin Dowex 1-x8 by $HNO_3$, HCl, $H_2SO_4$ and NaOH were determined. The solution ($5.0\times10^{-3}$ mol $dm^{-3}$ Re in 0.15 mol $dm^{-3}$ NaCl) was passed through a column containing 0.10 g of the resin. The total sorbed amount of rhenium was 0.20 g/g of the resin. It was then eluted by the corresponding eluent in the concentration range up to about 3.0 mol $dm^{-3}$. The highest elution efficiency and the most favourable elution profile were found with 3.0 mol $dm^{-3}$ $HNO_3$. Over 77 % of the sorbed rhenium was found in the first 5 ml of the eluate. Practically all the rhenium was recovered with 20 ml of the acid. Under the given experimental conditions, HCl and $H_2SO_4$ were less favourable while NaOH was not applicable, due to very low efficiency of rhenium elution.

*Keywords*: ion exchange; concentration; rhenium; elution efficiency; elution profile.

## INTRODUCTION

Low concentrations of elements often restrict their intended use. The recovery of a given element from very dilute solutions is often not simple. For routine practice, the procedure should preferably be simple, rapid and effective. There are reports in the literature describing several approaches to solve this problem. One of the most promising is based on ion exchange. The dilute solution is passed through a column containing either an inorganic or organic ion exchanger onto which the desired element is firmly sorbed.[1,2] Then, it is recovered in a much higher concentration by elution from the resin with an as small as possible volume of an appropriate eluent. The efficacy is determined by the elution efficiency, *i.e.*, by the ratio of the desorbed element in the first fractions of the eluate and by the elution profile representing the total volume of the eluent required to desorb practically the whole quantity of the element from the resin.

Such concentration procedures find wide application. They are also used in radiochemistry to achieve, for example, a high radioactive concentration of a given

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doi: 10.2298/JSC0803333L

radioisotope necessary for the preparation and the application of radiopharmaceuticals.[3,4]

The procedure under examination is based on the anion exchange resin Dowex 1-x8, onto which rhenium, in the form of perrhenate anions, was sorbed. The paper presents the results of the determination of the conditions of its effective desorption using mineral acids, *i.e.*, $HNO_3$, HCl and $H_2SO_4$, and sodium hydroxide. The determinations of rhenium elution profiles and of the total elution volume in dependence on the concentration of the eluents, are given.

The results of these experiments find application in the development and improvement of procedures for the production of concentrated solutions of the radioisotope $^{188}Re$, the physical properties of which are suitable for employment in therapeutic nuclear medicine.[3,5,6]

## EXPERIMENTAL

### *Reagents*

Potassium perrhenate ($KReO_4$, p.a., Aldrich) and the resin Dowex 1-x8, 100–200 mesh (Aldrich) were commercially purchased.

### *Chemical analyses*

The content of rhenium in the solutions was determined by direct current argon arc plasma atomic emission spectroscopy (DCP–AES) with an aerosol supply. The procedure was described in earlier papers.[6-8]

The experiments, repeated twice, were performed at room temperature.

### *Experiments*

The experiments were performed in a glass column (5.5 mm I.D., 40 mm length) containing 0.1 g of Dowex 1-x8. The bed height, $l$, was 0.69 cm. A freshly prepared Re solution containing $5.0\times10^{-3}$ mol dm$^{-3}$ in 0.15 mol dm$^{-3}$ NaCl was passed through the column. The total amount of sorbed rhenium was 0.20 g/g of resin. The flow rate was 3.0 ml min$^{-1}$.

The elution of rhenium was performed using various concentrations of $HNO_3$ (0.16, 0.9, 1.6, 3.0, 6.0 and 7.2 mol dm$^{-3}$), HCl (0.16, 1.6 and 3.0 mol dm$^{-3}$), $H_2SO_4$ (0.08, 0.16, 0.8, 1.5 and 3.0 mol dm$^{-3}$) and NaOH (0.16, 1.6 and 3.0 mol dm$^{-3}$).

The volume of the effluent solution was 5.0 ml. The flow rate (3.0 ml min$^{-1}$) was kept constant using a Masterflex C/L pump (Cole Palmer Instrument Company).

