

T. Kobayashi, S. Sekimoto<sup>1</sup> and S. Shibata<sup>1</sup>

College of Humanities and Sciences, Nihon University

<sup>1</sup>Research Reactor Institute, Kyoto University

**INTRODUCTION:** Technetium with atomic number 43 is an artificial radioactive element that is not found in nature, and it is used as a tracer in medicine and environmental analysis. In particular, technetium-95m (half-life: 61 days) and technetium-99m (half-life: 6 hours) are frequently used as tracers. Because commercially available technetium-95m is isolated from fission products, the influence of other technetium isotopes cannot be avoided. Technetium-99m, however, is obtained as a decay product of molybdenum-99, and it does not sustain any effects from other technetium isotopes. Technetium-99m, therefore, is superior as a tracer with its higher isotopic purity compared to technetium-95m. Nonetheless, the supply of technetium-99m from overseas has recently been unstable. Consequently, a variety of alternative efforts have been examined in Japan, such as the study of production methods using accelerators. The present research employed molybdenum metal to production molybdenum-99/technetium-99m through reactor neutron irradiation. The handling of molybdenum metal is easy, but the generated specific radioactivity is low. Thus, methods for efficient extraction of technetium from molybdenum must be studied, and the usability of the technetium extracted as a tracer must be confirmed.

**EXPERIMENTS:** Technetium-99m was determined to be obtained through the production and subsequent decay of its parent nuclide, molybdenum-99, as a decay product. Approximately 50 mg of natural molybdenum metal foil (0.05 mm in thickness) was used for the production of molybdenum-99. The foil was irradiated in a Pn-2 radiation tube of the Kyoto University Research Reactor for 240 minutes at an output of 1 MW. Upon cooling for approximately 2 hours after irradiation, the foil sample was heated and dissolved in 7 N nitric acid and aqueous hydrogen peroxide. The solution was left to cool, followed by adsorption to an Empore filter [1,2] (made by Sumitomo 3M Ltd.), and finally elution from the filter by varying the nitric acid concentration from 1 N to 8 N. The eluent was subjected to gamma-ray analysis at 739 keV emitted from molybdenum-99 and at 142.7 keV emitted from technetium-99m with a well-type HP-Ge detector to determine the filter adsorption and elution characteristics. The same chemical process was employed

respectively for the anion-exchanged resin, activated alumina, and TEVA resin [3,4] as adsorbents for a column volume of 2 ml. Filter adsorption and elution characteristics for these were also determined.

**SUMMARY:** To date, the irradiation was performed on four times, and the chemical separation on six times experiments. Although the results are preliminary, the experimental conditions enabled the production of the requisite amount of radioactivity for a tracer. Experimentation work will continue in 2013 for chemical separation in order to improve reproducibility and to determine the optimum separation conditions. Furthermore, comparison of the AnaLig Tc-02 method [5] with TEVA resin for Tc separation. Based on the current data, chemical separation employing the TEVA resin and anion-exchanged resin yielded better results for separation and recovery rates, in comparison to the activated alumina and Empore filter. The obtained technetium-99m as a tracer is planned for use in determining technetium-99 recovery yield from respective samples of tap water, sea water, soil, and sea weed. Quantitative analysis of the separated and collected technetium-99 is planning to use the liquid scintillation counter and ICP-MS.

#### REFERENCES:

- [1] S. C. Goheen, editor DOE Methods for Evaluating Environmental and Waste Management Samples.
- [2] Battelle Press, Columbus, OH(1997). Method RS551, Rapid isolation and measurement of technetium-99 using 3M Empore<sup>TM</sup> Technetium Rad Disks.
- [3] Horwitz, E.P., Dietz, M.L., Chiarizia, R., Diamond, H., Maxwell III, S.L., and Nelson, M., *Analytica Chimica Acta*, 310(1995)63-78.
- [4] Xialin Hou, M. Jensen, S. P. Nielsen, *Applied Radiation and Isotopes*, 65(2007)610-618.
- [5] V. Pauova, V. Drabova, J. Strisovska, S. Balogh, *J. Radioanal. Nucl. Chem.* 293(2012)309-312.

## Adsorptivity of Polyvinylpyrrolidone Irradiated by $\gamma$ -Ray in $\text{HNO}_3$ to Metal Ions in HCl

N. Miyata, K. Shunto, M. Nogami and N. Sato<sup>1</sup>

*Faculty of Science and Engineering, Kinki University*  
<sup>1</sup>*Research Reactor Institute, Kyoto University*

**INTRODUCTION:** It has been revealed that polyvinylpyrrolidone (PVPP) changes the chemical structure by  $\gamma$ -ray irradiation in  $\text{HNO}_3$ , where PVPP undergoes the cleavage of the pyrrolidone ring by the addition of oxygen atom originating from  $\text{HNO}_3$ , followed by the formation of chain compounds by the successive addition of oxygen, leading to the generation of a primary-amine-type weakly-basic anion exchange resin and oxalic acid, (see Fig. 1). It has also been found that the functional group (a) in Fig. 1 has uncommon chemical structures with multiple coordinative sites and is relatively stable under irradiation[1]. This means that it may be used as a novel type of chelating resin, particularly in acidic media originated from the multiple C=O groups in the structure. So far, adsorptivities of the irradiated PVPP to major metal ions in  $\text{HNO}_3$  media have been examined. As the results, it was found that many kind of metal ions are adsorbed from  $\text{HNO}_3$  of lower concentration range, and that those such Zr(IV), Mo(VI), and Pd(II) are adsorbed also from  $\text{HNO}_3$  of higher concentration range[2]. In the present study, adsorptivities of the irradiated PVPP were examined in HCl solutions, and compared with those for  $\text{HNO}_3$  system.

