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Production and isolation of homologs of flerovium and element 115 at the Lawrence Livermore National Laboratory Center for Accelerator Mass Spectrometry

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Abstract New procedures have been developed to isolate no-carrier-added (NCA) radionuclides of the homologs and pseudo-homologs of flerovium (Hg, Sn) and element 115 (Sb), produced by 12–15 MeV proton irradiation of foil stacks with the tandem Van-de-Graaff accelerator at the Lawrence Livermore National Laboratory Center for Accelerator Mass Spectrometry (CAMS) facility. The separation of ^{113}Sn from ^{nat}In foil was performed with anion-exchange chromatography from hydrochloric and nitric acid matrices. A cation-exchange chromatography method based on hydrochloric and mixed hydrochloric/hydroiodic acids was used to separate ^{124}Sb from ^{nat}Sn foil. A procedure using Eichrom TEVA resin was developed to separate ^{197}Hg from Au foil. These results demonstrate the suitability of using the CAMS facility to produce NCA radioisotopes for studies of transactinide homologs.

Keywords No-carrier-added · Homologs · Transactinide · Mercury · Tin · Antimony

Introduction

No-carrier-added (NCA) radionuclides play a crucial role in various science and technology fields [1]. In the field of nuclear medicine, radiopharmaceuticals having the ability to deliver a specific dose to a targeted region of the body must be prepared with high specific activity in order to administer in as small a volume as possible [2]. Additionally, radioanalytical chemistry and in particular nuclear forensic analysis makes use of NCA radionuclides as tracers in order to follow the behavior and measure the chemical yield of an element during a procedure [3]. A primary application of these types of radionuclides, described in this paper, is the study of transactinide elements.

The chemical investigation of the transactinide elements ($Z \geq 104$) presents challenges due to low production cross sections (nano- or picobarn) and short half-lives, which lead to studies on the one-atom-at-a-time scale [4]. Homolog studies of transactinides must, therefore, be carried out on-line by producing individual atoms at an accelerator, or with NCA, ultratrace amounts of radionuclides.

No-carrier-added radionuclides can be readily produced and isolated from charged-particle reactions since the target and the product can be different elements [5]. Typical reactions utilize proton bombardment of a stable target; however, heavier charged particles such as helium can also be used. Based on atomic number, flerovium belongs in Group 14 with its direct homologs Sn and Pb. From group trends, it is expected that flerovium would have an unstable 4+ oxidation state and the most stable 2+ state in the group [6]. This means that Hg could also be considered a pseudo-homolog of flerovium due to its similar oxidation state [6]. Similarly, Sb is a direct homolog of element 115

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based on atomic number. These elements (Sn, Hg, and Sb) can be produced by proton-induced reactions on natural-isotopic foils. The other homologs of flerovium and element 115 (Pb and Bi, respectively) can be obtained NCA by separation from the decay chains of ^{232,235,238}U and ^{228}Th [7]. Although excitation functions for the ^{124}Sn(p,n)^{124}Sb, ^{197}Au(p,n)^{197}Hg, and ^{113}In(p,n)^{113}Sn reactions have been reported in the literature, separation methods to obtain NCA activities from Sn, Au, and In target materials are lacking [8–10].

The reported production methods of NCA Sn isotopes are based on the isolation of parent ^{113,110}Sn for producing ^{113m,110}In generators in radiopharmaceutical applications [11, 12]. The production of NCA Hg from high-energy reactions designed to produce a packet of diverse radionuclides in Au targets with ^{7}Li and ^{12}C beams, and the subsequent separation of NCA products from the excess Au, has been described [13]. The production of ^{124}Sb is often not NCA, and the nuclide is commonly used as a gamma-ray calibration source and in radiopharmaceutical therapeutic methods [14].

The Lawrence Livermore National Laboratory (LLNL) Center for Accelerator Mass Spectrometry (CAMS) is well suited for the production of short-lived, NCA radionuclides. A 10-MV, model FN tandem Van-de-Graaff accelerator at CAMS can typically produce up to 15-MeV protons at beam currents of 100–400 nA ($\leq 2.5 \times 10^{12}$ pps). This energy range and current is suitible for the proton-induced reactions given above, all of which have peak cross-sections in the 10–15 MeV range [8–10].

