

RADIOCHEMICAL SEPARATION OF RHENIUM(VII) FROM TUNGSTEN(VI)

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The absorption of rhenium(VII) and tungsten(VI) ions on Al_2O_3 from HCl , HClO_4 , HNO_3 , H_2SO_4 , H_3PO_4 , NaOH , NH_4OH , NaCl , NaF , and Na-tartrate solutions by batch equilibration, as well as by passage through a chromatographic column, has been studied. The results show that rhenium(VII) can be effectively separated from tungsten(VI) using any of the acid or salt solutions investigated. The experimental data allowed to develop a simple procedure for the radiochemical separation of rhenium isotopes from an irradiated WO_3 sample.

Introduction

Irradiation of natural tungsten with thermal or epithermal neutrons gives several radioactive isotopes of tungsten and rhenium. As shown in the activation scheme given by GROSSE-RUYKEN and DÖGE,¹ the principal activities are due to ^{187}W , ^{185}W and ^{188}W , while ^{186}Re and ^{188}Re are the products of secondary reactions. Other stable tungsten isotopes give no interesting daughter nuclides in activation.

For the isolation of the rhenium isotopes from irradiated tungsten, GROSSE-RUYKEN and DÖGE¹ applied a solvent extraction procedure with pyridine, which had been earlier reported by GOISHI and LIBBY.² LEWIS and ELDRIDGE³ 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. HALDAR and WIIG⁴ separated rhenium, produced by the bombardment of tungsten with protons, with a solvent extraction procedure followed by the precipitation of rhenium as tetraphenylarsonium perrhenate or rhenium sulfide.

As stated previously,¹ the isolation of rhenium activity from high tungsten activities is very difficult. The procedures involving the extraction of rhenium with pyridine^{1,2,4} give relatively low decontamination factors, so that additional purification of the sample is necessary. The procedures based on the adsorption of tungsten on hydrous zirconium oxide^{3,5} give rather low rhenium yields. In the present work a method is described which, in a simple way, ensures practically complete separation of the radioactivities in question, and makes possible the complete recovery of radiorhenium produced by irradiation of natural tungsten.



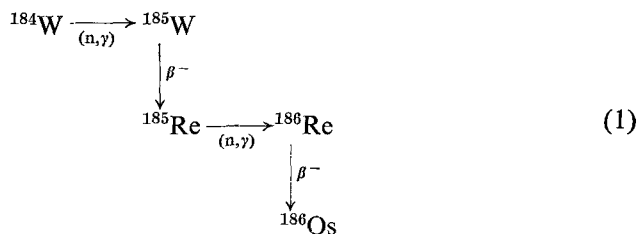
The Editorial Advisory Board and Publishers of the Journal of Radioanalytical Chemistry regret to announce that Professor LÁSZLÓ ERDEY, Regional Editor of the Journal, has suddenly died a few days after his sixtieth birthday.

LÁSZLÓ ERDEY, Member of the Hungarian Academy of Sciences, ordinary and honorary member of several chemical associations, member of the Analytical Committee of IUPAC, was Head of the Institute for General and Analytical Chemistry of the Technical University of Budapest from 1949 till the day of his death. He led extensive research work in the field of analytical chemistry, the results of which were published in several books and nearly 500 papers. His activity covered nearly all fields of analytical chemistry. In radioanalytical chemistry his interest mainly concerned the application of tracers, first of all in connection with radioactive precipitate exchange and isotope dilution methods.

He was one of the initiators in founding the Journal of Radioanalytical Chemistry. His contribution will be badly missed.

Irradiation data

When tungsten is irradiated with thermal neutrons, ^{186}Re and ^{188}Re are formed according to the following reactions:



and

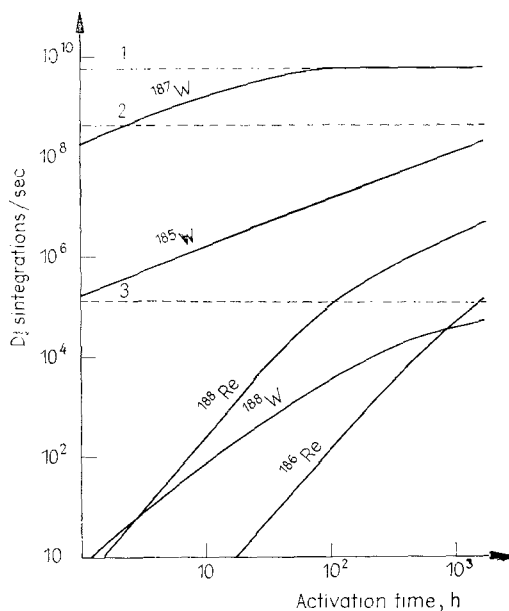
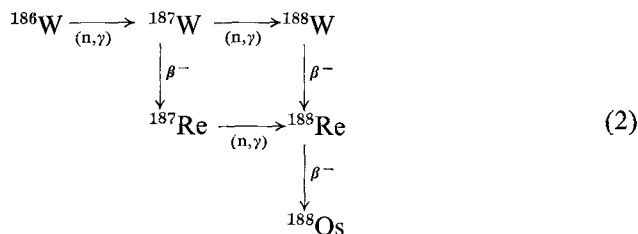


