

CO9-1 Investigation of coprecipitation with Sm hydroxide using KUR multitracer

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INTRODUCTION: Chemical researches on actinide and transactinide elements at the bottom of the periodic table are very important in inorganic chemistry. Owing to strong relativistic effect on the electronic shells of heavy elements, their chemical properties might be unique in the periodic table. It is, however, difficult to perform chemical experiment with heavy actinide and transactinide elements because these atoms must be produced at accelerators using heavy-ion induced nuclear reactions at low production rates. Furthermore, these nuclides have short half-lives. Thus, we need to establish new experimental methods with apparatuses specified for these elements. For such a purpose, it is important to perform fundamental chemical experiments (with and without apparatuses) using the lighter elements whose chemical properties are known.

We previously proposed the coprecipitation method with Sm hydroxide as a new methodology for heavy elements [1]. Indeed, suitable experimental condition for element 104, Rf, was successfully determined through fundamental experiments using homologues of Rf: Zr, Hf, and Th [2]. Additionally, in the coprecipitation experiment of various elements [1], multitracer produced by spallation reaction of Ta in RIKEN was used to investigate the coprecipitation behaviors of elements belonging to various groups in the periodic table. In this study, coprecipitation behaviors of the elements contained in KUR multitracer were studied. The KUR multitracer was produced by neutron-induced fission reaction of ²³⁵U. Thus, the product nuclides are different from those in RIKEN multitracer. We expect to obtain complementary data by this experiment.

EXPERIMENTS: The KUR multitracer sample was prepared by irradiating thermal neutrons on mixture powder sample of UO₂ and RbCl using the reactor at Institute for Integrated Radiation and Nuclear Science, Kyoto University [3]. Fission products implanted in RbCl were dissolved in 0.01 M HCl and were separated from the undissolved UO₂ by a suction filtration. A portion of the sample was subjected to γ -ray measurement by a Ge detector, and count rates of γ -ray peaks and their time dependences were measured to identify the nuclides in the sample.

In the precipitation experiment, 20 μ L (20 μ g) of Sm standard solution (1 M HNO₃) was added into the multitracer solution. After mixing it, 2 mL of basic solution was added to generate hydroxide precipitate. In the present experiment, we used dilute NH₃ solution, concen-

trated NH₃ solution, 0.1, 1, 6, and 12 M NaOH solutions as the basic solutions to observe the dependence of the precipitation yield on the concentration of the basic solution. Subsequently, the solution was stirred for 10 s and was soon filtrated with a polypropylene membrane filter. To check the complete precipitation of the samples, precipitate samples with stirring for 10 min after adding the basic solution were also prepared. The samples were then dried on heater at 100 degree C and were assayed for γ -ray measurements. Supernatant solutions were evaporated to dryness and were also subjected to measurements. The coprecipitation yields were determined from the results of the γ -ray measurements.

RESULTS: The product nuclides were identified from the γ -ray energies and the half-lives. To obtain precipitation yields, we exclude the nuclides whose decays are affected by their parent or daughter nuclide from the analysis of the coprecipitation yield. The nuclides of Na, Zr, Mo, Ce, Ba, Te are elements observed in RIKEN multitracer although the mass numbers of the nuclides are different from those in RIKEN multitracer. ⁹¹Sr, ¹⁰³Ru, ¹³³I, ¹⁵¹Pm, ^{198m}Au, and ²³⁹Np are newly observed elements in KUR multitracer. Especially, the ⁹¹Sr and ¹⁵¹Pm nuclides are of great importance for the establishment of the experimental method: Sr is comparative data for element 102, No, and Pm is near to Sm in the periodic table (Radioactive isotopes of Sm were not observed in both RIKEN and KUR multitracer). ¹³³I belongs to halogen and we had no data for halogen.

The coprecipitation yields were determined from the equation: $A_{\text{ppt}} / A_{\text{std}}$, where A represents the radioactivity of the nuclide, and ppt and std indicate the precipitate and standard, respectively. The yields of ¹⁴³Ce and ¹⁵¹Pm (lanthanides) were approximately 100% under all the conditions studied. This result means that the yield of Sm is considered to be 100% under all conditions which is favorable in the experiment. For transition metal elements and alkali metal element: Na, consistent results with those obtained for RIKEN multitracer were obtained. The yields of Np were similar to those of transition metal elements and not to lanthanides. These results are basically consistent with the hydroxide precipitation properties of the corresponding elements. It suggests that the present coprecipitation method is suitable to investigate the precipitation behaviors of the elements whose properties are unknown (heavy elements).

