Determination of Origin and Intended Use of Plutonium Metal Using Nuclear Forensic Techniques

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Abstract

Nuclear forensics techniques, including micro-XRF, gamma spectrometry, trace elemental analysis and isotopic/chronometric characterization were used to interrogate two, potentially related plutonium metal foils. These samples were submitted for analysis with only limited production information, and a comprehensive suite of forensic analyses were performed. Resulting analytical data was paired with available reactor model and historical information to provide insight into the materials' properties, origins, and likely intended uses. Both were super-grade plutonium, containing less than 3% ^{240}Pu , and age-dating suggested that most recent chemical purification occurred in 1948 and 1955 for the respective metals. Additional consideration of reactor modelling feedback and trace elemental observables indicate plausible U.S. reactor origin associated with the Hanford site production efforts. Based on this investigation, the most likely intended use for these plutonium foils was ^{239}Pu fission foil targets for physics experiments, such as cross-section measurements, etc.

Keywords: nuclear forensics, plutonium, Special Nuclear Materials, fission foil, chronometry, age dating

Introduction

After the dissolution of the Soviet Union in the early 1990s, a large number of incidents of illegal possession and trafficking of nuclear materials were reported[1]. Illicit activities involving nuclear materials still pose a great threat to international security as these materials have the potential to be used for nuclear terrorism. Nuclear forensics is a multi-disciplinary scientific field that was established to investigate the origin and intended use of interdicted nuclear materials[2–7]. Numerous analytical techniques are utilized in nuclear forensic investigations, including radiometric, mass spectrometric, microscopic, physical measurements, and computer simulations[2–12]. The use of particular analytical techniques depends on the characteristics of the material. A sample analysis plan developed on a case-by-case basis for individual samples identifies suitable analyses to answer questions being asked by the investigative agencies. The factors influencing the analysis plan are the nuclear material type, material burnup, quantity of the material, and material packaging[13]. The plan can be modified during the course of analysis in response to the most current findings.

One of the most important elements in nuclear forensics is plutonium (Pu) as it is one of the primary materials in defense applications[14]. This paper describes nuclear forensic analyses performed on plutonium metal samples. Several authors have published nuclear forensic work performed on plutonium oxide, plutonium metal, and plutonium sulfate tetrahydrate materials[2,3,11,12,15,16]. Plutonium is typically produced in a nuclear reactor through neutron capture of uranium (U) and subsequent beta decays. Therefore, the isotopic composition of seized plutonium material can be used to determine the irradiation history of the material, such as reactor type, irradiation condition, and enrichment of the starting material. The irradiation information will also assist in tracking back to the origin or source of the material. In addition, the isotopic abundance of ^{240}Pu directly determines the

“grade” of the plutonium. The plutonium grade (Table 1) often provides information on the intended use of the material.

Table 1 Plutonium grade[7]

Plutonium grade	²⁴⁰ Pu (%)
Super-grade	< 3%
Weapon-grade	< 7%
Fuel-grade	between 7% and 18% incl.
Reactor-grade	> 18%

The age or “model age” of the material is important in nuclear forensics as it can establish the production date or last separation date of the sample[17]. The age of a plutonium sample can be determined from the in-growth of plutonium progeny nuclides. The most commonly utilized chronometers for plutonium are ²³⁸Pu/²³⁴U, ²³⁹Pu/²³⁵U, ²⁴⁰Pu/²³⁶U and ²⁴¹Pu/²⁴¹Am[2]. The assumption in the age calculation is that initially the sample is free of progeny nuclides[18,19]. However, the uranium and americium (Am) separation from plutonium during the sample purification process can be incomplete and could result in an incorrect “model age” of the sample[20,21]. The advantage of using multiple chronometers is that systematic bias from incomplete separation of uranium and/or americium from reprocessing can be detected through inconsistent results[2,11,22]. In the present work, we investigated two nickel (Ni) clad plutonium metal foils for the origin and intended use of the samples.