Fig. 1. Activities produced by irradiation of 100 mg WO_3 with a neutron flux of $2 \cdot 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ as a function of the activation time. --- saturated activities: 1 for ^{187}W and ^{188}Re , 2 for ^{185}W and ^{186}Re and 3 for ^{188}W . The necessary nuclear data were taken from the literature¹

In order to obtain the activities of ^{186}Re and ^{188}Re as a function of the number of ^{184}W and ^{186}W atoms, the neutron flux, and the time of irradiation, the system of differential equations pertinent to Reactions (1) and (2) were solved. The necessary nuclear data were taken from the literature.¹

Fig. 1 shows the activities of various nuclides in a sample of 100 mg of WO_3 after irradiation with a flux of $\Phi_0 = 2 \cdot 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$. It is obvious that the radorhenium activity is mainly due to ^{188}Re . The calculations showed that nearly 98% of the latter is formed by the reaction $^{187}\text{Re}(\text{n}, \gamma)^{188}\text{Re}$ and 2% via ^{188}W only. For short activation times (~ 10 hrs) the activity ratio $^{188}\text{Re}/^{186}\text{Re}$ is $2.2 \cdot 10^3$, and it decreases with time, being about 750 after 100 hrs, and 50 after 1000 hrs of activation.

These conclusions cannot be applied to the epithermal activation of tungsten, where the yield for the ^{188}Re formation from ^{188}W is higher, as it was shown by LEWIS and ELDRIDGE³ who determined the effective resonance integrals of the $^{186}\text{W}(\text{n}, \gamma)^{187}\text{W}$ and $^{187}\text{W}(\text{n}, \gamma)^{188}\text{W}$ reactions.

Experimental

Preparation of aluminium oxide

Aluminium oxide used in this work was prepared by equilibrating commercial Al_2O_3 (aluminium oxide, Merck, neutral, act. I) with hot hydrochloric acid (1 : 1). The resulting oxide was washed thoroughly with distilled water, dried at 105°C for several hours and then screened with a DIN 1171 sieve. The fraction ranging between 2500 and 4900 mesh/cm² was used for both the batch experiments and column runs. Although the particle size was very small, all column experiments were carried out without suction or pressure. When 1 g of Al_2O_3 was shaken with 10 ml of distilled water, the resulting pH was 5.38. The apparent density was 0.97 g/cm^3 , while the picnometric one, determined in water, was 2.78 g/cm^3 . The product is partially hydrated and loses water when heated. Thermogravimetric analysis indicated continuous loss of water: 2.4% at 200°C and 1.2% between 200°C and 800°C .

Preparation of tracers

^{186}Re and ^{187}W were prepared by neutron activation of specpure KReO_4 and WO_3 (Johnson and Matthey). After irradiation, KReO_4 was dissolved in water and an appropriate aliquot was used for labelling the solution. The irradiated WO_3 was dissolved in hot 1M NaOH and then neutralized with conc. hydrofluoric acid. In all experiments, except in the cases of breakthrough capacity determinations, the initial W(VI) concentrations were lower than $1 \mu\text{g/ml}$.

Table 1
Distribution coefficients (D_W , D_{Re}) and distribution coefficient quotients ($\alpha = \frac{D_W}{D_{Re}}$) for different systems

