

## CO9-1 Search for the Ultraviolet Photons Emitted from $^{229\text{m}}\text{Th}$ Samples Reacted with HF Gas

Y. Yasuda, Y. Kasamatsu, Y. Shigekawa, T. Ohtsuki<sup>1</sup>, K. Takamiya<sup>1</sup>, A. Shinohara

Graduate School of Science, Osaka University

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

**INTRODUCTION:** Thorium-229m lies in the extremely low energy level and the excitation energy was reported to be  $7.8 \pm 0.5$  eV [1]. The energy corresponds to vacuum ultraviolet photon ( $\lambda=160$  nm). Because of the low energy, it is expected that  $^{229\text{m}}\text{Th}$  decays by internal conversion or gamma-ray transition depending on its chemical condition. Recently, it was reported that the  $^{229\text{m}}\text{Th}$  neutral atom decays by internal conversion with a half-life of 7  $\mu\text{s}$ , and that the  $^{229\text{m}}\text{Th}^{2+}$  ion in the isolated system decays with a half-life of longer than 60 s [2, 3]. It suggests that  $^{229\text{m}}\text{Th}^{2+}$  ion may decay by gamma-ray transition (photon emission). However, the photons from  $^{229\text{m}}\text{Th}$  have never been observed. To observe the photons, in this study we performed following experiments: First, we prepared  $^{229\text{m}}\text{Th}$  as recoil products (high valence  $^{229\text{m}}\text{Th}$  ions). Subsequently,  $^{229\text{m}}\text{Th}$  ions were directly reacted with hydrogen fluoride gas. Since the lowest binding energy of the outermost electron in  $\text{ThF}_4$  is 8.3 eV [4] which is larger than the  $^{229\text{m}}\text{Th}$  excitation energy, 7.8 eV, it is expected that  $^{229\text{m}}\text{Th}$  is not able to decay by internal conversion. Finally, the photon detection was performed for the sample.

**EXPERIMENTS:** To obtain  $^{229\text{m}}\text{Th}$  ions as recoil products, we prepared thin  $^{233}\text{U}$  sample by electrodeposition. A 10  $\mu\text{L}$  aliquot of the  $^{233}\text{U}$  solution in 0.1 M  $\text{HNO}_3$  (24  $\mu\text{g}/\mu\text{L}$  of  $^{233}\text{U}$ ) and 10 mL of isopropanol were placed into the 30-mm diameter electrodeposition cell. Using a Pt wire as the anode,  $^{233}\text{U}$  was electrodeposited on a Pt foil (0.02 mm thickness) with a current of 17 mA. The electrodeposition yield was determined by alpha spectroscopy to be 54% corresponding to  $17.8 \pm 0.3$   $\mu\text{g}/\text{cm}^2$  of  $^{233}\text{U}$  in thickness. The  $^{233}\text{U}$  sample was set in the Collection Apparatus for Recoil Products (CARP) [5]. In collecting  $^{229\text{m}}\text{Th}$  ions, He gas or He/HF mixture gas were guided into the CARP and the required voltage was applied to guide  $^{229\text{m}}\text{Th}$  ions onto the copper plate. After  $^{229\text{m}}\text{Th}$  was collected for several hours to 1 day, photon detection was performed. To detect the photons, we used the photomultiplier tube (PMT, HAMAMATSU R6836), which detects 4-10 eV photons. The PMT was cooled to about 10°C and set in vacuum.

**RESULTS:** In the result of photon detection for the  $^{229\text{m}}\text{Th}$  samples collected in He gas, weak decaying photon counts were observed as shown in Fig.1 (a). This time variation can be fitted with the decaying curve of two half-life components,  $^{212}\text{Pb}$  and  $^{213}\text{Bi}$ . However, this count rate was lower than the expected value (2 cps) for  $^{229\text{m}}\text{Th}$ , and therefore we tried to detect the photons emit-

ted from the  $^{229\text{m}}\text{Th}$  sample reacted with HF gas. In this case, decaying photons were also observed as shown in Fig.1 (b). However, the count rate of photon emitted from this sample was almost the same as that from the sample collected in He gas. This fact indicates that these photons mainly originated from daughter nuclides such as  $^{213}\text{Bi}$ ,  $^{209}\text{Tl}$ ,  $^{212}\text{Bi}$ , and  $^{208}\text{Tl}$ . Thorium-229m might not be reacted sufficiently. To reduce the photons induced by daughter nuclides, we will use the electrodeposited sample of newly purified  $^{233}\text{U}$ .

