Radiochronometric analysis of a mock ^{224}Ra pigment sample: Towards a nuclear forensic analysis of a historical ^{226}Ra pigment sample

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In 2008, the International Atomic Energy Agency identified ^{226}Ra as a potential nuclear security threat due to its potential usage in radiological dispersal devices [1]. Despite this, nuclear forensic literature on ^{226}Ra-containing samples remains nonexistent. This work addresses this underexplored area by developing a methodology for the nuclear forensic analysis of a historical ^{226}Ra pigment sample, a commercial product commonly used in the early 1900s watch dial industry [2]. This work aims to estimate the sample's age or "time since purification" by determining the absolute quantities of decay products ^{210}Pb and ^{210}Po relative to the parent, ^{226}Ra. This approach involves the dissolution and separation of the pigment sample, chromatographic separation of the constituents, and assay by radiation detection methods. Preliminary findings from the developed processes are presented.

To develop and validate all analytical procedures, a mock ^{224}Ra pigment sample was prepared in anticipation of receiving only a limited quantity of historical material. The mock pigment consisted primarily of ZnS (>99% w/w) and a ^{224}Ra salt (<1% w/w), with additional radiotracers (^{133}Ba, ^{209}Po, ^{207}Bi, and ^{65}Zn) to validate procedural efficiency [2-4]. ^{65}Zn was chemically integrated into the ZnS lattice to simulate the behavior of matrix-bound Zn. As part of the final preparations for the pigment, ^{224}Ra was chemically purified from its daughter, ^{212}Pb, to reset the forensic clock so that subsequent ^{212}Pb ingrowth will serve as a chronometric signature for dating. Dissolution was executed by dissolving ~40 mg of mock pigment using a mixed solution of 0.8 M tetrakis (hydroxymethyl)-phosphonium chloride (THPC) and 2 M NH4Cl, stirred at 70-80 °C for 2 hrs, a method based on previous reports [5-7]. Gamma spectrometry using an HPGe detector was used to quantify radionuclide recovery. The dissolution efficiencies for ^{133}BaCl2 (γ = 356 keV), ^{224}RaCl2 (γ = 240 keV), ^{212}PbCl2 (γ = 238 keV), and ^{65}ZnS (γ = 1115 keV) were 99 ± 3%, 100 ± 3%, 100 ± 2%, and 98 ± 2%, respectively. Therefore, mixed solutions of THPC and NH4Cl are effective for the quantitative dissolution of the mock ^{224}Ra pigment sample.

Following dissolution, a separation scheme was developed to isolate radionuclides from the THPC/NH4Cl matrix. Given the limited literature available for this unique matrix, converting the radionuclides into a more well-studied matrix, such as HCl, was advantageous for their further chemical separation and assay. Previous work [5] evaluated the weight distribution coefficient (Dw) of all target elements (^{224}Ra, ^{212}Pb, ^{133}Ba, ^{65}Zn, ^{207}Bi, and ^{210}Po) in solutions of THPC/NH4Cl and HCl on Chelex-100 resin. Batch studies showed that adjusting the pH between 3.8 and 4.5 enabled quantitative recovery of ^{224}Ra, ^{133}Ba, ^{65}Zn, ^{207}Bi, and ^{210}Pb in their respective eluents [5]. To continue, the nuclides ^{224}Ra, ^{133}Ba, ^{212}Pb, and ^{65}Zn were recovered from Chelex-100 using 1 M HCl, and then ^{207}Bi was recovered using 10 M HCl. ^{224}Ra, ^{133}Ba, ^{212}Pb, and ^{65}Zn elute in the same fractions, so their further chemical purification was necessary, especially to prepare ^{224}Ra for assay via alpha spectrometry. These fractions were diluted to 0.5 M HCl using H_2O and loaded onto a preconditioned Dowex 50x8 column. ^{212}Pb and ^{65}Zn have slight

separation in 0.5 M HCl, but because they are both assayed via gamma spectrometry, complete separation of these radionuclides is not of utmost importance. By using 3 mL of 1 M HCl following the 0.5 M HCl eluent, the last remnants of ^{65}Zn were recovered. Separating ^{224}Ra from ^{65}Zn was the ultimate goal to achieve improved resolution of the stippled sample for alpha spectrometry. ^{224}Ra and ^{133}Ba were finally recovered from the column using 5 mL of 5 M HCl. A 1% aliquot was removed and assayed via alpha spectrometry, and the peak resolution FWHM was measured to be ~30 keV, deemed an acceptable resolution for analysis.