Experimental

Material

Two plutonium foils were received encapsulated in nickel cladding designed to negate the potential spread of radioactivity and to provide protection from oxidation of the plutonium metal. Visual inspection showed discoloration on the nickel on both samples but the cladding was fully intact with no sign of exposed plutonium. There were numbers written on the nickel surface; foil 1 had “4” written on both sides in black and had a red line on one side, whereas foil 2 had “9” and “16” written on one side

and nothing on the other side. Sample images are shown in Figure 1 and complete physical measurements of both are summarized in Table 2. These samples have similar physical dimensions with Foil 2 being slightly larger and heavier than Foil 1.

Figure 1 Nickel clad plutonium foils showing surface markings. (A) Foil 1, (B) Foil 2

Table 2 Sample masses and physical dimensions

Sample	Mass (g)	Diameter (cm)	Thickness (cm)
Foil 1	0.44795 ± 0.00001	1.2657 ± 0.0003	0.0363 ± 0.0003
Foil 2	0.51856 ± 0.00001	1.2779 ± 0.0003	0.0498 ± 0.0003

Gamma-ray spectroscopy

Plutonium samples were evaluated using a coaxial, electrically cooled 40% relative efficiency high-purity germanium (HPGe) detector (Model GMX40P, ORTEC, Oak Ridge, USA) with a beryllium (Be) end window. The resolution (FWHM) for the detector was 1.90 keV at 1.33 MeV. The detector system was energy and peak resolution calibrated using NIST traceable ^{166m}Ho calibration source procured from Eckert & Ziegler Analytics (Atlanta, GA, USA). Gamma-ray spectroscopy was mainly used as a screening tool and was performed within the first 24 hours of receipt of the samples. Gamma-ray spectra were

evaluated using Los Alamos National Laboratory (LANL) developed Fixed-Energy, Response Function Analysis with Multiple Efficiency (FRAM) 5.2 code[23,24] to determine plutonium isotopic abundances along with ^{241}Am and ^{237}Np concentrations.

Light Microscopy

Two digital light microscopes were used to supplement and assist in using the μXRF imaging capabilities more effectively. The two microscopes used were: a Dino-Lite AM7013MZTS (New Taipei City, Taiwan) and a Dino-Lite AM7013MZT4 (New Taipei City, Taiwan). These digital microscopes have the capability of determining dimensions in collected images by calibrating with a micro-scale ruler.

Micro X-ray fluorescence spectrometry (μXRF)

An EDAX Orbis PC micro-XRF (μXRF) instrument was used in the experiment for a non-destructive elemental analysis. High spatial resolution data were acquired using a polycapillary optic producing a 30 micron diameter X-ray beam (FWHM intensity measured at the Mo $K\alpha$ energy). The instrument uses a 50 W rhodium X-ray anode and a 30 mm² silicon drift detector. X-ray source filters were used to improve the signal-to-background ratios. All spectra were collected with air in the instrument chamber to eliminate any possibility of radioactive contamination. The foils were mounted with the foil edge to be analyzed facing up toward the X-ray tube. The upright foil was then placed inside a plastic cup which was sealed with 6 micron Mylar on the analysis side. After analyzing a cut edge of each foil, they were remounted with the outer, intact edge facing up and analyzed again.

Sample dissolution

The sample dissolution was a two-step process as the plutonium metal was encapsulated in a nickel protective cover. Samples were first placed in 8M Optima grade nitric acid (HNO_3) (Fisher Scientific, NH, USA) to remove the nickel layer from the plutonium metal. The reaction was initially slow and low heat was applied to speed up the reaction. After a few minutes on the hot plate, the samples started to rapidly react with the HNO_3 and the solution turned to light green. The foils were removed from the hot

plate then rinsed with 8 M HNO_3 . The foils were transferred to an inert glovebox and mechanically polished to remove the plutonium oxide layer. The samples were then rinsed with high purity ethanol to remove any residue and then were allowed to dry. The cleaned plutonium foils were then dissolved in 6M Optima grade hydrochloric acid (HCl) (Fisher Scientific, NH, USA).

