Dissolution of a ^{224}Ra mock sample for future nuclear forensic analyses of a ^{226}Ra pigment sample

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Radium pigments and paints were popularized in the early 1900s due to their attractive, self-luminescent properties with applications in the watch dial industry, the military, and households [1-3]. Many biological and environmental hazards have been identified with the use of these products [1,3,4]. Consequently, the IAEA has identified ^{226}Ra, the major radioactive component of radium pigments and paints, as a potential threat in nuclear terrorism events in the form of radiological dispersive devices [4,5]. To combat such events, the field of nuclear forensics was created as a method of determining source attribution of materials of unknown origins and intentions [5]. Many nuclear forensic techniques used to analyze nuclear materials are well documented in the literature [3]; however, literature pertaining to ^{226}Ra pigments and paints regarding nuclear forensics is nonexistent. This work aims to develop a methodology for the nuclear forensic analysis of ^{226}Ra pigment and paint samples. This report will detail necessary procedures for recreating the radium pigment sample in addition to procedures for the dissolution of said sample. Preliminary results are reported here.

For this project, the main nuclear forensic signature will be derived from a radiochronometric analysis of a historical ^{226}Ra pigment sample. The chosen radiochronometric parent/daughter pairs are ^{210}Pb/^{226}Ra and ^{210}Po/^{226}Ra due to the daughters' long half-lives (22 y and 138 d, respectively) and favorable decay characteristics (easily detected γ line and α particle, respectively). Although the historical ^{226}Ra pigment sample has already been received, the sample is very limited in quantity; thus, it is necessary to attempt to recreate the sample based on a literature description of these samples in the early 1900s for initial tests. The predicted composition of the sample is ~ 99% ZnS and ~1% ^{226}RaX$_2$ (X=Cl or Br) [1]. To replicate this mixture, ^{224}Ra/^{133}Ba (Ba is the homolog of Ra chemically) will be substituted for ^{226}Ra as they are more available commercially. The procedure for creating the mock radium pigment sample is as follows: First, ^{224}Ra is eluted via a ^{228}Th generator. ^{228}Th is loaded in conc. HCl solution to a DGA-branched resin column with 1 mL of resin. The column is then rinsed with 5 mL of conc. HCl. The eluate then contains the ^{224}Ra. The eluate is evaporated to dryness and then reconstituted with 2 mL of Millipore Omnitrace 18.2 MΩ H$_2$O. this solution is evaporated to dryness once more. Next, it is reconstituted with 1 mL of Millipore 18.2 MΩ Omnitrace H$_2$O. To this solution, ~40 mg of ZnS is added and the slurry is evaporated to leave a radioactive material containing ZnS powdered sample. The ^{224}Ra in this sample has a half-life of 3.66 d, so the sample will usually last a maximum of 30 days.

Before any radiochronometric analysis can be performed, it is necessary to convert the sample into a form that can easily be manipulated via dissolution. Surprisingly, dissolving this sample was not straightforward. Due to very dissimilar chemical properties between ZnS and RaX$_2$ (in addition to all its daughters), mineral acids which are commonly used to dissolve many radiological samples are ineffective in this case [6,7]. Various chelators such as EDTA have been explored as well with no success. In recent literature, phosphonium salts have tested for their effectiveness on FeS scales in oil fields with promising results [8]. The dissolution of FeS scales using a mixture of tetrakis(hydroxymethyl)phosphonium sulfate

(THPS) and ammonium chloride (NH$_4$Cl) at temperatures of approximately 85 °C resulted in ≥90% efficiency [6]. In hopes of achieving similar results, these methods were tested on the mock ^{224}Ra pigment sample in addition to a mock ^{133}Ba pigment sample. A 1 M solution of tetrakis(hydroxymethyl)phosphonium chloride (THPC) was mixed with NH$_4$Cl in a ratio of 10:1 by mass followed by the mock pigment sample (0.08% by mass of the total solution) and stirred at ~85 °C for 2-4 h. Overall, the dissolution efficiencies for ^{133}BaCl$_2$, ^{224}RaCl$_2$, and ^{212}PbCl$_2$ (^{212}Pb is a daughter in ^{224}Ra's decay chain) were 103 ± 8%, 100 ± 3%, and 103 ± 3% respectively. As for ZnS, the solid qualitatively appears to dissolve completely, but the dissolution efficiency has yet to be measured. This will involve tracing ZnS with ^{65}Zn which will be part of future studies. Overall, this mixture of THPC and NH$_4$Cl will be used for future studies with the mock pigment sample.