Due to its unique chemical behavior, Po required a distinct separation pathway. Its interaction with Chelex-100 differed from all other elements, as it was not as strongly adsorbed ($D_w \approx 60$) in dilute solutions of THPC/NH4Cl on Chelex-100 resin. However, in HCl media, Po exhibits strong retention across all concentrations, effectively preventing its recovery once bound to the resin. As such, Po could not be reliably assayed following contact with Chelex-100. An alternative strategy for Po recovery was pursued, which involved its known spontaneous deposition onto Ni foil, notably in 0.1-1 M HCl with heat and stirring [8, 9]. 210Po deposition onto Ni foil in solutions of THPC/NH4Cl has not been studied previously in the literature; thus, kinetic uptake studies were conducted in a mixed solution of 0.8 M THPC and 2 M NH4Cl with heat and stirring over 2 hrs. The result of this study was relative recoveries of ~46%. Subsequent experiments with a small addition of 0.01 M HCl significantly enhanced recovery, leading to a final deposition efficiency of 92 ± 1% after five trials. These results demonstrate that spontaneous deposition onto Ni foil is a viable and reproducible strategy for isolating Po from THPC/NH4Cl matrices. This method will be applied to recover ^{210}Po as part of the radiochronometric analysis of the historical ^{226}Ra pigment sample, providing a practical alternative to the resin-based separation.

All developed methods were applied to determine the age of a mock ^{224}Ra pigment sample with a known purification time and date of 2331 hrs on 04/07/25. The reference measurement point for age determination was defined as the time of complete dissolution, 1743 hrs on 04/08/25, when the sample's liquid geometry matched that of the ^{152}Eu calibration source used for absolute quantification. At this point, ^{212}Pb activity was measured by gamma spectrometry, and the ^{212}Pb/^{224}Ra activity ratio was used to calculate the time since purification using first- and fourth-order Bateman equations. The measured age was 19 ± 2 hrs, in agreement with the known time interval of 18 hrs, validating the accuracy of the radiochronometric approach. Fig. 1 illustrates the results of the radiochronometric analysis.

A complete methodology was developed for the dissolution, separation, and radiochronometric analysis of a mock ^{224}Ra pigment sample. These procedures enabled successful radiochronometric dating of the mock ^{224}Ra pigment with a known purification date, demonstrating accuracy and reproducibility. The validated method is now being applied to the forensic analysis of a historical pigment sample, and a dissertation and publications on this work are currently in preparation.

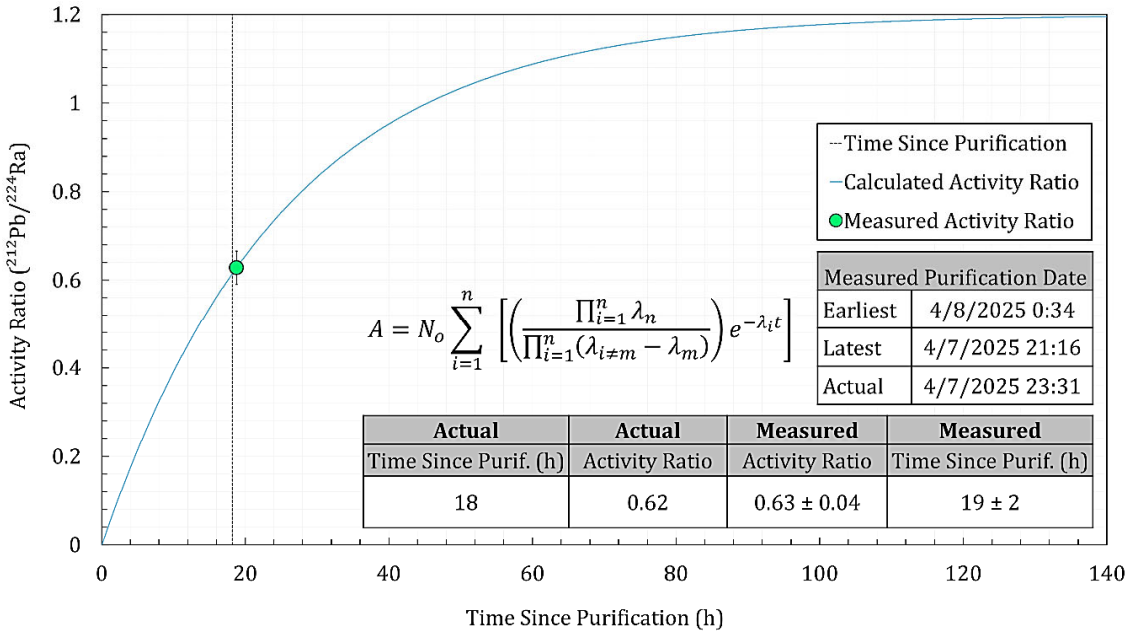

Fig. 1. Radiochronometric analysis of the 224Ra pigment sample. The blue, solid curve represents the calculated 212Pb/224Ra activity ratio over time based on the first- and fourth-order Bateman equations. The measured activity ratio is shown as a single data point. The vertical, dashed line represents the actual time since purification.

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