

Coprecipitation Behaviors of Zr, Hf, and Th with Sm Hydroxide for Chemical Study of Element 104, Rf†

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Owing to significant relativistic effects on electron orbital shells for heavy elements, the chemical properties of the superheavy elements are expected to deviate from the characteristic periodicity of the lighter homologues in the periodic table, and their chemical studies have attracted much attention. However, experimental evaluation of these species is fraught with difficulties. Because of the extremely low production rates and short half-lives (within a few min) of these heavy nuclides, chemical evaluations of the superheavy elements must be rapidly conducted on a one-atom-at-a-time basis. Thus, simple chemistry employing partition methods such as solvent extraction and ion-exchange chromatography have been utilized and the chemical separations were repeated hundreds or thousands of times under identical conditions. This approach requires a rapid chemistry apparatus. Additionally, for unambiguous identification of superheavy nuclides, it is necessary to measure the energies and lifetimes of α or sometimes spontaneous fission decays.

The purpose of the present study is to establish a new experimental methodology for investigating the chemical properties of superheavy elements, specifically, the coprecipitation properties of ²⁶¹Rf ($T_{1/2} = 68$ s) by the formation of hydroxide and ammine complexes. Herein, we applied a simple coprecipitation method with Sm hydroxide, which facilitates α spectrometry with high energy resolution,¹⁾ to the investigation of the coprecipitation behaviors of the homologues of Rf: Zr, Hf, and Th. In addition, a semiautomatic apparatus for repetitive preparation of precipitate samples was developed and tested using the gas-jet transport system of nuclear products.

We used ⁸⁸Zr, ¹⁷⁵Hf, and ²²⁸Th radiotracers to prepare coprecipitated samples with Sm hydroxide. A 20 μ L aliquot of the Sm standard solution (Sm 1000 ppm, 1 M HNO₃) was added into 220 μ L of an aqueous solution (~0.4 M HCl) containing the radiotracers in a polypropylene (PP) beaker. The solution was stirred and 2 mL of the basic solution (dilute and concentrated aqueous NH₃ and 0.1, 1.0, 6.0, and 12.0 M NaOH solutions) was then added to produce the precipitate. After aging the precipitate for 10 s or 10 min at 25 °C, the precipitate sample was subjected to suction filtration with a PP membrane filter (eichrom, Resolve®

Filters 0.1 μ m). The obtained sample was dried on a heater at 100 °C, and was subjected to γ -ray and α -particle measurements. The radioactivities of the filtrate and PP beakers used were also measured. We determined precipitation yields, Y , and the percent adsorption on the PP beaker, R_{ad} , from the radioactivities.

A computer-controlled suction filtration apparatus for the preparation of precipitated samples of heavy elements was developed. The online experiment using the apparatus was performed with relatively short-lived nuclides ^{89m,g}Zr (4.2 min and 78.4 h) and ¹⁷³Hf (23.6 h) produced using the AVF cyclotron at RCNP. These nuclides were rapidly and continuously transported from the nuclear reaction chamber to the chemistry laboratory using the He/KCl gas-jet system. Using the apparatus, the products were dissolved by 200 μ L of dilute HCl and the precipitate samples were prepared at room temperature in a manner similar to that used in the above tracer experiment with stirring for 10 s.

The R_{ad} values of Zr, Hf, and Th for samples aged for 10 s was generally less than 3%, which suggests that physical adsorption of these group 4 elements during coprecipitation with Sm hydroxide was small enough to be negligible in the determination of the coprecipitation yields. The Y values of Zr, Hf, and Th obtained with 10-min and 10-s aging are in good agreement with each other. This suggests that the chemical reactions during coprecipitation of these elements are fast, and the present conditions are suitable for evaluating the coprecipitation behavior of 68-s ²⁶¹Rf. Almost complete coprecipitation of Zr and Hf with Sm hydroxide was achieved when aqueous NH₃ solutions and 0.1 M NaOH were used. These results are consistent with the well-known properties of these elements, i.e., hydroxide precipitation in basic solutions. With the use of more highly concentrated NaOH solutions, these yields decreased, whereas the Th yields were constant at ca. 100%. This is attributed to the fact that Zr and Hf form hydroxide complex ions in high [OH⁻] solutions.

The Y values obtained in the online experiments and their dependence on the composition of the added basic solution are consistent with those in offline experiment. This suggests that the present experimental method using the apparatus under the present conditions should be applicable to the coprecipitation experiment of Rf.

Reference

1) H. Kikunaga et al., Appl. Radiat. Isot. **67**, 539 (2008).

† Condensed from the article in J. Nucl. Radiochem. Sci. **14**, 7 (2014).

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