Thermal Ionization Mass Spectrometry (TIMS)

Both samples were analyzed on either a VG-Sector 54 (Thermo Fisher, MA, USA) or VG-Isoprobe-T (Isotopx, Cheshire, UK) TIMS instrument; both instruments are equipped with numerous variable position Faraday cup detectors and a fixed-position axial Daly detector. Plutonium and uranium isotopic and IDMS measurements were made via total evaporation using triple, rhenium filament assemblies. Americium IDMS and gallium IDMS were performed using single rhenium filament assemblies and ion counting on the center Daly collector.

Plutonium, uranium, ^{241}Am , and gallium (Ga) content in each sample was determined by isotope dilution mass spectrometry (IDMS) using well-characterized ^{244}Pu , ^{233}U , ^{243}Am , and ^{71}Ga spikes, respectively.

These elements were purified from potential interfering elements using Lewatiit MP 5080 ion exchange resin (Bayer AG, Germany). The precision and accuracy of IDMS measurements were evaluated using two reference materials as QC standards: New Brunswick Laboratory (NBL) Certified Reference Material (CRM) 126A for plutonium assay and National Bureau of Standards (NBS) U960 for uranium content.

Plutonium and uranium isotopic abundances were determined by TIMS following the separation of isobaric interferences by ion exchange. NBL CRM 126 and 126A were processed as plutonium isotopic quality control (QC) standards and NBL CRM U630 and U930 were processed as uranium isotopic QCs with samples to provide TIMS isotopic measurement quality assurance. The ^{243}Am working standard that was used in the ^{241}Am measurement was calibrated against the National Institute of Standards and Technology (NIST) SRM ^{241}Am standard. Process blanks were also run with the samples to assess any plutonium or uranium concentration and isotopic background. Uranium concentrations and isotopics

were measured from 4 aliquots of each sample. ^{241}Am and gallium concentrations were also measured with 4 aliquots.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Trace elemental analysis was performed by a VG Elemental PlasmaQuad PQ-S (Thermo Scientific, Waltham, MA, USA) ICP-MS. This instrument was modified so that the vacuum chamber and the quadrupole are interfaced with a glove box at the service panel. The ICP torch box and the auto-sampler are located inside the glove box to handle the radiologically contaminated samples. Electronic control system and vacuum pumps reside outside of the glove box. More detailed instrument configuration and operating conditions have been described elsewhere[25].

For ICP-MS analysis, the dissolved plutonium solution was diluted to a volume of 5.0 mL with 2% (v/v) HNO_3 . Another 20X dilution was performed after the addition of the internal standard solution containing ^{45}Sc , ^{103}Rh , and ^{169}Tm . The final solution contained approximately $250\text{ }\mu\text{g mL}^{-1}$ of sample and 100 ng mL^{-1} of each internal standard element with an acidity of 1% (v/v) HNO_3 . External calibration at 0, 20, and 100 ng mL^{-1} levels was performed daily. Instrument tuning for gas flow and ion lens settings was performed before each analytical run to ensure the maximum sensitivity and stability for the m/z range of 7 to 238.

Samples were run in batches of 10 to 15 and bracketed by two sets of calibration verification standard/blank. Calibration verification standards were prepared from SPEX CertiPrep (Metuchen, NJ, USA) standard solutions with Fisher Optima (Pittsburgh, PA, USA) ultrapure grade nitric acid and $>18\text{ M}\Omega$ resistivity de-ionized water that was produced by a Barnstead (Dubuque, IA, USA) E-pure system. One spike sample, in which known amount of NIST traceable multi-element standards were added to a randomly selected post dilution sample, was analyzed for each analytical run. Processed blank was also evaluated along with the multi-element calibration standards. The internal standards were prepared from Inorganic Ventures (Christiansburg, VA, USA) standard solutions for ICP-MS analysis.