System	Coefficient	Normality, N						
		$1 \cdot 10^{-2}$	$3 \cdot 10^{-2}$	$1 \cdot 10^{-1}$	$3 \cdot 10^{-1}$	1.0	2.0	4.0
HCl	D_W	250	340	770	895	670	170	37
	D_{Re}	20	10	3	1.2	0.1	< 0.1	< 0.1
	α	12.7	34	256.6	745	6700	> 1700	> 370
HNO ₃	D_W	485	265	300	740	195	60	25
	D_{Re}	25	10	5	0.8	0.25	< 0.1	< 0.1
	α	19.4	26.5	60	925	780	> 600	> 250
H ₂ SO ₄	D_W	775	1465	1685	620	100	30	10
	D_{Re}	20	4	1	0.4	< 0.1	< 0.1	< 0.1
	α	38.7	366	1685	1550	> 1000	> 300	> 100
H ₃ PO ₄	D_W	220	200	390	1340	905	265	50
	D_{Re}	35	10	2	0.7	< 0.1	< 0.1	< 0.1
	α	6.3	20	195	1918	> 9050	> 2650	> 500
HClO ₄	D_W	210	135	330	580	985	395	122
	D_{Re}	25	20	10	3	1	0.5	0.2
	α	8.4	6.7	33	193	985	790	610

NaOH	D_W	1965	3	0	0	0	0	0
	D_{Re}	10	0.3	0	0	0	0	0
	α	196.5	10	0	0	0	0	0
NH ₄ OH	D_W	1555	190	10	2	0.7	—	—
	D_{Re}	10	0.5	< 0.1	< 0.1	< 0.1	—	—
	α	155.5	380	> 100	> 20	> 7	—	—
NaCl	D_W	680	1255	2555	1855	1165	—	—
	D_{Re}	10	2	0.1	< 0.1	< 0.1	—	—
	α	68	612	$2.5 \cdot 10^4$	$> 1.85 \cdot 10^4$	$> 1.16 \cdot 10^4$	—	—

System	Coefficient	Normality, N							
		$1 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$3 \cdot 10^{-3}$	$4 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	$1.5 \cdot 10^{-2}$	
NaF	D_W	330	835	—	1950	—	3235	50	
	D_{Re}	45	30	—	15	—	0.5	0.1	
	α	7.3	27.8	—	130	—	6470	500	
Na ₂ C ₄ H ₄ O ₆	D_W	860	—	4805	4500	5209	6190	380	
	D_{Re}	40	—	20	12	10	1	< 0.1	
	α	21.5	—	240	375	520	6190	> 3800	

Determination of the distribution coefficient

Batch experiments were carried out by equilibrating 1 g of Al_2O_3 for 1 hr with 10 ml of labelled solution in a centrifuge tube. After equilibration and centrifugation, an aliquot of the supernatant was withdrawn and its radioactivity measured. The amount of the element bound on Al_2O_3 was calculated as the difference of the supernatant activity before and after equilibration. The results are presented in terms of the distribution coefficient D , defined by

$$D = \frac{(1-x)V}{xm}$$

where

- x — experimentally determined fraction of the element remaining in the solution
- $1-x$ — the fraction sorbed on Al_2O_3
- V — the volume of the aqueous phase, ml
- m — the amount of Al_2O_3 used, g.

Column experiments

The breakthrough capacities of Al_2O_3 for tungsten were determined for the studied acidic and salt solutions at concentrations exhibiting the optimum values of distribution coefficient quotients. For this purpose, the chosen solution containing from 5 μg to 500 μg of W(VI) and labelled with ^{187}W was passed through the column (10 mm diameter, 100 mm length; bed: 1 g of Al_2O_3) at a flow rate of 1 ml/min. In the elution experiments of radiorhenium this column was packed with 3.5 g of Al_2O_3 . The same acid and salt solutions as in the case of determination of the breakthrough capacity were used as eluents. After the sorption of 1 ml of the studied eluent labelled with ^{187}W and ^{186}Re , the radiorhenium was eluted by it at a rate of 1 ml/min. The course of elution was followed radiometrically. The volumes required to elute more than 98% of radiorhenium are given in Table 2.

Proposed procedure for the isolation of radiorhenium from irradiated WO_3 targets

The results suggest the following procedure for the isolation of $^{188,186}\text{Re}$ activity from an irradiated WO_3 sample: 100 mg of specpure WO_3 is sealed in a silica tube and irradiated for about 50 hrs with a thermal neutron flux of $2 \cdot 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$. The irradiated sample is dissolved in 1 ml of hot 1M sodium hydroxide, the excess of NaOH is neutralized with hydrofluoric acid, and the solution diluted with 0.1M NaCl to 50 ml. To remove radiorhenium, this solution is passed through an Al_2O_3 column (18 mm diameter, 170 mm length; bed: 30 g of Al_2O_3) at a flow rate of 1 ml/min.