Total experimental error is up to 1 %.

## RESULTS AND DISCUSSION

The main residence or contact time ($\tau_c$) between the solution and the resin can be calculated by:[9]

$$\tau_c = \varepsilon\, l/u \qquad (1)$$

where: $\varepsilon$ is the extra particle bed porosity or void fraction of the sorbent bed (for the resin, the calculated value of $\varepsilon$ was $\approx 0.33$) and $u$ is the linear or interstitial velocity (m s$^{-1}$).

For a value of $u$ of 12.5 cm min$^{-1}$ (*i.e.*, a flow rate of 3.0 ml min$^{-1}$), the calculated contact time $\tau_c$ is 1.1 s.

It can be seen that the contact time between the solution and the resin is very short in comparison with the value between the solution and alumina, which was found to be about ten seconds.[6]

The calculated theoretical sorption capacities of the resin Dowex 1-x8 (100––200 mesh) for the corresponding anions are given in Table I. In practice, the values are about 50 % lower than those calculated.

TABLE I. The theoretical sorption capacities of the resin Dowex 1-x8 (100–200 mesh) for the corresponding anions

| Anion | Theoretical capacity, g/g of the resin |
|---|---|
| $ReO_4^-$ | 0.85 |
| $NO_3^-$ | 0.21 |
| $Cl^-$ | 0.12 |
| $SO_4^{2-}$ | 0.16 |
| $OH^-$ | 0.06 |

Experimentally, the dependence of the elution efficiency of rhenium from the resin on the nature and the concentration of the influent solution were examined. The elution profiles of Re, *i.e.*, the ratio of the total sorbed rhenium found in the first 5.0 ml of the eluate and in the total volume of the eluate (20 ml) was determined for the different concentrations of the chosen eluents. The results obtained with nitric acid in the concentration range of 0.16–7.2 mol $dm^{-3}$ are given in Table II.

TABLE II. The dependence of the elution efficiency of rhenium from Dowex 1-x8 on the concentration of the eluent $HNO_3$

| Sample No. | $V$ / ml | Eluted rhenium, % | | | | | |
|---|---|---|---|---|---|---|---|
| | | $c_M$ ($HNO_3$) / mol $dm^{-3}$ | | | | | |
| | | 0.16 | 0.9 | 1.6 | 3.0 | 6.0 | 7.2 |
| 1 | 5.0 | 5.6 | 55.4 | 65.7 | 77.2 | 63.2 | 66.4 |
| 2 | 5.0 | 12.2 | 24.6 | 20.9 | 15.9 | 20.7 | 21.5 |
| 3 | 5.0 | 12.6 | 10.4 | 9.2 | 5.7 | 10.1 | 4.9 |
| 4 | 5.0 | 11.8 | 5.3 | 4.5 | 2.1 | 5.2 | 2.3 |
| Total | 20 | 42.2 | 95.7 | 100.3 | 100.9 | 99.2 | 95.1 |

From the results presented in Table II, it can be seen that the best results are obtained when the rhenium was eluted by 3.0 mol $dm^{-3}$ $HNO_3$. In this case, the highest amount of rhenium was desorbed and found in both the first 5.0 ml and in the total volume of the eluate (20 ml).

The effect of the concentration of $HNO_3$ on the elution efficiency of rhenium is presented in Fig. 1, from which it can be seen that the efficiency first rises, reaches the highest levels at about 3.0 mol $dm^{-3}$ $HNO_3$ and then decreases with the further increase in the concentration of the acid.

The results obtained with HCl, $H_2SO_4$ and NaOH are given in Tables III–V.

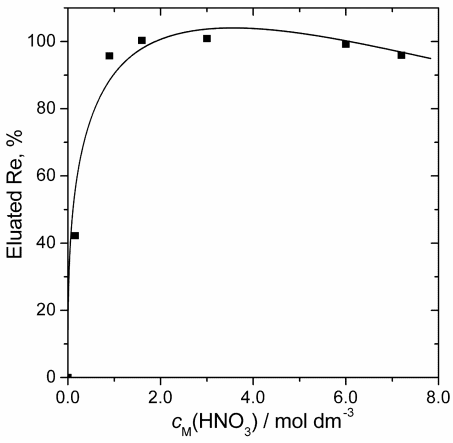


Fig. 1. The dependence of the efficiency of rhenium elution on the concentration of the eluent $HNO_3$.

