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Dynamic properties on ^{99}Mo adsorption and ^{99m}Tc elution with alumina columns

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Abstract. The Mo adsorption/^{99m}Tc elution properties of alumina used as Mo adsorbents are examined for the development of ^{99}Mo/^{99m}Tc generators using ^{99}Mo produced by the (n, γ) method. MoO_3 is irradiated by the Kyoto University Research Reactor (KUR). The alumina columns are filled with three types of alumina made from different raw materials. In this paper, elongated tubes are used as columns and the properties under Mo dynamic adsorption conditions on alumina are compared with those under static adsorption conditions. The results obtained suggest that the ^{99}Mo/^{99m}Tc ratio specified by the Minimum Requirements for Radiopharmaceuticals of Japan (MRRP) is greatly affected by the method of adsorbing Mo on alumina.

1. Introduction

Technetium-99m (^{99m}Tc) is most commonly used as a radiopharmaceutical. ^{99m}Tc is produced by the decay of molybdenum-99 (^{99}Mo). Currently, ^{99}Mo is mostly produced by the fission of uranium (generally called "(n, f) method"). From the viewpoint of uranium usage restrictions, such as nuclear non-proliferation and nuclear security, the target transition from High- to Low-Enriched Uranium (HEU to LEU) is progressing. However, the production of ^{99}Mo using the LEU targets also has drawbacks, including plutonium production and increased fission product waste.

Therefore, the production of ^{99}Mo by the activation method (generally called the "(n, γ) method") is attracting attention as an alternative to the (n, f) method. However, because the specific activity of ^{99}Mo produced by this method is lower than that of the (n, f) method, ^{99m}Tc needs to be concentrated. The medical ^{99}Mo/^{99m}Tc generator (hereinafter called "generator") is one of the devices that concentrates ^{99m}Tc. The development of a Mo adsorbent with high adsorption capacity is indispensable for the practical application of a generator using (n, γ)^{99}Mo. Alumina (Al_2O_3) is commonly used as a Mo adsorbent for generators. Therefore, the development of Alumina with a high Mo adsorption capacity is necessary. The previous study has developed alumina with a higher Mo adsorption capacity than existing

alumina. However, the ^{99m}Tc solution obtained by milking didn't meet the Minimum Requirements for Radiopharmaceuticals of Japan (hereinafter referred to as the "MRRP") requirements [1].

In this study, we focused on the method of adsorbing Mo to alumina in order to obtain ^{99m}Tc solutions that meets the requirements of the MRRP. The Mo adsorption/^{99m}Tc elution properties were examined under dynamic adsorption condition using MoO_3 irradiated in the Kyoto University Research Reactor (KUR). Elongated tubes were used as columns and the properties obtained under dynamic adsorption conditions were compared to those obtained under static adsorption conditions.

2. Experimental

2.1. Materials of Alumina

The raw material of alumina used is aluminum hydroxide and the crystalline phase of alumina produced depends on the crystalline phase of aluminum hydroxide (gibbsite, p-boehmite, bayerite, etc.) and the sintering temperature [2].

The Alumina specimens were prepared by the following procedure. The mixtures of 5 wt.% alumina sol, water and each aluminum hydroxide powder were extruded. The moldings were dried at 200-300 °C for the hour, ground and sorted by a 50-100 mesh sieve (opening: 150-300 μm). Finally, they were sintered at 300 °C for the hour. Now, the alumina specimens prepared from different aluminum hydroxide crystal phases (gibbsite, p-boehmite, bayerite) are referred to as D-201-300, V-V-300, and V-B-300, respectively. Additionally, commercial medical alumina (Medical Alumina) used in the current generator, with (n, f)^{99}Mo, was also prepared as a comparative specimen. Table 1 shows the basic properties of each Alumina specimen [3].

Table 1. The basic properties of Alumina specimens.

Specimens	Crystal structure	Specific surface (m^2/g)	Particle size(D_{50}) (μm)
D-201-300	χ-Al_2O_3 + Boehmite	311	283
V-V-300	p-Boehmite	270	285
V-B-300	η-Al_2O_3 + Boehmite	417	238
Medical Alumina	χ-Al_2O_3 + γ-Al_2O_3	116	103

2.2. Neutron irradiation of MoO_3

The MoO_3 pellets were made by mixing MoO_3 powder with 2 wt.% camphor and ethanol, and molding into pellets with a uniaxial press. The moldings were sintered at 650 °C. The MoO_3 pellets were roughly crushed after they were sufficiently dried, and about 1.5 g of MoO_3 pieces were used for the neutron irradiation test.

