

Development of a radiochronometric procedure for the analysis of ^{226}Ra pigment and paint samples for nuclear forensics

J.R. Garcia and C.M. Folden III

Radium pigments and paints were used in the early 1900s for the watch dial industry, military instrumentation, and household applications due to their attractive, self-luminescent properties [1-3]. These pigments and paints are no longer used modern day as they pose many health hazards [1,3,4]. In addition, the International Atomic Energy Agency (IAEA) has identified ^{226}Ra , the main radioactive component within the sample, as a potential threat in the use of radiological dispersive devices (RDDs) [4,5]. To combat nuclear terrorism events, nuclear forensic analytical techniques are used for origin attribution in interdicted samples [5]. Many techniques used to analyze nuclear materials are well documented; however, forensic techniques used to analyze ^{226}Ra radiological samples are nonexistent within the literature. This work focuses on developing a methodology for the radiochronometric analysis of these pigments and paints. Preliminary results are reported here.

For this project, chosen radiochronometers were $^{210}\text{Pb}/^{226}\text{Ra}$ and $^{210}\text{Po}/^{226}\text{Ra}$ due to their long half-lives that are useful for performing relatively long chemical separations which will be necessary for this project. In preparation for assaying the radioisotopes of interest, a “mock” sample was created as a surrogate for the real radium pigment sample. Activity for this project is yet to be received and in addition, the sample will be very limited in quantity. Based on the literature regarding the components of the sample, it is predicted to consist of 99% ZnS , ~1% RaBr_2 , and <<1% PbBr_2 ; Ba will be substituted for Ra in this case due to their very similar chemical properties. With the mock sample, the dissolution properties were examined and an attempt was made to isolate the components from one another. Samples were also assayed using ICP-MS.

Due to very dissimilar properties of the chemical components of the pigment sample, dissolution was not a trivial problem. This sample did not dissolve to completion in any mineral acids (rather new, more insoluble products formed such as PbS) and was determined to dissolve in an unsafe manner with concentrated acids (violent sputtering). Various chelators were explored with little success as well. The chemical reagents that have shown the best results are a combination of tetrakis (hydroxymethyl) phosphonium sulfate (THPS) and ammonium chloride (NH_4Cl). This mixture was found to qualitatively dissolve to completion in ~30% THPS, ~10% NH_4Cl , and ~60% H_2O followed by an addition of concentrated HCl (after 24 h). Dissolution efficiency will be determined for this procedure using ICP-MS in the near future.

After the sample is completely dissolved, elemental separation is possible using column chromatography. The first step is to determine the separation factors of the elements of interest; an attempt was made to measure the k' values, retention factors, of Ba and Pb in a solution of THPS/ $\text{NH}_4\text{Cl}/\text{HNO}_3$ and LN resin (see Table I). Unfortunately, initial results were not reproducible. One likely possibility for this inconsistency is due to the Fe (~5 ppm), Ba (~5 ppb), and Pb (~5 ppb) contamination that is present in the starting reagents, THPS and NH_4Cl . These reagents cannot be purchased ultrapure, so procedures are being developed for the ultra-purification of these materials using PFA materials and recrystallization techniques (see Fig. 1). Recrystallization is a basic technique to purify

Table 1. Measured k' values for lead and barium in the THPS/NH₄Cl/HNO₃ matrix and LN resin with varying concentration of HNO₃. The upper limits of the k' values are provided due to high errors amongst triplicate measurements.

[HNO ₃] (M)	Pb k'	Ba k'
0.01	< 0.4	< 0.5
0.05	< 0.4	< 0.1
0.1	< 0.4	< 0.1
0.5	< 0.1	< 0.1
1	< 1	< 0.7

a chemical product by using a solvent that does not change the chemistry of your product at hot temperatures. For both THPS and NH₄Cl, acetic acid was found to have the necessary properties for the recrystallization of both. The acetic acid would need to be ultra-purified first before recrystallization to minimize the number of impurities that could incorporate into the crystal structures. Currently, our primary focus is to recrystallize the starting reagents to minimize the contamination of elements that may be interfering with the k' results. Once these reagents have been cleaned, the dissolution efficiency and k' values will be re-measured and hopefully will be more consistent. Once these studies are complete and the Ra samples are received, the final forensics analysis can begin



Fig. 1. Recrystallization of NH₄Cl using acetic acid after 1 week of crystal growth.

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