TABLE III. The dependence of the elution efficiency of rhenium from Dowex 1-x8 on the concentration of the eluent HCl

| Sample No. | $V$ / ml | Eluted rhenium, % | | |
|---|---|---|---|---|
| | | $c_M$ (HCl) / mol dm$^{-3}$ | | |
| | | 0.16 | 1.6 | 3.0 |
| 1 | 5 | 0.5 | 12.6 | 34.0 |
| 2 | 5 | 1.6 | 12.2 | 19.3 |
| 3 | 5 | 3.0 | 8.7 | 10.7 |
| 4 | 5 | 3.9 | 6.4 | 7.1 |
| Total | 20 | 9.0 | 39.9 | 71.1 |

According to the data given in Tables II–V, it can be concluded that both the elution efficiency and the profile depend on the nature and the concentration of the eluent. The most favourable results were obtained with 3.0 mol dm$^{-3}$ $HNO_3$. In this case, the highest amount of rhenium was found in the first 5.0 ml of the eluate. The total sorbed rhenium was recovered with 20 ml of the eluent. The shape of the dependence of the elution efficiency on the concentration of nitric acid is shown in Fig. 1.

TABLE IV. The dependence of the elution efficiency of rhenium from Dowex 1-x8 on the concentration of the eluent $H_2SO_4$

| Sample No. | $V$ / ml | Eluted rhenium, % | | | | | |
|---|---|---|---|---|---|---|---|
| | | $c_M$ ($H_2SO_4$) / mol dm$^{-3}$ | | | | | |
| | | 0.08 | 0.16 | 0.80 | 1.5 | 1.6 | 3.0 |
| 1 | 5 | 0.5 | 1.7 | 12.2 | 21.4 | 22.6 | 19.4 |
| 2 | 5 | 1.5 | 3.0 | 14.4 | 14.7 | 15.2 | 13.3 |
| 3 | 5 | 2.4 | 3.8 | 11.5 | 9.6 | 10.3 | 9.4 |
| 4 | 5 | 3.0 | 4.1 | 9.2 | 7.7 | 8.0 | 6.9 |
| Total | 20 | 7.4 | 12.6 | 44.3 | 53.4 | 56.1 | 49.0 |

For the other employed eluents, except for HCl, the pattern of the dependence of the efficiency of rhenium elution on concentration was the same as that

shown in Fig. 1. The concentration of 3.0 mol dm$^{-3}$ HCl was found to be too low to reach the maximal elution efficiency. However, higher concentrations of the acid would be very unsuitable for further handling.

TABLE V. The dependence of the elution efficiency of rhenium from Dowex 1-x8 on the concentration of the eluent NaOH

| Sample No. | $V$ / ml | Eluted rhenium, % | | |
|---|---|---|---|---|
| | | $c_M$ (NaOH) / mol dm$^{-3}$ | | |
| | | 0.16 | 1.6 | 3.0 |
| 1 | 5 | 0.24 | 0.64 | 0.25 |
| 2 | 5 | 0.11 | 0.53 | 0.11 |
| 3 | 5 | 0.09 | 0.55 | 0.11 |
| 4 | 5 | 0.09 | 0.59 | 0.14 |
| Total | 20 | 0.53 | 2.31 | 0.61 |

In the case of NaOH, the elution efficiency of rhenium was very low. Hence, this eluent can be neglected in the further considerations.

The elution efficiencies of rhenium when 20 ml of 3.0 mol dm$^{-3}$ $HNO_3$, HCl and $H_2SO_4$, respectively, were passed through the column at a flow rate of 3.0 ml min$^{-1}$ are presented in Table VI.