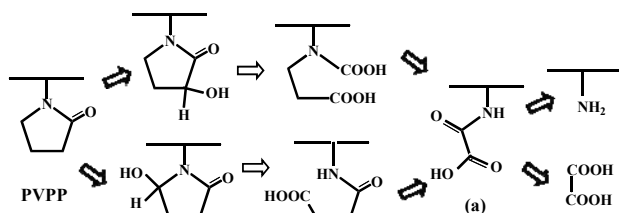


Fig. 1. Expected major route of change in chemical structure of PVPP by  $\gamma$ -ray irradiation in  $\text{HNO}_3$ .

**EXPERIMENTS:** Similarly to the earlier work[2], PVPP (Sigma-Aldrich) and  $\text{HNO}_3$  (6 mol/dm<sup>3</sup> (= M)) were mixed in a Pyrex sample tube, and the mixture was irradiated by the <sup>60</sup>Co source at maximum 10 kGy/h up to 2.3 MGy at room temperature under ambient atmosphere. Adsorptivities of the irradiated PVPP to various metal ions at equilibrium were examined by the batch method. Samples of the conditioned adsorbent (wet 0.25 g) and 5 cm<sup>3</sup> of 0.1 - 3 M HCl solutions containing a metal ion (10 mM each) were shaken at 298K in a thermostatic shaking bath for 24 h. Adsorptivities were evaluated by the distribution ratio,  $K_d$ , defined as,

$$K_d = \frac{C_0 - C}{C} \times \frac{V}{W} \quad (\text{cm}^3/\text{g}) \quad (1)$$

where  $C_0$  and  $C$  denote the concentrations of the nuclide in the solution before and after contact with the adsorbent, respectively.  $V$  and  $W$  represent the volume of the solution and the weight of the dry adsorbent, respectively.

**RESULTS:**  $K_d$  values were found to basically increase with increasing dose for many examined metal ions, which was similar to that for  $\text{HNO}_3$  system.  $K_d$  values for various metal ions as a function of HCl concentration for PVPP irradiated at 1.3 MGy are shown in Fig. 2. It can be seen that Zr(IV) and Mo(VI) have high adsorptivities under all examined HCl concentrations. In particular, the  $K_d$  value for Zr(IV) in 0.1 M HCl is large. Pd(II), Fe(III) and Re(VII) also show relatively large  $K_d$  values. On the other hand, adsorption of Nd(III) is found to be weak.

For both HCl and  $\text{HNO}_3$  systems,  $K_d$  values for each acid concentration were found to have similar tendency, except smaller  $K_d$  values for Mo(VI) in HCl system compared with  $\text{HNO}_3$ . Such a similarity is of great interest, because the dominant chemical species of each metal ion including valences differ depending on concentration of HCl and  $\text{HNO}_3$ . Considering the extraction behavior and adsorptivity of conventional extractants and anion exchange resins in HCl and  $\text{HNO}_3$  systems, respectively, different sites of the functional group may participate in the adsorption. Namely, the contribution of oxygen atoms is greater for  $\text{HNO}_3$  system, while that of the nitrogen atom takes the more important role for HCl system. Further investigations are necessary for understanding the adsorption mechanisms.

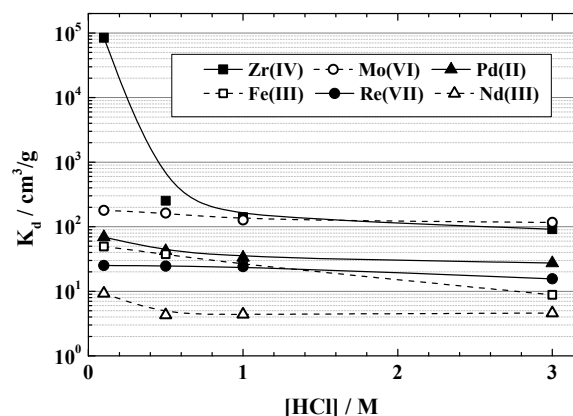


Fig. 2. Adsorptivity of PVPP irradiated in 6M  $\text{HNO}_3$  at 1.3 MGy to various metal ions in HCl.

### REFERENCES:

- [1] M. Nogami *et al.*, J. Radioanal. Nucl. Chem., **296** (2013) 423-427.
- [2] N. Miyata *et al.*, KURRI Progress Report 2010 (2011) 258.