Chemical Studies on Radioactive Indicators. XXIV. Separation of Rhenium from Technetium by the Distillation Method

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It has been considered that technetium has much resemblance in chemical properties to rhenium and the latter element has often been used as a carrier in the analysis of the former. An appropriate method is needed for the separation and the determination of technetium which is supposed to be present in natural ores or meteorites and also for the preparation of carrier-free rhenium or technetium produced by the bombardment of nuclear particles. Although several methods for separation, i. e., precipitation method(1), ion exchange method(2) and paper chromatography(3) have been proposed, it can not be said that any one of them is satisfactory in the analysis of the samples containing technetium and rhenium over a wide range of quantity.

The distillation of rhenium as Re_2O_7(4,5) has been a powerful method in the isolation from various elements other than technetium but the attempt to separate rhenium from technetium has not appeared yet.

In the previous paper(6), the author pointed out that the distillation of technetium from sulfuric acid is promoted by the addition of an oxidizing agent, such as nitric acid or potassium bichromate, and delayed by the addition of a reducing agent, such as hydroxylamine.

The resistance for the distillation of technetium in the presence of a reducing agent would be due to the formation of a lower oxidation state than +7. A similar experiment was performed on rhenium and it was found that reducing agent showed no effect on the distillation.

In this experiment, several kinds of gas were passed through the distilling flask as carrier and it was found that steam was the most effective on the separation of rhenium from technetium. The experiments were carried out with the solutions of carrier-free ^{95m}Tc, ^{97m}Tc, ^{183}Re and ^{184}Re in the presence or the absence of rhenium carrier.

The results were quite satisfactory as shown in Tables I and II.

Experimental

Reagents and Apparatus.—*Isotopes.*—^{95m}Tc(60d) and ^{97m}Tc(90d) were isolated as pertechnetate, from the proton-bombarded molybdenum target(6). ^{183}Re(71d) and ^{184}Re(50d) were isolated as perrhenate from the proton-bombarded tungsten target(7).

Stable Rhenium.—Metallic powder of rhenium was obtained from Yokozawa Chemicals Co. and was converted to perrhenate by fusing it with sodium hydroxide and sodium peroxide in a nickel crucible.

Distilling Apparatus. — A pyrex glass distilling apparatus shown in Fig. 1 was prepared. Junctions were connected without grease.

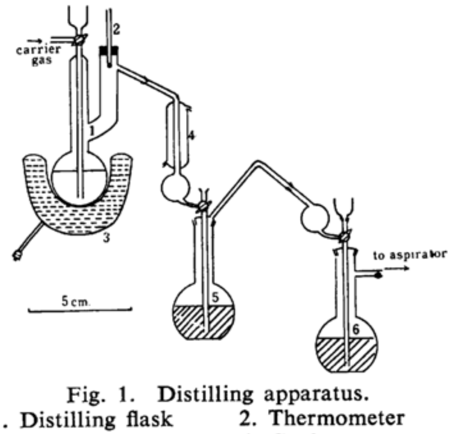

Fig. 1. Distilling apparatus.
1. Distilling flask 2. Thermometer
3. Mantle heater 4. Cooler
5. Receiver-1 (10 ml. of water)
6. Receiver-2 (20 ml of 4 N NaOH)

Counters.—A single channel γ-ray spectrometer (crystal: NaI(Tl), 1×1 inch) made by Kobe Kogyo Co., Ltd. and a G. M. counter (Tube: G. M. 132A, mica window 1.95 mg./cm^2) made by Metro Denki Co., Ltd. were used.

Procedure.—Six milliliters of the sample solution was taken in the distilling flask and heated with a mantle heater whose temperature was controlled with a transformer.

Carrier gas was conducted at the rate of 60

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1) C. Perrier and E. Segrè, *J. Chem. Phys.*, **5**, 712 (1937).
2) E. Jacobi, *Helv. Chim. Acta*, **61**, 2118 (1948).
3) M. Lederer, *Anal. Chim. Acta*, **12**, 146 (1955).
4) W. Geilmann and E. Weibke, *Z. anorg. u. allgem. Chem.*, **199**, 120 (1931).
5) W. Geilmann and H. Bode. *Z. anal. Chem.*, **130**, 323 (1950).
6) M. Ishibashi, T. Fujinaga and M. Koyama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 1260 (1960).
7) M. Ishibashi, T. Fujinaga and M. Koyama, ibid., **82**, 185 (1961).

bubbles per minute. Receivers were cooled with ice water, whenever necessary. Any adhering activity inside the cooler was washed out into the receiver with a small amount of water before the measurements of the activities of the distillate. All the solutions were brought to a known volume in a volumetric flask and an aliquot was taken in a 5 ml. glass counting dish and was mounted for the γ-ray measurement.

