Development of a procedure for the radiochronometric analysis of a mock ^{224}Ra sample: towards a nuclear forensic analysis of a historical ^{226}Ra pigment sample

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^{226}Ra was identified as a potential threat in nuclear terrorism events by the International Atomic Energy Agency in 2008 for usage in radiological dispersive devices [1]. In the field of nuclear forensics, literature pertaining to ^{226}Ra radiological samples is nonexistent. This work aims to develop a methodology for the nuclear forensic analysis of ^{226}Ra pigment samples, a common product of the early 1900s from the watch dial industry [2]. As part of this analysis, the pigment sample age, or "time since purification," will be determined by measuring absolute quantities of ^{210}Pb and ^{210}Po (daughters in the ^{226}Ra decay chain) relative to ^{226}Ra. To perform a radiochronometric analysis, the solid pigment sample must be quantitatively dissolved, separated via chromatographic methods, and assayed by the respective radiation detector. Preliminary results of the dissolution and separation procedure will be discussed.

A mock ^{224}Ra pigment sample comprised of ZnS (>99% w/w) and a ^{224}Ra salt (<1% w/w) [2-4] was used to develop all procedures for dissolution and separation. Other radiotracer salts such as ^{133}Ba, ^{212}Pb, ^{209}Po, ^{207}Bi, and ^{65}Zn (where ^{65}Zn was chemically incorporated into the lattice structure of ^{nat}ZnS) were incorporated into the pigment. The mock pigment sample was dissolved using a mixture of 0.8 M tetrakis(hydroxymethyl)phosphonium chloride (THPC) solution and 2 M NH_4Cl solution stirred at ~85 °C for 2 h. A small quantity of mock pigment (~0.005 g) was dissolved using 5 mL of the dissolution solution, and radionuclide quantities were assayed by gamma spectrometry with an HPGe detector. The dissolution efficiencies for $^{133}BaCl_2$ (γ = 356 keV), $^{224}RaCl_2$ (γ = 240 keV), $^{212}PbCl_2$ (γ = 238 keV), and ^{65}ZnS (γ = 1115 keV) were 103 ± 8%, 100 ± 3%, 103 ± 3%, and 100 ± 2%, respectively. Mixed solutions of THPC and NH_4Cl have proven effective for the quantitative dissolution of the mock ^{224}Ra pigment sample.

There is significant literature on column chromatography of many elements and their behaviors with various resin and acid systems [5]. However, THPC and NH_4Cl are uncommon reagents, so the literature is very sparse. In this case, removing all elements from the THPC/NH_4Cl matrix and converting to a more commonly studied medium (such as HCl or HNO_3) is advantageous. Batch studies were performed to determine the chemical behavior of Ra, Ba, Pb, Bi, Po, and Zn in the THPC/NH_4Cl matrix. Chelex-100 was the selected resin due to its effective ability to remove metal ions from dilute salt solutions [6]. Weight distribution coefficient values, D_w, were measured to be ≥ 1000 for all studied elements in dilute solutions of THPC/NH_4Cl (0.008 M and 0.02 M, respectively) indicating retention onto the resin under these conditions. Next, the common ion in the matrix is Cl^-, so it was desirable to switch to HCl media for elemental separation after retention on Chelex-100. Batch studies were performed for all elements between 0.01 M and 10 M HCl on Chelex-100 resin. These data showed retention of all elements under dilute conditions (0.01 M HCl). Furthermore, 1 M HCl allowed for the desorption of Ra, Ba, Pb, and Zn and retention of Bi on the resin; Bi was recovered using 10 M HCl. Using this information, a separation scheme was determined. Starting from dissolution, a 500 µL cocktail mixture of