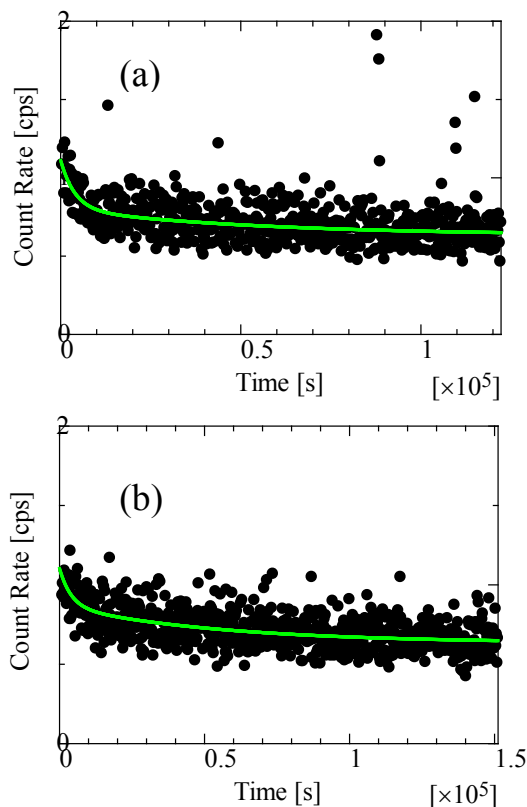


Fig. 1. The photon counts for the  $^{229\text{m}}\text{Th}$  samples. Solid curves describe the fitted curves containing two decaying components. Fig.1 (a) shows the counts for  $^{229\text{m}}\text{Th}$  sample prepared in He gas for about 15 h and (b) shows that reacted with HF gas for about 25 h.

### REFERENCES:

- [1] B. R. Beck *et al.*, LLNL-PROC-415170(2009).
- [2] L. von der Wense *et al.*, Nature **533** (2016) 47-51.
- [3] B. Seiferle *et al.*, Phys. Rev. Lett. **118** (2017) 042501.
- [4] N. Trautmann, J. Alloys Compd. **213/214** (1994) 28.
- [5] Y. Shigekawa *et al.*, Rev. Sci. Instrum. **87**(2016) 053508.

## CO9-2 Stability of Triphosphine Trioxide Extractant against $\gamma$ -Ray Irradiation in $\text{HNO}_3$

M. Nogami, E. Tamaru, S. Maeda and N. Sato<sup>1</sup>

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

**INTRODUCTION:** We have been paying attention to one of triphosphine trioxides, 1,1,3,5,5-pentaphenyl-1,3,5-triphosphapentane trioxide (PPTPT : Fig. 1) for a potential versatile extractant [1,2]. The most distinguished nature of PPTPT would be its unusual high selectivity to U(VI) in  $\text{HNO}_3$  of very low concentrations [3]. Another expected nature of PPTPT is higher chemical stability in acid media. In principle, phosphine oxides do not undergo acid hydrolysis unlike compounds not containing phosphorus such as diamides, and ester phosphates such as tri-*n*-butylphosphate (TBP). In addition, PPTPT has no ether bonds which are known to decrease the stability of extractants in acid media[4], although they have been sometimes included in chemical structures of extractants to increase extraction properties. Based on the above, radiation stability of PPTPT was investigated mainly from the identification of degradation products in this study.

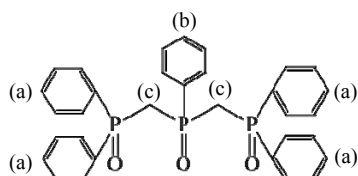


Fig. 1. Chemical structure of PPTPT.

**EXPERIMENTS:** For  $\gamma$ -ray irradiation to PPTPT, the samples were prepared by mixing PPTPT of white crystal with  $\text{H}_2\text{O}$ , 3 and 9 mol/dm<sup>3</sup> (= M)  $\text{HNO}_3$ , respectively. The mixture was put in a Pyrex tube and irradiated by the <sup>60</sup>Co source at ca. 3.7 kGy/h up to 1.6 MGy at room temperature under ambient atmosphere. Irradiated samples were analyzed by <sup>1</sup>H and <sup>13</sup>C NMR.