The MoO_3 pieces were irradiated at 5MW for 20 min using the irradiation hole of pneumatic tube Pn-2 (thermal neutron flux: 2.8×10^{17} n/m^2/s) of KUR. The irradiated MoO_3 pieces were attenuated for 4 days and used in the experiment.

2.3. Mo adsorption/^{99m}Tc elution property test

The Mo adsorption/^{99m}Tc elution property test was carried out by two types of Mo adsorption methods; static adsorption and dynamic adsorption.

About 1.5 g of the irradiated MoO_3 pieces were dissolved in 3.75 mL of a 6 mol/L-NaOH aqueous solution. The solution was adjusted to pH 4 by adding 2 mol/L-HCl and the Mo concentration of the solution was adjusted to 10 g-Mo/L by adding deionized water. The prepared aqueous solutions of sodium molybdate (Mo solution) was used for two types of Mo adsorption/^{99m}Tc elution property tests. The milking was carried out for 3 days.

The samples for activity measurement were prepared by dropping 100 μL of the sample solution on paper discs (φ10 mm) and enclosing them in polyethylene bags. The activities were measured using a γ-ray spectrometer made by Mirion Technologies (Canberra) KK. The Mo adsorption capacities of each

Alumina specimen were calculated from the value obtained by subtracting the Mo contents in the solution after adsorption from the one in the solution before adsorption. The Mo adsorption capacities (mg-Mo/g) were calculated based on the ^{99}Mo specific activity at the start of adsorption.

2.3.1. The static adsorption. 30 mL of Mo solutions were added to 1 g of each alumina specimen. They were immersed at room temperature for 3 hrs and shaken every 30 min during this time. The Alumina specimens and the supernatant were separated. The activities of the solution containing the supernatant and the wash solution were measured. The washed Alumina specimens were packed in a polypropylene column (ID 5-5.5 mm ×H 42 mm) and further washed with 50 mL of deionized water. The columns packed with each Alumina specimen were washed with 50 mL of saline to remove ^{99m}Tc and ^{99}Tc. After 24 h, the columns were milked with 1.5 mL of saline six times and 10 mL once for a total of 19 mL to examine the elution properties of ^{99m}Tc. The activities of ^{99}Mo and ^{99m}Tc in the obtained an aqueous solution of sodium pertechnetate (^{99m}Tc solution) were measured. The flow speeds of saline were approximately 210 mL/h.

2.3.2. The dynamic adsorption. The 1g of each alumina specimen was filled in PFA tubes (ID 1.59 mm × approx. 1 m). The alumina specimens in the tubes were fixed by the upper and lower glass wools. The alumina columns were connected to a peristaltic pump and 10 mL of Mo solutions were flowed through the columns. 30 mL of deionized water for washing and 30 mL of saline for removing ^{99m}Tc and ^{99}Tc were flowed through the columns. The activities of ^{99}Mo in the Mo solution, deionized water and saline after flowing through the columns were measured, respectively. After 24 h, the columns were milked with 1.5 mL of saline six times for a total of 9 mL to examine the elution properties of ^{99m}Tc. The activities of ^{99}Mo and ^{99m}Tc in the obtained ^{99m}Tc solution were measured. The flow speeds of the solution flowed through each alumina columns are shown in table 2.

Table 2. The flow speeds of the solution flowed through each alumina column in dynamic adsorption.

Specimens	Flow speed (mL/h)					
	Mo adsorption	Column washing	Conditioning	Miking		
				Day 1	Day 2	Day 3
D-201-300	24	25.7	27.7	22.5	16.9	27.0
V-V-300	24	25.7	27.7	22.5	24.5	27.0
V-B-300	20	26.9	26.5	15.4	24.5	15.4
Medical Alumina	20	25.4	22.5	4.0	3.6	3.6

3. Result and discussion

3.1. Irradiation properties

The activity of ^{99}Mo was calculated by the Covell method from the energy peak of 739.469 keV specified in MRRP. Table 3 shows the specific activity of ^{99}Mo in the Mo solution for about 100 hrs after irradiation.