High-purity natural In, Sn, and Au foils were irradiated at the LLNL CAMS facility to produce NCA Sb, Sn, and Hg radionuclides for homolog studies of flerovium and element 115. The production routes, as well as the methods for rapidly separating the NCA activities from the bulk target materials, are described in this work. These novel procedures were developed for the isolation of NCA ^{124}Sn, ^{113}Sn, and ^{197}Hg from their corresponding production targets.

Experimental

Reagents and materials

High-purity, natural Sn and In foils (each 0.05-mm thick, 99.999 %) were obtained from Goodfellow, and Au foils (0.025-mm thick, 99.95 %) were obtained from Alfa Aesar. All were used as received. Reagents for the separations were prepared from trace-metal grade, ultrapure acids and deionized water (18.2 MΩ cm). Maximum stable isotope contamination from reagents used was <1 ppb. Eichrom TEVA resin (50–100 μm, 40 % w:w) and BioRad AG 1 × 8 (100–200 mesh) and AG 50W×8 (100–200 mesh) resins were cleaned prior to use.

Production of radionuclides

Foils were cut into 8 × 8-mm squares weighing 20–50 mg each and mounted in a target chamber (Fig. 1). Foils of different elements were separated by 0.01-mm Ta catcher foils. Separate irradiations were performed with various different stacks comprising Au, In, and Sn foils. The foil stacks were irradiated for 6–8 h with 12–15 MeV protons at currents of 100–400 nA ($\leq 2.5 \times 10^{12}$ pps) at the CAMS tandem Van-de-Graaff accelerator. A cesium-ion sputter source was utilized to produce negatively charged hydrogen ions, which were injected into the tandem accelerator at ~40 keV and accelerated through a stripper gas to generate 12–15 MeV protons for irradiation of the target materials. The foils were allowed to cool for 8–12 h after an irradiation before removal from the target chamber.

Radiochemical separation of no-carrier-added activities

The procedure for the isolation of ^{113}Sn from irradiated ^{nat}In foil is based on results presented in Refs. [12, 15]. The In foil was dissolved in 4 mL of concentrated HCl and evaporated to moist dryness at 90 °C, the temperature chosen to minimize volatilization of Sn. The residue was reconstituted in 4 mL of 1 M HCl, with 0.5 mL of 30 % H_2O_2 added to oxidize the Sn to the Sn(IV) state. A 2-mL (4 cm long by 0.4 cm inner diameter) column of AG 1 × 8 anion-exchange resin was prepared and conditioned with 10 mL of 1 M HCl. The solution containing the dissolved foil was then loaded onto the column under gravity. The empty sample container was rinsed twice with 4 mL of 1 M HCl, and also passed through the column. Under these conditions, the In target material was expected to pass through the column while the NCA ^{113}Sn would be retained. An additional four 4-mL fractions of 1 M HCl were passed through the column to ensure that all In was eluted, and each such fraction was collected and individually analyzed by HPGe gamma spectroscopy for ^{113m}In content. The ^{113}Sn was then eluted with five 4-mL fractions of 3 M HNO_3, each analyzed for ^{113m}In content initially and then after 1 day to allow ^{113m}In to reach secular equilibrium with ^{113}Sn. The ^{nat}In fractions were also counted 1 day later to ensure that all of the ^{113m}In had decayed to background, indicating the absence of ^{113}Sn. Separations were performed approximately 1 day after irradiation to ensure equilibrium between ^{113m}In and ^{113}Sn.

The isolation of ^{124}Sb from ^{nat}Sn was based on distribution ratios presented in Refs. [16, 17]. The Sn foil was dissolved in 1 mL of concentrated HCl, with 20 μL of

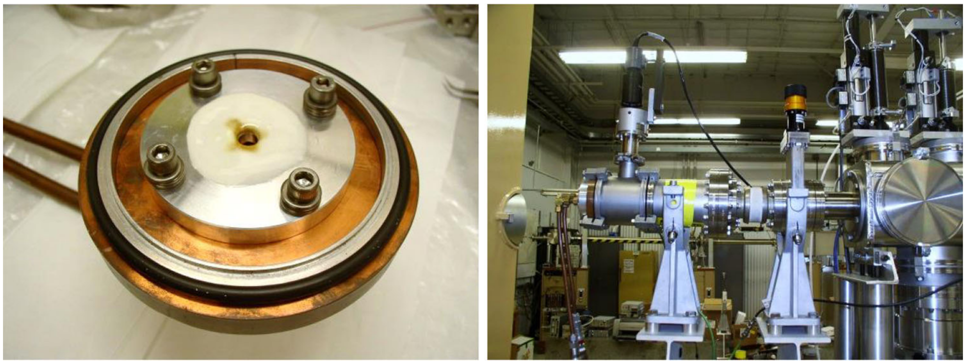

Fig. 1 CAMS target chamber for irradiations of stable metal foils: copper cooling block with aluminum clamp to hold foil stack in place (*left*) and the irradiation chamber as installed at the CAMS beamline (*right*)