Results and Discussion

Both samples were first measured with gamma-ray spectroscopy as part of the NDA. This technique was used as a screening tool, so count times were relatively short and resulted in relatively large uncertainties in minor plutonium isotope measurements. The samples were confirmed to be primarily plutonium. Also, no activation or fission products were observed in the spectra. Plutonium isotopes, ^{241}Am , and ^{237}Np concentrations (Table 3) were also measured and calculated using gamma-ray spectroscopy and the FRAM code. The gamma results show that these foils are super-grade plutonium. The $^{241}\text{Pu}/^{241}\text{Am}$ chronometer results indicate the foils were produced in the 1950s. Plutonium isotopic abundances were similar for both samples but still statistically distinct with Foil 1 showing a greater abundance of ^{239}Pu and reduced ^{240}Pu relative to Foil 2. The ^{242}Pu isotopic values reported in Table 3 are not from a direct gamma-ray measurement but from a FRAM built-in empirical correlation equation as no adequate gamma rays exists for ^{242}Pu [24].

Table 3 Sample isotopic properties measured via gamma-ray spectrometry (k=2)

Sample	^{238}Pu (wt %)	^{239}Pu (wt %)	^{240}Pu (wt %)	^{241}Pu (wt %)	^{242}Pu (wt %)	^{241}Am ($\mu\text{g/g Pu}$)	^{237}Np ($\mu\text{g/g Pu}$)
Foil 1	0.0013 ± 0.0004	99.043 ± 0.079	0.953 ± 0.080	0.0019 ± 0.0002	0.0010 ± 0.0002	434 ± 52	53 ± 1
Foil 2	0.0017 ± 0.0002	98.379 ± 0.039	1.642 ± 0.040	0.0017 ± 0.0005	0.0019 ± 0.0001	419 ± 18	66 ± 3

After the gamma-ray spectroscopy, samples were sectioned with pliers. These pliers were pre-cleaned with ethanol to remove any organic contaminants from the cutting edges. Sectioning of the samples revealed the cross-section of nickel encasing plutonium, and the cross sectional view of the samples were examined with an optical microscope. Dimensions determined from optical microscopy (Figure 2) show that the thicknesses of the plutonium foils were not uniform as the edges are thinner than the center. Also, the nickel cladding thicknesses were not uniform either.

Figure 2 A cross sectional view, obtained via optical microscopy, of (A) Foil 1 in 249x magnification and (B) Foil 2 in 215x magnification

A quarter was cut from each of the two foil disks for μ XRF analysis (Figures 3 and 4) which were used to examine elemental heterogeneity. Relatively high signal intensity (higher elemental concentration in that region) was depicted as brighter pixels and lower intensity as darker pixels. The elemental analysis of the cross-sectional view of the foil shows measureable gallium in the plutonium layer. Gallium was only present in the plutonium section and not in the cladding region. The cladding was composed of mostly nickel although a minor amount of Fe was also detected in the cladding and not in the plutonium metal in both samples (Figure 4 and 5). No plutonium was detected on the uncut edge which indicates that there was no plutonium leakage on the sections analyzed with μ XRF.

The initial non-destructive analyses were used to refine the destructive sample analysis plan. Since the qualitative μ XRF analysis indicated that the plutonium metals contained measureable gallium, a quantitative gallium analysis was determined to be important to fully understand the provenance of the plutonium foil samples.

Figure 3 μ XRF elemental imaging of foil 1 shows Ga in Pu layer and Fe in Ni cladding

Figure 4 Foil 2, intact edge μ XRF elemental images (2.51 mm x 1.97 mm)

Figure 5 A thin iron layer (green) can be seen on portions of the nickel cladding (red)

Isotopic Analysis

Following NDA efforts, foil samples were dissolved for destructive analysis. Plutonium isotopic abundance measurements were performed using the total evaporation method[26]. Plutonium isotopic compositions were measured with two aliquots of each sample, and they revealed several important features in these foil samples (Table 4). The isotopic compositions were similar for both foils but not identical, indicating that the samples were prepared from two different starting materials with different reactor irradiation conditions. Both foils have over 98% ^{239}Pu and less than 2% ^{240}Pu , which supports NDA measurements suggesting that these foils were produced from extremely low burnup material. Plutonium with low ^{240}Pu concentration is typically produced in reactors with soft neutron spectra, such as heavy-water and graphite moderated reactors[5].