Results and Discussion

Effect of the Concentration of Sulfuric Acid.—Carrier-free rhenium was used in the experiments for testing the effect of the concentration of sulfuric acid on the distillation of rhenium. Rhenium was not distilled out from the pure water solution. On heating the sulfuric acid solution, the temperature remained at about 98~100°C during the distillation of water. After the water was distilled over, the temperature decreased once and again rose gradually to about 250°C, while sulfuric acid began to be distilled. The distilling temperature (250°C) was changeable depending on the heating and bubbling conditions.

In Fig. 2, the amounts of distilled rhenium are plotted against the amounts of distilled sulfuric acid. When 60% of the total amount of sulfuric acid was distilled, nearly 100% of rhenium was distilled out, irrespective of the initial concentration of sulfuric acid. The rate of distillation of rhenium was the greatest with 6 N sulfuric acid and the smallest with 30 N sulfuric acid. However, no quantitative distillation could be expected by the use of dilute sulfuric acid, because the volume of distilling solution became too small to dissolve the residual materials in the course of distillation.

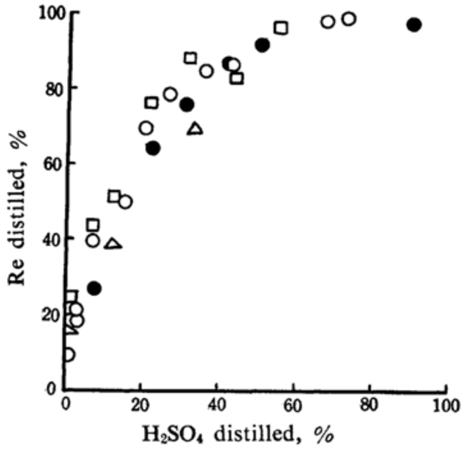

Fig. 2. Relationship between amount of Re distilled and that of H_2SO_4.
△ 6 N H_2SO_4 ○ 18 N H_2SO_4
□ 24 N H_2SO_4 ● 30 N H_2SO_4

Therefore, 18 N sulfuric acid was used in the following experiments.

Effects of Reducing Agent and Carrier Gas on the Distillation of Rhenium and Technetium.—In order to examine the effects of the atmosphere in the distilling flask on the distillation rate of rhenium and technetium, three kinds of gas, i. e., air, hydrogen and carbon dioxide, were bubbled respectively through the flask during the distillation.

Stannous chloride and hydroxylamine were used as the reducing agent, but the former

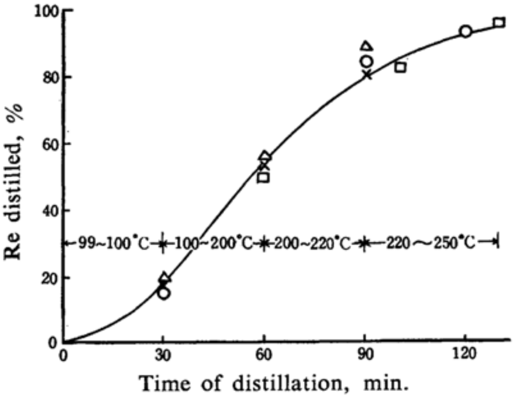

Fig. 3. Distillation rate of Re from 18 N H_2SO_4 in the presence or the absence of reducing agents.

	Reducing agent	Carrier gas
○	None	Air
□	〃	CO_2
×	10% $SnCl_2$ 1 ml.	〃
△	10% $NH_2OH \cdot HCl$ 1 ml.	〃

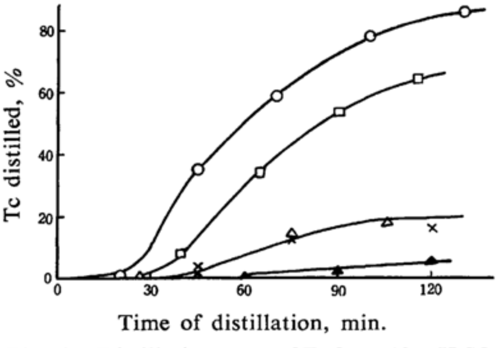

Fig. 4. Distillation rates of Tc from 18 N H_2SO_4 in the presence or the absence of reducing agents.

	Reducing agent	Carrier gas
○	None	Air
□	10% $NH_2OH \cdot HCl$ 0.5 ml.	〃
△	〃	CO_2
×	〃	H_2
▲	10% $NH_2OH \cdot HCl$ 2 ml.	CO_2

TABLE I. DISTILLATION RATES OF RHENIUM

Solution	Redistilled (%) at various times						
	20 min.		40 min.		60 min.		Spot tests of residual solution
	c.p.m.	%	c.p.m.	%	c.p.m.	%	
Carrier-free Re alone	3570	61.6	5540	95.6	5780	99.8	—
	3790	65.4	5250	90.5	5740	98.9	
Carrier-free Re+10% $NH_2OH\cdot HCl$ 2 ml.	3210	55.4	5170	89.2	5790	99.9	—
Re 1 mg.+ 10% $NH_2OH\cdot HCl$ 2 ml.	2450	42.2	5200	89.6	5780	99.7	None
	3090	53.2	5480	94.5	5790	99.8	None
Re 10 mg.+ 10% $NH_2OH\cdot HCl$ 2 ml.	890	15.4	5450	94.5	5740	99.0	$1\gamma>Re$
	2200	38.2	5220	90.7	5790	99.9	$1\gamma>Re$

* Carrier gas: steam, Total volume of solution to be distilled: 6 ml. of 18 N H_2SO_4, Radioactive Re added: 5800 c.p.m.