30 % H_2O_2 added to ensure oxidation to Sb(V) and Sn(IV). A 2-mL (4 cm long by 0.4 cm inner diameter) column of AG 50W×8 cation-exchange resin was prepared and conditioned with 10 mL of concentrated HCl. The solution containing the dissolved Sn foil was added to the column, followed by ten 1-mL fractions of concentrated HCl. Under these conditions the Sn was expected to pass through the column, while the Sb would be retained. The Sb was then stripped off the column with ten 1-mL fractions of concentrated HCl + 0.05 M HI. The Sb activity was monitored by HPGe gamma spectroscopy of ^{124}Sb, whereas the Sn was monitored by ^{117m}Sn from the decay of ^{117}Sb ($t_{1/2} = 2.80$ h [18]). The separations were also performed approximately 1 day after irradiation, allowing the ^{117m}Sn to reach equilibrium with ^{117}Sb. A second experiment was additionally performed to assess elution curves. There, an activated Sn foil was allowed to decay until only ^{124}Sb activity remained; then, the same separation method was executed with an aliquot of purified ^{113}Sn added as tracer.

The separation of ^{197}Hg from Au target material was based on the Aliquot 336 liquid–liquid extraction described in Ref. [13]. Eichrom TEVA resin, containing 40 % w:w Aliquot 336 as extractant and acting as a selective anion exchanger, was chosen for this separation. Initially, batch experiments were performed to establish the uptake of Hg and Au on Eichrom TEVA resin. To 1.5-mL centrifuge vials, 5–10 mg of TEVA resin were weighed, and appropriate volumes of HNO_3 from 0.001 to 16 M were added. The resin was then placed on a rotary mixer for 1 h for preconditioning. A 20-µL spike, containing either ^{195}Au or ^{197}Hg in 2.0 M HNO_3, was added to the wet resin. The solutions were equilibrated for 3 h on the mixer, each sample counted with a HPGe detector for sufficient time to give ≥1000 counts in the desired photopeak, and then filtered through a 0.45-µm polytetrafluoroethylene (PTFE) filter to separate resin from solution. A 700-µL aliquot of each filtered solution was added to 320 µL of deionized water in a 1.5-mL centrifuge vial (to maintain initial counting geometry) and counted with the HPGe detector. The experimental parameters for the column study were based on the results from this batch study.

The Au foil was dissolved in 800 µL of aqua regia and evaporated to approximately 300 µL total volume. This solution was diluted to 2 mL by adding 1.7 mL of 1 M HNO_3. Two prepacked, 2-mL vacuum-flow TEVA columns were deployed in tandem to accomodate the target Au mass. A 24-hole polycarbonate vacuum box (Eichrom, Darien, IL, USA) with a pressure regulator was used to accelerate the elution process and maintain a flow rate of ~1 mL/min. The columns were conditioned with 10 mL of 1 M HNO_3 prior to use. The Au foil solution was added to the column, and two 2-mL rinses with 1 M HNO_3 were performed. The ^{197}Hg was then stripped off the column with 12 mL of 12 M HNO_3. This fraction was analyzed via HPGe gamma spectroscopy to ensure that ^{197}Hg had been eluted and that no ^{198}Au (produced from scatttered neutrons during the irradiation) was present in this fraction. Under these conditions the Au foil was verified to have been retained by the column.

Results and discussion

The speciation of In in the 1 M HCl column load solution should be dominated by the neutral $InCl_3$ complex, which is not retained on anion-exchange resin [15]. However, Sn(IV) in 1 M HCl forms a stable anion complex, $SnCl_6^{2-}$, which is strongly retained by the column [15, 19]. Since ^{113}Sn ($t_{1/2} = 115.1$ days [18]) has only weak characteristic gamma-rays, its activity is measured by its daughter, ^{113m}In ($E_\gamma = 391.69$ keV, $t_{1/2} = 1.658$ h [18]) when in secular equilibrium. The ^{nat}In was also measured through ^{113m}In activity, by counting early (soon after irradiation) before its ingrowth from ^{113}Sn, and by counting later (after secular equilibrium) to verify its absence (thus indicating no ^{113}Sn contamination). Figure 2 shows the gamma-ray spectrum of the activated ^{nat}In foil.