Once the sample could be dissolved, it was necessary to determine a separation pathway of elements within the pigment to appropriately isolate the radiochronometers of interest (^{210}Pb/^{226}Ra and ^{210}Po/^{226}Ra). Generally, column chromatography is the most commonly used technique for separation of elements and there is significant literature on various elements and their behaviors with various resins and acid systems [9, 10]. However, THPC and NH$_4$Cl are less common reagents to work with and literature is very sparse [11] so converting the THPC/NH$_4$Cl solution to a more commonly studied medium (such as HCl or HNO$_3$) is not plausible. Additional research is necessary to study the behavior of the elements in this system (Ra, Ba, Pb, Po, Bi, and Zn) in solutions of THPC and NH$_4$Cl on various resins to best separate them. Weight distribution ratios, D_w, are used to quantify an element's affinity to a particular resin under certain conditions (such as acid concentration). These values can be experimentally measured using batch studies given a specific acid media, resin, and element of interest. In Fig. 1, the D_w values for ^{133}Ba were measured in solutions of THPC on Chelex-100 ion exchange resin. The results of this
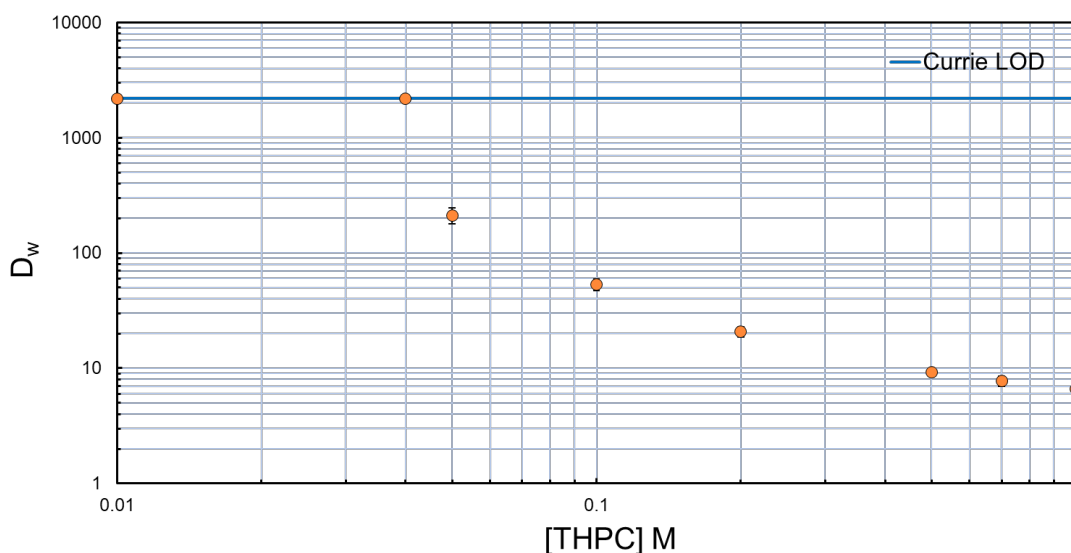

Fig. 1. Measured D_w values for ^{133}Ba on Chelex-100 in solutions of THPC. High D_w values indicate a strong affinity to the resin while low values indicate low uptake of ^{133}Ba. The Currie LOD illustrates the limits of detection. [12].

experiment showed that Ba does not have a strong affinity for Chelex-100 at higher concentrations of THPC.

Currently, the information on an effective pathway for separation of elements of interest is incomplete. Future work will be focused around performing more batch studies including ^{65}Zn in solutions of THPC and NH$_4$Cl with various resins because Zn is 99% of the sample matrix. Its elimination is important so that it does not affect the chemistry of elements in much lesser quantities (such as Ra, Pb, Po, and Bi). If further batch studies show no promise in separating these elements given the current THPC/NH$_4$Cl solution they are dissolved in, it may be necessary to find a way to digest the THPC and convert the solution to more commonly studied media.

In all, this work aims to perform a nuclear forensic analysis of a historical ^{226}Ra pigment sample. Presently, this work has discussed efforts made toward performing a radiochronometric analysis including the dissolution and separation of a mock, ^{224}Ra pigment sample. After successfully producing a procedure for making a mock pigment sample, the dissolution of the sample has shown ~100% dissolution efficiency. Investigation of the separation capabilities of various resins and THPC/NH$_4$Cl solutions are still ongoing and a full radiochronometric analysis on the mock sample is to be accomplished in the near future. In conclusion, this work aims to aid in overall national security by pioneering the field of ^{226}Ra nuclear forensics.

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