TABLE II. DISTILLATION RATES OF TECHNETIUM

Solution	Tc distilled (%) at various times									
	20 min.		40 min.		60 min.		80 min.		100 min.	
	c.p.m.	%	c.p.m.	%	c.p.m.	%	c.p.m.	%	c.p.m.	%
Tc alone	4470	12.4	704	18.6	765	20.2	795	21.0	—	—
	628	16.6	784	20.7	832	22.0	835	22.0		
Tc+10% $NH_2OH\cdot HCl$ 2 ml.	0	0	0	0	0	0	20	0.5	—	—
	0	0	0	0	0	0	10	0.3		
Tc+Re 10mg+ 10% $NH_2OH\cdot HCl$ 2 ml.	0	0	0	0	0	0	0	0	—	—
	0	0	0	0	0	0	0	0		
Tc+HNO_3 1 ml.	1470	38.8	2000	52.8	2020	53.0	3090	81.7	3500	92.4
	1360	35.0	2360	62.3	2380	63.0	3190	84.5	3350	88.6

* At the same condition as in the case of rhenium.
Tc added: 3800 c.p.m.

was partially distilled out. In Fig. 3, it can be seen that the distillation rate of rhenium from sulfuric acid is independent of the presence of hydroxylamine and bubbling gas. The fact that the addition of hydroxylamine had no effect on the distillation rate of rhenium shows that hydroxylamine can not reduce perrhenate[8].

In the case of technetium, the decrease in the distillation rate was distinctly observed by the addition of hydroxylamine, even when air was used as carrier gas.

In the same experiment, the bubbling of hydrogen or carbon dioxide caused a marked decrease in the distillation rate, especially in the period of the distillation of water, little technetium being found in the receiver.

The difference of the distillation rates between the use of air and that of carbon dioxide or hydrogen seems to be due to the difference of oxidizing ability against hydroxylamine. After the water was consumed in the flask, technetium gradually came to appear in the distillate. The increase in the amounts of hydroxylamine caused the decrease of the distillation rate of technetium.

Separation of Rhenium from Technetium.—In the foregoing method, as an appreciable amount of hydroxylamine is decomposed by heating with sulfuric acid solution, much hydroxylamine has to be added for the quantitative separation of rhenium from technetium.

To achieve smooth distillation, it is desirable to keep the amount of hydroxylamine as small as possible. Utilizing the fact that much rhenium but no technetium could be found in the distillate, the steam distillation method in the presence of hydroxylamine was examined.

Table I shows the distillation rates of rhenium obtained by steam distillation in the presence or the absence of hydroxylamine. It was found that by passing steam only at 100°C, little rhenium was distilled out, however, with gentle heating of the flask above 105°C, rhenium came to be distilled out with the steam.

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[8] S. Tribalat, *Ann. chim.*, **4**, 289 (1949).

After distillation for 60 min., more than 99% of the rhenium was recovered. In the case when the distillation was carried out with stable rhenium, a spot test for the rhenium⁹⁾ remaining in the flask proved to be less than 1γ of rhenium as shown in Table I.

The presence of hydroxylamine also had no effect on the distillation rate of rhenium in this method. In Table II, the distillation rates of technetium in the same condition as in the case of rhenium are shown. Distillation rates of technetium from 18 N sulfuric acid were smaller than that of rhenium even in the absence of hydroxylamine. In the presence of hydroxylamine no technetium appeared in the receivers, while most of the rhenium had been distilled off.

On the other hand, it was also observed that the presence of nitric acid promoted the distillation of technetium in the steam distillation. Therefore the separation of rhenium from technetium followed by the separation of technetium from other non-volatile materials by the distillation method could be attained by the proper use of hydroxylamine and nitric acid.

Summary

The separation of rhenium from technetium was investigated. Pertechnetate is reduced to non-volatile species by the use of hydroxylamine, but perrhenate is not reduced by such an agent. Rhenium is distilled out with steam from sulfuric acid medium and technetium remains in the solution containing hydroxylamine. Rhenium from carrier-free amounts up to 10 mg. can be separated quantitatively from technetium by this method.

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9) E. B. Sandell, "Colorimetric Determination of Traces of Metals", Interscience Publishers, New York (1959), p.754.