known quantities of ^{244}Ra, ^{133}Ba, ^{212}Pb, ^{207}Bi, and ^{65}Zn dissolved in H_2O was added to a round bottom flask containing a 5 mL solution of THPC and NH_4Cl (0.008 M and 0.02 M, respectively). A 0.3 g Ni foil was added to the mixture to simulate the auto-deposition of ^{209}Po for its separation from the solution. After 2 h of heating (~75 °C) and stirring, 100 µL was removed and diluted to 10 mL with H_2O. The pH of the resulting solution was adjusted to 4.5 using a 1.0 M solution of NaOH. After 30 min, this solution was loaded onto the reverse preconditioned (10 M HCl, 1 M HCl, 0.01 M HCl, and diluted THPC/NH_4Cl solution, in that order) Chelex-100 column (8 mm diameter; 3 cm bed height). The column was rinsed with 5 mL of 0.01 M HCl to retain ^{224}Ra, ^{133}Ba, ^{212}Pb, ^{207}Bi, and ^{65}Zn to switch from THPC/NH_4Cl media to HCl. Next, the column was rinsed with 5 mL of 1 M HCl to elute ^{224}Ra, ^{133}Ba, ^{212}Pb, and ^{65}Zn. Finally, the column was rinsed with 5 mL of 10 M HCl to recover ^{207}Bi. The results of this experiment are shown in Fig. 1.

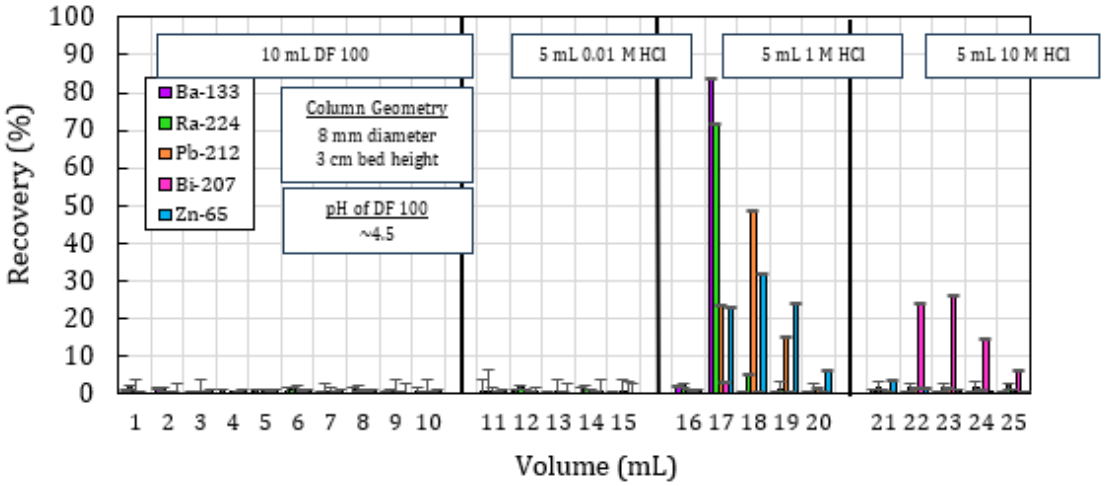

FIG.1. Chromatographic separation of ^{224}Ra, ^{133}Ba, ^{212}Pb, ^{207}Bi, and ^{65}Zn using Chelex-100 resin. The load solution of diluted THPC/NH_4Cl (dilution factor, DF, of 100) was adjusted to pH 4.5 and equilibrated for 30 min before separation. Each element appeared in their anticipated fractions according to batch study experiments.

Overall, according to the batch study experiments, this experiment has shown recovery of all elements that appear in the anticipated fractions. In addition, all elements could be recovered from the THPC/NH_4Cl matrix, making alpha spectrometry a feasible assay technique (THPC/NH_4Cl previously formed a residue that inhibited α particles from reaching the detector [7]).

In future work, ^{209}Po will be incorporated into the dissolution and separation procedures to confirm its auto-deposition and removal from THPC/NH_4Cl matrices. Additionally, milligram quantities of ^{nat}ZnS will be used for the combined dissolution and separation procedure to ensure possible separation even with large quantities of Zn. These procedures will ultimately be applied to the mock ^{224}Ra pigment sample for the radiochronometric determination of the known sample age. Finally, these procedures will be used to age date a historical ^{226}Ra pigment sample.

A dissertation based on the results discussed above is currently being written.

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