TABLE VI. Elution efficiency of rhenium when 20 ml of 3.0 mol dm$^{-3}$ $HNO_3$, HCl and $H_2SO_4$ were employed as the eluents

| Eluent | $c_M$ / mol dm$^{-3}$ | Eluted Re, % |
|---|---|---|
| $HNO_3$ | 3.0 | 100.9 |
| HCl | 3.0 | 71.1 |
| $H_2SO_4$ | 3.0 | 49.0 |
| $H_2SO_4$ | 1.5 | 53.4 |

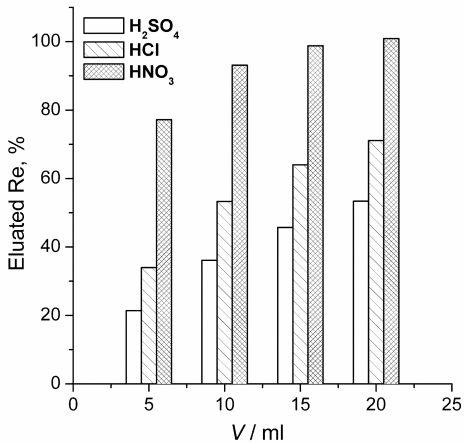


Fig. 2. Elution efficiency of rhenium in dependence on the volume of $HNO_3$, HCl and $H_2SO_4$.

By comparing the results obtained with acids of the same concentration, it can be seen that the highest elution efficiency was obtained when nitric acid was the eluent. The anions are bound on the resin in the following order: $NO_3^- > Cl^- > SO_4^{2-}$.

The same conclusions were obtained when the other concentrations of the acids, given in Tables II–V, are compared. In all cases, the highest elution yield of rhenium was obtained with nitric acid.

The dependences of the elution efficiency of rhenium on the elution volume of the acid eluents are presented in Fig. 2, from which it can be seen that the most favourable elution profile was obtained with nitric acid. Much higher volumes of the other eluents were required for the recovery of rhenium.

## CONCLUSIONS

The results presented in this paper showed that perrhenate anions sorbed on Dowex 1-x8 can be desorbed by the mineral acids $HNO_3$, HCl and $H_2SO_4$. The experiments were performed with concentrations of the eluent up to 3.0 mol $dm^{-3}$. The total elution volume of the corresponding eluate was 20 ml. In the examined range of concentrations, the highest efficiency of rhenium elution and the most favourable elution profile were obtained when using 3.0 mol $dm^{-3}$ $HNO_3$. In this case, practically all the sorbed rhenium was eluted in 20 ml of the acid. The elution yields were lower if HCl or $H_2SO_4$ of the same concentrations were used. In addition, the elution profiles were less favourable. The results showed that NaOH, under the given experimental conditions, was not useful for the intended purpose due to very low efficiency of rhenium elution.

Thus, the applicability of the proposed concept of concentration based on the sorption of rhenium from dilute solutions on an anion exchanger and its subsequent elution by acid was confirmed. However, further investigations are required before its introduction into routine practice.

*Acknowledgements.* This work was financially supported by the Ministry of Science of the Republic of Serbia, under Project No.142004B.

## ИЗВОД

## КОНЦЕНТРИСАЊЕ РЕНИЈУМА ИЗ РАЗБЛАЖЕНИХ РАСТВОРА НАТРИЈУМ-ХЛОРИДА

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Одређивани су услови десорпције ренијума са анјонске измењивачке смоле Dowex 1-x8 са $HNO_3$, HCl, $H_2SO_4$ и NaOH. Раствор ренијума ($5{,}0\times10^{-3}$ mol $dm^{-3}$ Re у 0,15 mol $dm^{-3}$ NaCl) је пропуштан кроз колону са 0,10 g смоле. Укупна сорбована количина ренијума била је 0,20 g по граму смоле. Ренијум је затим елуиран одговарајућим елуентом у опсегу концентрација до 3,0 mol $dm^{-3}$. Највећа ефикасност елуирања и најповољнији профил елуирања добијени су са $HNO_3$ концентрације 3,0 mol $dm^{-3}$. У првих 5 ml елуата налази се преко 77 % сорбованог ренијума. Практично сва количина се елуира са 20 ml киселине. Под датим експерименталним условима, примена HCl и $H_2SO_4$ је мање повољна док NaOH није примењив због врло ниске ефикасности елуирања.

(Примљено 24. маја 2007)

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