The "Day 1 Sn" in Fig. 3 shows the counts in each fraction immediately following the elutions of In and

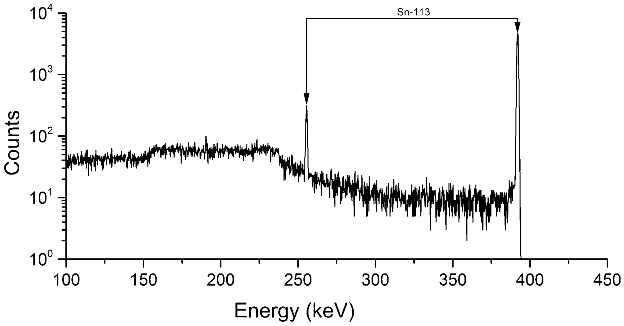

Fig. 2 Gamma-ray spectrum of activated ^{nat}In containing ^{113}Sn

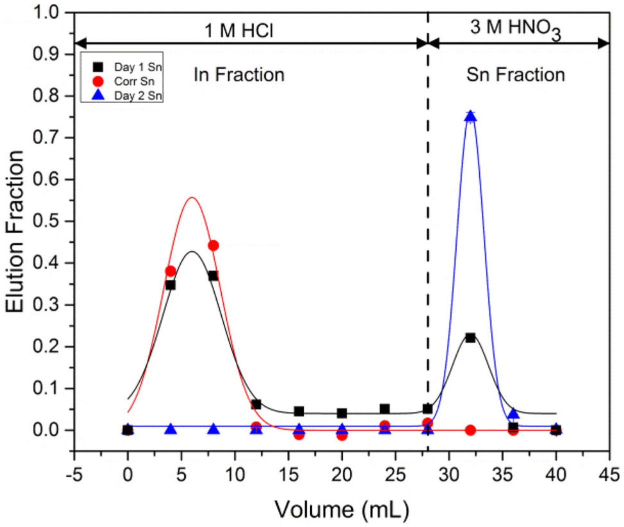

Fig. 3 Elution curves for ^{nat}In/^{113}Sn separation: In fraction from initial-day counts of ^{113m}In and ^{113}Sn fraction from day-two counts after equilibration of ^{113m}In

^{113}Sn. The ^{113}Sn elution is given by the "Day 2 Sn" curve after ^{113m}In has reached secular equilibrium with ^{113}Sn. The corrected day-one curve, "Corr Sn," reflects both the growth of ^{113m}In in the presence of ^{113}Sn on the column and the decay of ^{113m}In in the ^{nat}In fraction during counting and elution times. From this curve, it is apparent that all of the ^{nat}In, as traced by the ^{113m}In activity, resides in the In fraction, while the ^{113}Sn fraction is free of any independent In. After evaporation of the ^{113}Sn fraction, it was also observed that no visible residue was present, whereas the In fraction contained the solid ^{nat}In upon evaporation to dryness. The total recoveries of In and Sn were: (100 ± 20) and (78.7 ± 1.4) %, respectively. The uncertainties are 1σ standard deviation and were based only on counting statistics. The losses of Sn were attributed to the amount remaining on the column, possibly due to slow elution kinetics. It was impossible to quantify the In in the ^{113}Sn fraction due to the ingrowth of ^{113m}In during the slow elution process; this also made decay correction of the ^{113m}In in the In fraction more problemmatic and led to the larger uncertainty in In recovery.

Speciation of Sb(V) in concentrated HCl is presumably as $SbCl_6^-$, which contrary to conventional thinking, exhibits high retention on the cation exchange-resin AG 50W×8 (as described by Kraus et al. [17]). This is in contrast to Sn(IV), which forms the stable $SnCl_6^{2-}$ complex in HCl concentrations above 0.7 M and subsequently passes through the column under a concentrated HCl load solution [19]. Figure 4 shows an HPGe gamma spectrum of an activated Sn foil soon after irradiation and after the Sb radiochemical separation. Sn activity was monitored by ^{117m}Sn ($E_\gamma = 158.6$ keV, $t_{1/2} = 13.60$ days [18]) and Sb activity by both ^{120m}Sb ($E_\gamma = 1171.3$ keV, $t_{1/2} = 5.76$ days [18]) and ^{124}Sb ($E_\gamma = 602.8$ keV, $t_{1/2} = 60.20$ days [18]).