Table 3. Activities of ^{99}Mo in the Mo solution after approximately 100 h from irradiation completion. (1: for D-201-300 and V-V-300, 2: for V-B-300 and Medical Alumina)

		Activity (MBq/g-Mo)
Static	1	14.59
	2	14.88
Dynamic		14.59

3.2. Evaluation of Mo adsorption properties

Table 4 shows the Mo adsorption capacities of each alumina specimen obtained by static adsorption and dynamic adsorption. The Mo adsorption capacities (mg-Mo/g-Al_2O_3) were calculated from the ^{99}Mo adsorption capacities (mg-^{99}Mo/g-Al_2O_3). Here, the specific activities of ^{99}Mo at the start of adsorption was used, which is obtained by attenuation correction from the specific activities shown in Table 5. The prepared alumina specimens have Mo adsorption capacities far exceeding that of Medical Alumina. In particular, V-B-300 has about twice the Mo adsorption capacity of Medical Alumina. However, the difference in these Mo adsorption capacities is small compared to the difference in these specific surfaces. This may be due to the lack of preliminary preparation of alumina specimens.

Comparing the Mo adsorption capacities obtained by dynamic adsorption and static adsorption, the Mo adsorption capacities by dynamic adsorption decreased as compared with static adsorption. Therefore, the result was shown that dynamic adsorption using an elongated column doesn't affect the improvement of Mo adsorption capacity.

Table 4. The Mo adsorption capacities of each alumina specimen obtained by static adsorption and dynamic adsorption.

Specimens	Adsorption capacity (MBq-^{99}Mo/g-Al_2O_3)		(mg-Mo/g-Al_2O_3)	
	Static	Dynamic	Static	Dynamic
D-201-300	0.91	0.83	58.4	51.9
V-V-300	0.88	0.69	56.4	48.7
V-B-300	1.17	0.38	74.1	63.8
Medical Alumina	0.59	0.36	37.2	27.0

3.3. Evaluation of ^{99m}Tc elution properties

The activity of ^{99m}Tc was calculated by the Covell method from the energy peak of 140.509 keV specified in MRRP. Figure 1 shows the ^{99m}Tc elution properties obtained by static adsorption. The total ^{99m}Tc elution rate on the vertical axis means the ratio of the activity of ^{99m}Tc present on the alumina column at the start of milking to the activity of ^{99m}Tc eluted. D-201-300 and Medical Alumina didn't reach 100 % of ^{99m}Tc elution rate even with 9 mL of milking on day 1, and D-201-300 remained low ^{99m}Tc elution rate on days 2 and 3. Figure 2 shows the ^{99m}Tc elution properties obtained by dynamic adsorption. Only 1.5 mL of milking gave 100 % of ^{99m}Tc elution for all alumina specimens. Therefore, dynamic adsorption by an elongated column is effective in improving ^{99m}Tc elution properties. However, dynamic adsorption involves the effects of ^{99m}Tc generated during milking since the milking using an elongated column took a long time. Obtaining more accurate ^{99m}Tc elution properties requires consideration of the amount of ^{99m}Tc generated during milking.

3.4. Quality evaluation of the ^{99m}Tc solution

MRRP specifies the standard pH value of ^{99m}Tc solution as pH 4.5-7.0. Figure 3 shows the pH of the ^{99m}Tc solutions obtained from each alumina specimen in static adsorption. The ^{99m}Tc solutions up to 9 mL were mixed and measured. All ^{99m}Tc solutions obtained from day 1 to day 3 were close to pH 4.5, which is the lower limit of the pH standard value. Since the pH of some ^{99m}Tc solutions obtained from Medical Alumina used in the current generators deviates from the standard value, the Mo adsorption method of this test and current generators are different. Figure 4 shows the pH of the ^{99m}Tc solutions obtained from each alumina specimen in dynamic adsorption. The ^{99m}Tc solutions from 0 to 4.5 mL and 4.5 to 9.0 mL were mixed and measured, respectively. The pH of the ^{99m}Tc solution obtained from V-V-300 and Medical Alumina was not significantly different from that of static adsorption, but the pH of the ^{99m}Tc solution obtained from D-201-300 and V-B-300 was approaching the neutral. Therefore, the elongated column increases the contact area between alumina and deionized water and efficiently cleans alumina. In addition, since the dynamic adsorption shortened the contact time between the alumina and

the Mo solution (pH 4), the dynamic adsorption may be suppressed the effect of the acidic solution on the alumina surface.