Table 4 Pu and U assay and atomic isotopic abundances in foil samples

Sample	Pu concentration (g/g)	^{238}Pu (%)	^{239}Pu (%)	^{240}Pu (%)	^{241}Pu (%)	^{242}Pu (%)
Foil 1	0.9839 ± 0.0013	0.001855 ± 0.000099	98.244 ± 0.011	1.751 ± 0.011	0.002418 ± 0.000092	0.000655 ± 0.000059
Foil 2	0.9809 ± 0.0013	0.001750 ± 0.000093	98.4136 ± 0.0099	1.5818 ± 0.0099	0.001856 ± 0.000071	0.000526 ± 0.000048
Sample	U concentration	^{233}U (%)	^{234}U (%)	^{235}U (%)	^{236}U (%)	^{238}U (%)

	(μg/g)					
Foil 1	1745.5 ± 2.1	< 0.0023	0.59602 ± 0.00066	93.257 ± 0.030	6.1258 ± 0.0061	0.019158 ± 0.000045
Foil 2	1929.7 ± 2.3	< 0.0023	0.55607 ± 0.00062	93.735 ± 0.031	5.5484 ± 0.0055	0.15826 ± 0.00027

U isotopic abundances and ^{241}Am concentration were measured using the total evaporation method and IDMS, respectively (Table 4 and 5). These data along with plutonium isotopics were used to age date the samples (i.e. the age since the last chemical separation). The model age of foil samples were determined using $^{238}\text{Pu}/^{234}\text{U}$, $^{239}\text{Pu}/^{235}\text{U}$, $^{240}\text{Pu}/^{236}\text{U}$, and $^{241}\text{Pu}/^{241}\text{Am}$ chronometers (Table 6). The model ages from the four chronometers are in agreement for both samples. The model ages were about 6 years apart for the samples based on $^{239}\text{Pu}/^{235}\text{U}$ and $^{240}\text{Pu}/^{236}\text{U}$ chronometers. The plutonium in Foil 1 was produced around 1955, and the plutonium in Foil 2 was produced around 1948. The different production dates are a strong indication that these foils were produced from different batches of starting material under different reactor operation conditions. All results in Table 4 through 6 are reported with GUM compliant uncertainties at a coverage factor of $k=2$ [27].

Table 5 ^{241}Am , ^{237}Np , and gallium concentrations in samples

	^{241}Am concentration (μg/g)	^{237}Np concentration (μg/g)	Gallium concentration (mg/g)
Foil 1	365.4 ± 1.1	48 ± 10	10.458 ± 0.067
Foil 2	370.0 ± 1.2	60 ± 12	10.210 ± 0.065

Table 6 The radiometric model ages and production age of foils using several chronometric pairs

Sample	Chronometric pair	Radiometric age* (yrs)	Production date
Foil 1	$^{238}\text{Pu} - ^{234}\text{U}$	57.9 ± 3.8	November 1956 ± 3.8 years
	$^{239}\text{Pu} - ^{235}\text{U}$	59.51 ± 0.13	March 1955 ± 1.6 months
	$^{240}\text{Pu} - ^{236}\text{U}$	59.58 ± 0.56	March 1955 ± 6.7 months
	$^{241}\text{Pu} - ^{241}\text{Am}$	59.00 ± 1.20	October 1955 ± 1.2 years
Foil 2	$^{238}\text{Pu} - ^{234}\text{U}$	62.3 ± 4.0	June 1952 ± 4.0 years
	$^{239}\text{Pu} - ^{235}\text{U}$	66.22 ± 0.15	July 1948 ± 1.8 months
	$^{240}\text{Pu} - ^{236}\text{U}$	66.22 ± 0.60	July 1948 ± 7.2 months
	$^{241}\text{Pu} - ^{241}\text{Am}$	64.19 ± 1.10	July 1950 ± 1.1 years