The elution curves shown in Fig. 5 are from separation of an activated Sn foil performed long after the decay of all short-lived Sb products (approximately 1 month). Only ^{117m}Sn (low statistics) and ^{124}Sb were detectable, and a small aliquot of ^{113}Sn tracer was used to assay the Sn foil.

As shown in Figs. 4 and 5, an efficient separation of ^{124}Sb from the irradiated ^{nat}Sn foil was developed. Due to slow Sb elution kinetics and the desire to minimize elution volume, since evaporating the (very volatile) ^{124}Sb fractions was required to change the solution matrix, $\leq$10 mL of the concentrated HCl/0.05 M HI solution was used. As a result, only (71.2 ± 7.7) % ^{124}Sb was recovered, while the rest presumably remained on the column.

The extractant Aliquat 336 sorbed on the TEVA resin is an anion-exchange medium. In the 1 M HNO_3 column-load solution, it was expected that Hg would form an anionic complex and be retained by the resin, while at higher concentrations form a non-anionic compelx and be eluted [13]. Under these conditions, Au forms species strongly absorbed by the resin, as observed in other anion-exchange systems [13, 20]. The Hg behavior was assessed by gamma spectroscopy of the ^{197m}Hg ($E_\gamma = 133.99$ keV, $t_{1/2} = 23.8$ h [18]) isotope. Because of scattered neutrons

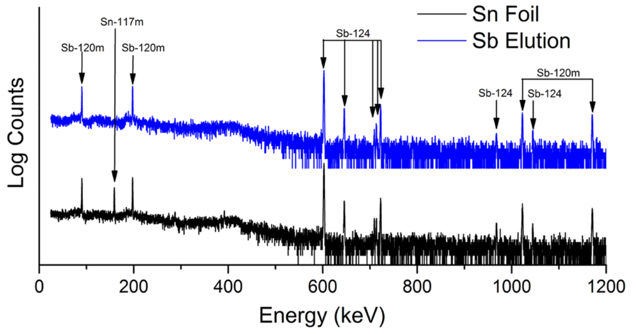

Fig. 4 Gamma-ray spectra of the irradiated ^{nat}Sn foil (*bottom trace*) and the Sb combined elution fraction after separation (*top trace*)

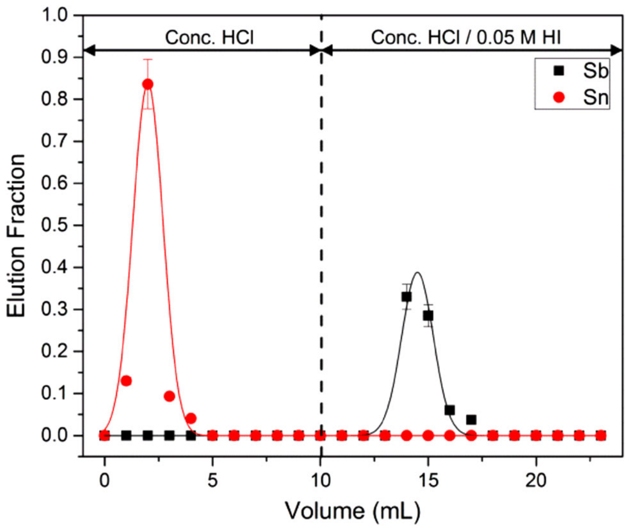

Fig. 5 Elution curves for Sn and Sb. Uncertainties are 1σ

at the target chamber, ^{198}Au ($E_\gamma = 411.80$ keV, $t_{1/2} = 2.70$ days [18], formed via ^{197}Au(n,γ)^{198} Au) was also produced during bombardment, yielding a convenient tracer for quantifying the Au content in the elution fractions. Figure 6 shows the gamma-ray spectra of the irradiated Au foil and the separated ^{197}Hg elution fraction.

As seen in Fig. 7, both Au and Hg have strong uptake at 1 M HNO_3 (chosen as the load solution for the column separation), but Hg retention is negligible above 10 M HNO_3 while Au is still reasonably sorbed up to $\sim$13 M HNO_3. Because the Au foil was left on the TEVA columns, no elution curve was obtained; however, the macroscopic Au band visible on the columns migrated only to approximately 1/3rd of the way through the lower tandem column. Table 1 summarizes the results from three individual Au foil separations.