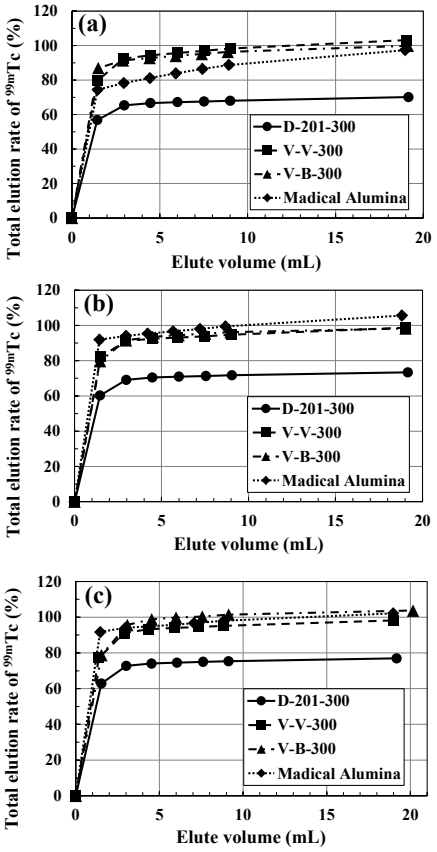

Figure 1. The ^{99m}Tc elution properties of alumina specimens obtained by static adsorption, (a) Day 1, (b) Day 2, (c) Day 3.

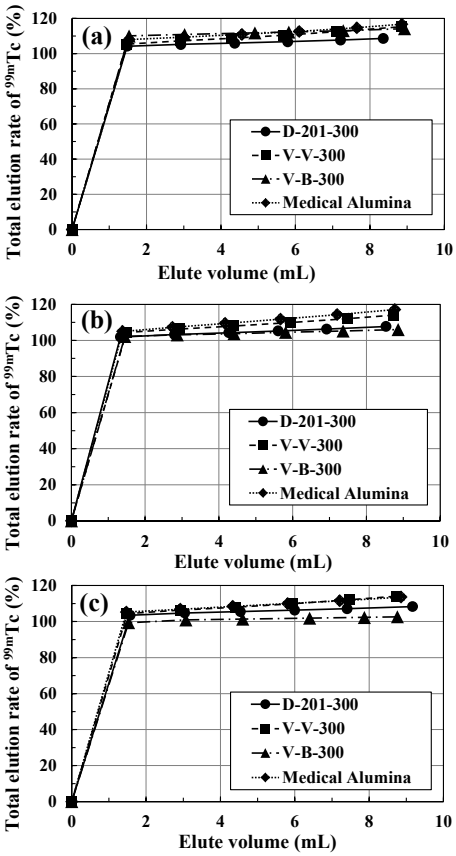

Figure 2. The ^{99m}Tc elution properties of alumina specimens obtained by dynamic adsorption, (a) Day 1, (b) Day 2, (c) Day 3.

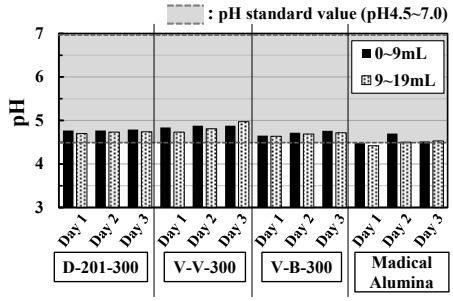

Figure 3. The pH of the ^{99m}Tc solution on alumina specimens obtained by static adsorption.

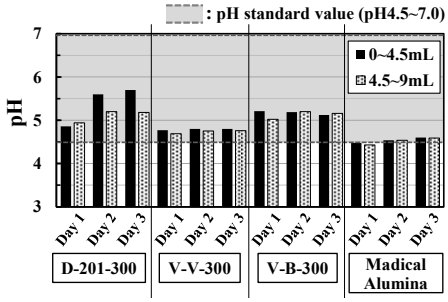

Figure 4. The pH of the ^{99m}Tc solution on alumina specimens obtained by dynamic adsorption.

In MRRP, the amount of ^{99}Mo desorbed in a ^{99m}Tc solution is specified using the ^{99}Mo/^{99m}Tc ratio as an index. The standard value is ^{99}Mo/^{99m}Tc < 0.015%. Figure 5 shows the ^{99}Mo/^{99m}Tc ratio in the ^{99m}Tc solution obtained from each alumina specimen in static adsorption. The ^{99}Mo/^{99m}Tc ratio was well above the standard value for all alumina specimens. Figure 6 is the ^{99}Mo/^{99m}Tc ratios in the ^{99m}Tc solution obtained from each alumina specimen in dynamic adsorption and the enlarged figure of that. The ^{99}Mo/^{99m}Tc ratio of dynamic adsorption is significantly reduced, compared to that of static adsorption. Therefore, efficient washing by using elongated columns effectively suppresses Mo desorption resulting

in a significant reduction in the ^{99}Mo/^{99m}Tc ratio. The decrease in the amount of Mo adsorbed by dynamic adsorption seems to be the result of removing excess Mo that was not adsorbed on alumina or was weakly adsorbed. However, although the ^{99}Mo/^{99m}Tc ratio was improved, it didn't meet the standard value of MRRP, and further improvement is needed.