* Reference date is October 2nd 2014

230 $^{238}\text{Pu}/^{234}\text{U}$ model age of both samples was slightly lower than the other chronometers and had a larger
 231 uncertainty than the rest of the chronometers. The ^{238}Pu measurement was performed with TIMS and
 232 could be affected by isobaric interference from ^{238}U and tailing of ^{239}Pu signal[28,29]. Ideally, alpha
 233 spectroscopy could be performed for the ^{238}Pu measurement to eliminate interferences from ^{238}U and
 234 ^{239}Pu , which would also lower the uncertainty of the model age from the chronometer. The ^{234}U
 235 concentration is typically very low in low burn plutonium as it can be seen in Table 4. The low
 236 concentration of ^{234}U also contributed to the large uncertainty of the $^{238}\text{Pu}/^{234}\text{U}$ model age. The process
 237 blank data was also examined for any possible contamination during the analysis and showed no
 238 significant contamination of plutonium or uranium to affect the measurements. Plutonium and uranium
 239 concentrations in blanks were 32 part-per-trillion (ppt) and 119 ppt, respectively.
 240 The $^{241}\text{Pu}/^{237}\text{Np}$ pair is a less common chronometer for a plutonium material. The model age calculated
 241 from this chronometer is 68 years for Foil 1 and 75 years for Foil 2. These ages were vastly older than
 242 the model ages calculated from major plutonium chronometers. The model age for Foil 2 is clearly
 243 wrong as it even precedes the discovery of plutonium by Glenn Seaborg[30]. The inaccurate age
 244 determination may point towards incomplete purification of Np from the material. The initial ^{237}Np
 245 concentration for each sample was calculated by using the model age from the $^{241}\text{Pu}/^{241}\text{Am}$
 246 chronometer. The initial ^{237}Np concentrations were 23 ± 10 and 32 ± 12 ppm for Foil 1 and Foil 2,
 247 respectively. These values were within measurement uncertainty and may indicate that the starting
 248 materials used in the production of these materials were similarly processed in terms of chemistry[4].
 249 The gallium IDMS measurement confirms the presence of gallium observed by μXRF (Table 5). Gallium is
 250 used to stabilize the face-centered cubic (fcc) δ -phase of plutonium over a large temperature range[31].
 251 The soft and ductile nature of the δ -phase makes alloyed plutonium much easier to cast and shape than
 252 the unalloyed metal[32]. Use of an alloyed metal likely means that samples were prepared from rolled
 253 metal sheets by punching out the circular foils[33]. Plutonium foils were likely clad after the

punching process. The shape of the foils and isotopic characteristics indicate that the foils were possibly designed and prepared for a ^{239}Pu neutron physics experiment to measure cross-sections etc. The thin nickel coating was likely applied to keep fission gases within the confinement as fission targets are typically clad with metal such as nickel and aluminum to prevent fission gas from escaping[34–36]. The reactor modelling was used to predict the reactor irradiation history of plutonium incorporated into these foil samples. This technique is well developed and known in the nuclear forensics community as previously discussed in multiple publications[4,37,38] and have been performed at LANL for decades. The simulations were performed using the Monte Carlo transport and burnup codes MCNP (Monte Carlo N-Particle Transport Code) and MonteBurns[39,40]. Isotopic results from simple burnup calculations with cross sections and fluxes for graphite and heavy water reactor models were examined to determine the type of reactors that were used to produce these plutonium samples[41]. The modelling data shows that the plutonium was produced about 60 years ago in a graphite reactor. The irradiation was followed by chemical purification with minimal cooling time. The model results confirm the sample model ages calculated using major plutonium chronometers ($^{239}\text{Pu} - ^{235}\text{U}$ and $^{240}\text{Pu} - ^{236}\text{U}$). The Hanford site is the likely site for any super grade plutonium production in the U.S. in the 1940s. Both Hanford and Savannah River Site were producing plutonium in the 1950s. Nine production reactors were built at the Hanford Site between 1944 and 1963[42] (Table 7). All these reactors had similar designs with graphite moderator and light-water cooling with low-enriched uranium metal fuel [43]. Savannah River Site reactors had different designs with a heavy water moderator and cooling medium. Based on the modeling information, which indicated production from graphite moderator reactor, these two foil samples were likely produced from Hanford reactors. The first eight Hanford reactors are possible candidates for the production of Foil 1, and B, D, and F reactors are possible candidates for Foil 2. The startup date for the N reactor was outside of the model age of both Foil samples and can be ruled out.