Results

Table 1 presents the dependence of the distribution coefficients of Re(VII) and W(VI) on the concentrations of the various acids, bases and neutral salts in the starting solutions. The results clearly show that Al_2O_3 is a much better adsorbent for W(VI) than for Re(VII). In the concentration range investigated, the distribution coefficients of Re(VII) decrease, in all cases, with increasing concentration of the electrolyte in the initial solution. The same can be stated for W(VI) in alkaline solutions, whereas in acid and neutral solutions the distribution coefficients first increase, reach a maximum, and then decrease. An inspection

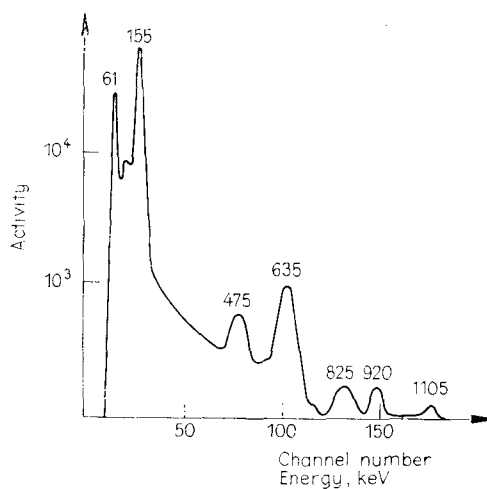


Fig. 2. γ -ray spectrum of the isolated rhenium activity

Table 2

Breakthrough capacities for W(VI) and elution volumes for Re(VII)

Solution normality, <i>N</i>	Breakthrough capacity, mg $\text{WO}_3/\text{g Al}_2\text{O}_3$	Elution volume, ml
1.0 HCl	0.19	15
0.3 HNO_3	3.28	15
0.1 H_2SO_4	0.50	10
1.0 HClO_4	0.25	20
0.3 H_3PO_4	2.52	20
0.1 NaCl	4.41	15
0.01 $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$	1.89	10
0.01 NaF	0.13	10

tion of the distribution coefficient quotients, α , in Table 1 shows that, except in alkaline solutions, the satisfactory separation of W(VI) from Re(VII) is feasible.

A survey of Table 2 leads to the conclusion that among the solutions studied 0.1M NaCl is the most suitable medium for the separation of rhenium from tungsten. As a result, for the isolation of $^{186,188}\text{Re}$ activity from an irradiated WO_3 sample, the procedure given in Experimental was developed with the decontamination factor of $^{187}\text{W} > 10^4$.

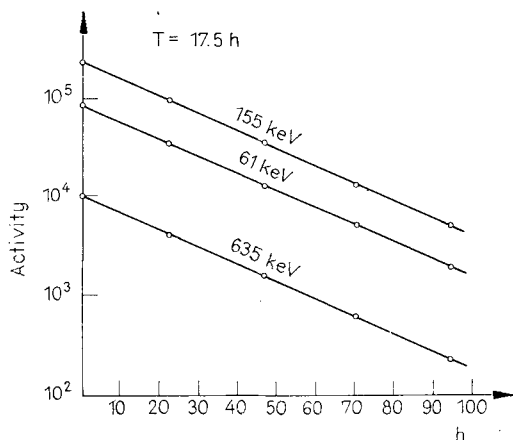


Fig. 3. Decay curves of separated rhenium

The efficiency of the separation procedure proposed is shown by the γ -spectrum of the eluate, presented in Fig. 2, which reveals the presence of peaks due to ^{188}Re only. The absence of peaks belonging to ^{186}Re is in agreement with Fig. 1, showing that the ratio of disintegration rates of $^{186}\text{Re}/^{188}\text{Re}$ is lower than 0.1%, which is insufficient for ^{186}Re detection. The same applies to the decay curves of activities at photopeaks 61 keV (characteristic of the ^{188}Re X-ray peak), 155 and 635 keV presented in Fig. 3, which all exhibit slopes in accordance with the half-life of ^{188}Re .⁶

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References

1. H. GROSSE-RUYKEN, H. G. DÖGE, *Talanta*, 12 (1965) 73.
2. W. GOISHI, W. F. LIBBY, *J. Am. Chem. Soc.*, 74 (1952) 6019.
3. R. E. LEWIS, J. S. ELDRIDGE, *J. Nucl. Med.*, 7 (1966) 792.
4. B. C. HALDAR, E. O. WIIG, *Phys. Rev.*, 105 (1957) 1285.
5. V. J. PLOTNIKOV, V. Z. KOCHETKOV, *Zh. Analit. Khim.*, 21 (1966) 1260.
6. D. STROMINGER, J. M. HOLLANDER, G. T. SEABORG, *Rev. Mod. Phys.*, 30 (1958) 762.