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INTRODUCTION: Stability of pyrrolidone derivatives (NRPs) which are potential precipitants for uranium(VI) species in nitric acid media has been investigated. Irradiation to HNO₃ solutions up to 6 mol/dm³ (= M) containing 2 M *N-n*-butyl-2-pyrrolidone (NBP : Fig. 1), one of NRPs has revealed that the residual ratios of NBP in the samples of HNO₃ up to 3 M decreased identically and linearly. On the other hand, the degradation of the samples irradiated in 6 M HNO₃ has been found more distinguished. It was proposed from the analyses of degraded compounds that the degradation of NBP in HNO₃ by γ -ray irradiation started from the cleavage of the pyrrolidone ring by the addition of oxygen atom originating from HNO₃, followed by the formation of chain compounds by the successive addition of oxygen, leading to the generation of oxalic acid and acetic acid. Some of the oxalic acid further decompose to CO₂[1]. In order to know more about the degradation mechanism of NRP, degradation property of NBP in hydrochloric acid media was investigated in the present study.

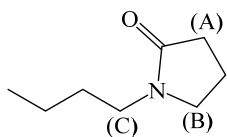


Fig. 1. Chemical structure of NBP.

EXPERIMENTS: 0.1, 3, and 6 M HCl solutions containing 0.5 M NBP, respectively, were prepared in Pyrex tubes for the samples for γ -ray irradiation. Irradiation was carried out by the ⁶⁰Co source up to 0.45 MGy at room temperature under ambient atmosphere, similarly to the earlier study[2]. Irradiated samples were analyzed by ¹H NMR. DMSO-d₆ containing a known weight of TMS which is a standard material was used as the NMR solvent. The residual ratio of NBP was calculated by the area ratio of each signal with that of TMS.

RESULTS: The sample solutions were found to turn yellow with increasing concentration of HCl and dose. In a ¹H NMR spectrum, neat NBP showed three signals; (A)2.3, (B)3.2, (C)3.3 ppm in Fig. 1, respectively. The calculated residual ratios of the sample vs. dose are shown in Fig. 2, together with the relationship between the position of hydrogen in the structure of NBP and that of the signal. The residual ratios calculated from the three signals show a nearly identical trend regardless of the concentration of HCl, where the residual ratios decrease linearly with an increase in dose, and the residual ratios are ca. 70 % at 0.3 MGy. The residual ratios for the of HNO₃ up to 3 M was ca. 90 %[1], indicating that the stability of NBP against γ -ray irradiation in HCl is lower

than that in HNO₃ of lower concentrations. The reason why no dependence of degradation property on HCl concentration would result from the absence of oxygen atoms supplied for the above-mentioned HNO₃ system.

No new signals attributed to the decomposition products were observed for the ¹H NMR spectra in the irradiated samples, although some NBP was degraded. A possible degraded compound may be oxalic acid like the case for HNO₃ system, because the proton of oxalic acid is hardly detected in a ¹H NMR spectrum. What happened to NBP in the HCl system during irradiation remains unclear.

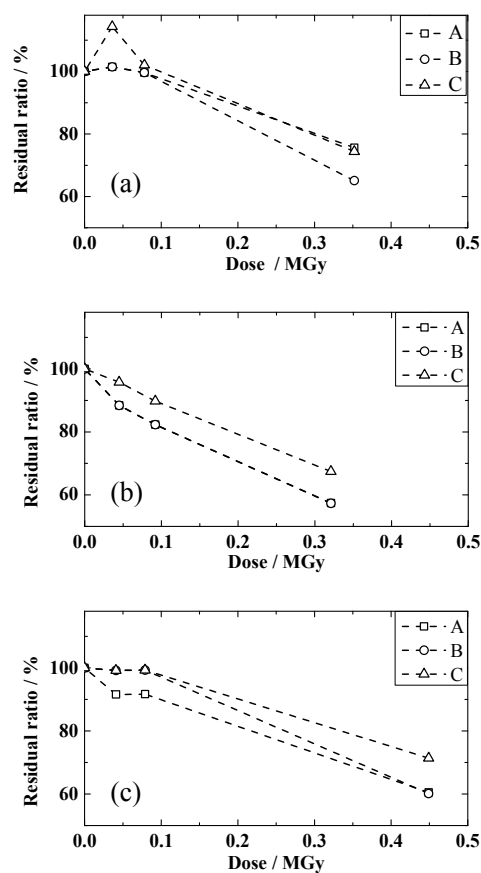


Fig. 2. Dependence of residual ratio of NBP in (a) 0.1 M, (b) 3 M, (c) 6 M HCl on dose.

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