In each ^{197}Hg fraction, no detectable ^{198}Au was observed, indicating an effective separation of Hg from Au. The second column in Table 1 is a calculated limit based on the minimum detectable activity [21]. Upon evaporation of the Hg fraction, no visible residue was observed.

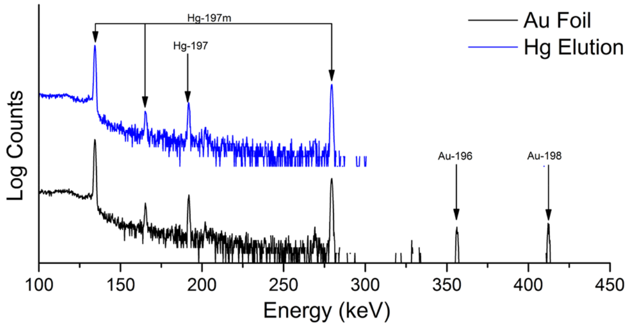

Fig. 6 Gamma-ray spectra of the irradiated Au foil (*bottom trace*) and the separated ^{197}Hg elution fraction (*top trace*)

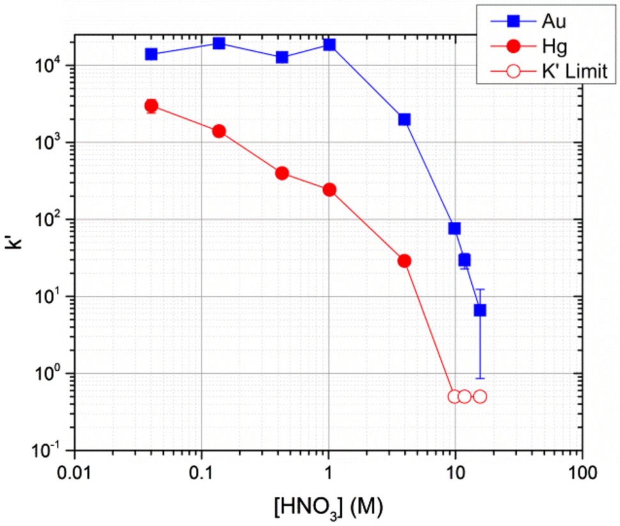

Fig. 7 The batch uptake (k′) of ^{195}Au and ^{197}Hg as a function of nitric acid media on TEVA resin with a 3-h equilibration time

Table 1 Summary of Au/Hg separation on Eichrom TEVA resin

Au foil	Au in Hg fraction (%)	Hg recovery (%)
Au1	<3.2	85.8 ± 0.6
Au2	<4.7	87.1 ± 0.6
Au3	<3.9	87.8 ± 0.6

Conclusions

No-carrier-added radionuclides of flerovium and element 115 homologs and pseudo-homologs (Sn, Hg, and Sb) were produced at the LLNL CAMS facility via bombardment of natural-isotopic foils with 12–15 MeV protons for 0.6–4 μA-h ($\leq 2.5 \times 10^{12}$ pps). The following reactions were used for isotope production: ^{nat}Sn(p,n)^{124}Sb, ^{197}Au(p,n)^{197}Hg, and ^{nat}In(p,n)^{113}Sn.

Separation procedures for the isolation of the NCA activities were established. An anion-exchange method in hydrochloric and nitric acid solutions was developed to separate the ^{113}Sn radiotracer from ^{nat}In targets. A cation-exchange method in hydrochloric and mixed hydrochloric/hydroiodic acid matrices was used to isolate ^{124}Sb from ^{nat}Sn. A separation based on Eichrom TEVA resin, which used Aliquot 336 as the extractant, was developed to separate ^{197}Hg from target Au. Batch distribution studies were performed to establish the affinity of Au and Hg for the TEVA resin, and those results were implemented in the experimental design. In all cases, NCA radionuclides were obtained and confirmed by HPGe gamma spectroscopy.

The 10–MV, tandem Van-de-Graaff accelerator at the LLNL CAMS facility was demonstrated to be sufficient for the production of these NCA tracers for transactinide homolog studies. The target chamber used for these experiments can be deployed with a wide range of specific metal foils for production of various NCA radionuclides. This feature is useful for the synthesis of other transactinides or tracers for use in chemical yield measurements and other procedures in radiochemistry experiments.

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