These results suggest that the ^{99}Mo/^{99m}Tc ratio and pH of the ^{99m}Tc solution specified by MRRP are greatly affected by the Mo adsorption method on alumina.

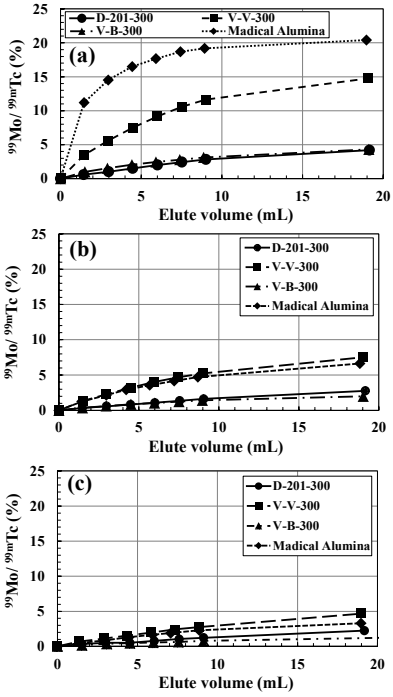

Figure 5. The ^{99}Mo/^{99m}Tc ratio of the ^{99m}Tc solution obtained by static adsorption, (a) Day 1, (b) Day 2, (c) Day 3.

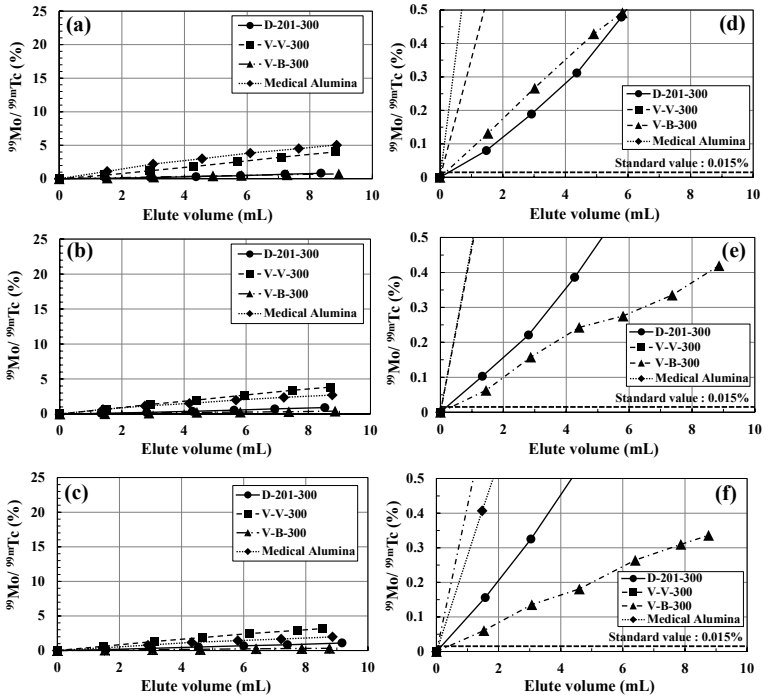

Figure 6. The ^{99}Mo/^{99m}Tc ratio of the ^{99m}Tc solution obtained by dynamic adsorption, (a) Day 1, (b) Day 2, (c) Day 3, and the enlarged figure of them, (d) Day 1, (e) Day 2, (f) Day 3.

4. Conclusions

The results of this work showed that dynamic adsorption using elongated columns increased the contact area between alumina and the solution. Increasing the contact area results in improved ^{99m}Tc elution properties of alumina columns, pH and ^{99}Mo/^{99m}Tc ratio of the ^{99m}Tc solution obtained from alumina columns. These results suggest that changing the Mo adsorption method (e.g., the column shape, the linear flow rate, etc.) on alumina helps to improve the ^{99}Mo/^{99m}Tc ratio and pH of the ^{99m}Tc solution specified by MRRP.

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