**RESULTS:** PPTPT irradiated in  $\text{H}_2\text{O}$  showed powdered state. While, those irradiated in 3 and 9 M  $\text{HNO}_3$  turned into brown viscose oil. <sup>1</sup>H NMR spectra of neat PPTPT and that irradiated in 9 M  $\text{HNO}_3$  are shown in Fig. 2. It can be seen that the signal at ca. 1.5 ppm which is

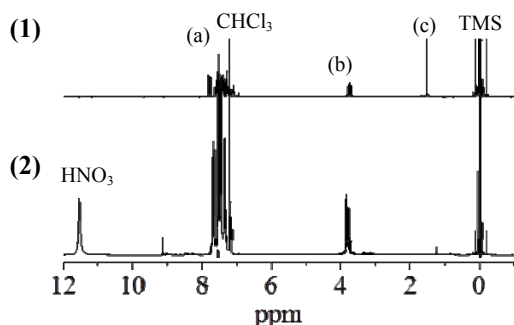


Fig. 2. <sup>1</sup>H NMR of PPTPT : (1) neat, (2) irradiated in 9 M  $\text{HNO}_3$  (solvent :  $\text{CDCl}_3$ ).

attributed to the hydrogen atoms at (c) in Fig. 1 is significantly decreased after irradiation. This suggests that the bond cleavage occurred between phosphorus and methylene carbon.

For comparison, PPTPT was treated with 9 M  $\text{HNO}_3$  containing 10 mM Nd(III) or Fe(III), or 3 %  $\text{H}_2\text{O}_2$  at boiling temperature for 6 h. It was also treated similarly with conc.  $\text{HNO}_3$ . Under these conditions, little structure changes were observed for <sup>1</sup>H NMR spectra. This would indicate high chemical stability of PPTPT in  $\text{HNO}_3$  media. On the other hand, <sup>1</sup>H NMR analysis for PPTPT treated with aqua regia at room temperature for 1 day suggests the similar bond cleavage to the irradiated PPTPT. Further <sup>1</sup>H and <sup>13</sup>C NMR analyses for PPTPT treated with aqua regia suggest that formic acid and two kinds of phenylphosphoric acid were generated as the degraded compounds (Fig. 3). Large portion of formic acid might be decomposed to CO and  $\text{H}_2\text{O}$ . Such a pathway of degradation was similar to some extent to that of octylphenyl-*N,N'*-diisobutylcarbamoylmethyl phosphine oxide (CMPO), a conventional bidentate phosphine oxide extractant, by  $\gamma$ -ray irradiation [5].

So far, the detailed pathway of degradation for irradiated PPTPT is not confirmed. However, it is expected that the pathway is close to that shown in Fig. 3.

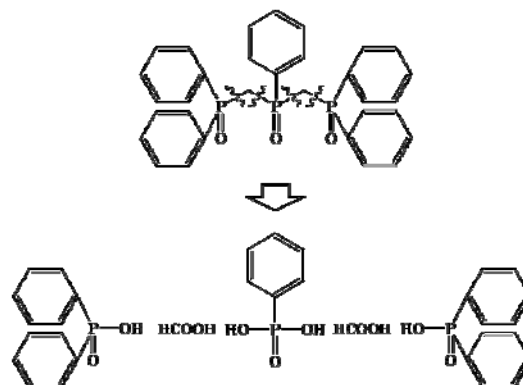


Fig. 3. Expected structure change in PPTPT by treatment with aqua regia.

### REFERENCES:

- [1] M. Nogami *et al.*, Energy Procedia, **71** (2015) 123-129.
- [2] K. Hashimoto, *et al.*, Abst. ASNFC 2015, Tokyo, Japan, 2B-24 (2015).
- [3] M. Nogami, *et al.*, J. Radioanal. Nucl. Chem., **284** (2010) 195-199.
- [4] C. Madic, *et al.*, Nuclear science and technology, Final report, EUR19149, European Commission, 44 (2000).
- [5] J. N. Mathur, *et al.*, Sep. Sci. Technol., **33** (1998) 2179-2196.