Table 7 Hanford site nuclear reactors[44]

Name	Startup Date	Shutdown Date
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B-Reactor	September 1944	February 1968
D-Reactor	December 1944	June 1967
F-Reactor	February 1945	June 1965
H-Reactor	October 1949	April 1965
DR-Reactor	October 1950	December 1964
C-Reactor	November 1952	April 1969
KW-Reactor	December 1954	February 1970
KE-Reactor	February 1955	January 1971
N-Reactor	December 1963	January 1987

Trace element analysis

Trace element contents in these foil samples were measured by the ICP-MS method. The intent was to measure nickel concentration to assess the sample dissolution procedure for complete cladding removal. In addition, the analysis also provided concentrations of other trace elements in each sample. The quantity of trace elements in the sample could potentially indicate any process signatures. First of all, both samples had similar trace element content except for Pt and Sn as shown in Table 8. Foil 2 had higher concentration of Pt and Sn than Foil 1. The trace element concentrations in two foil samples were compared to the values from other plutonium metals reported in literatures[45–48] . These previous studies were not a part of nuclear forensics analysis, but the trace element data were used for comparison purposes. Nickel (Ni) content was slightly elevated compared to other reported plutonium specimens in Table 8. However, nickel concentration was not significantly higher than other plutonium specimens, which is indicating the chemical method used to remove the cladding was effective. From the trace element analysis, it is also seen in Table 7 that aluminum and boron (B) concentrations were noticeably high in both foil samples compared to other plutonium specimens reported in the literatures. A high aluminum concentration can be attributed to the use of aluminum fuel claddings to contain fission product gases[49,50], and aluminum nitrate ($\text{Al}(\text{NO}_3)_3$) is used in redux process to strip plutonium from the organic phase[51]. However, boron is not a typical element to be present in plutonium metal. ^{10}B has a high thermal neutron cross section and is used as a neutron poison[49]. There is a possibility of using boron in similar capacity in these foils as reported in other publications[52,53].

299 It had been reported that even with the same process, difference in processing flowsheets may leave
300 different signatures on plutonium metals[54]. The similarity between the two foil samples in trace
301 element concentrations but difference in plutonium isotopic abundances show that two samples were
302 likely from different batches but possibly processed using the same or similar techniques at the same
303 facility[9].

304

305 Table 8 Trace elemental contents in the Foil samples and other Pu samples reported in the literatures.

	Foil 1 (ppm)	Foil 2 (ppm)	Pu specimen 1 (ppm)[45]	Pu specimen 2 (ppm)[45]	Pu specimen 3 (ppm)[46]	Pu specimen 4 (ppm)[47]	Pu specimen 5 (ppm)[48]
Al	130 ± 26	130 ± 26	10	25	15	22	40
B	805 ± 161	675 ± 135	< 0.5	< 0.5	-	< 0.5	-
Be	0.93 ± 0.20	0.85 ± 0.17	< 0.1	< 0.1	-	< 0.05	-
Bi	0.30 ± 0.07	0.21 ± 0.05	< 1	< 1	-	< 5	-
Co	1.6 ± 0.3	1.7 ± 0.3	< 10	< 10	1	-	-
Cr	37 ± 8	22 ± 4	< 10	< 20	28	< 3	< 20
Cu	26 ± 5	28 ± 6	7	10	1	3	2
La	0.21 ± 0.05	0.41 ± 0.08	< 10	< 10	-	< 50	-
Li	<5	<4	< 0.2	< 0.2	-	-	-
Lu	0.07 ± 0.02	0.07 ± 0.02	-	-	-	< 2	-
Mg	6.0 ± 1.2	10 ± 2	< 5	20	7	3	-
Mn	22 ± 4	33 ± 7	8	3	4	3	< 2
Mo	1.9 ± 0.4	2.1 ± 0.04	-	-	-	< 5	-
Nd	0.34 ± 0.09	0.22 ± 0.04	-	-	-	< 100	-
Ni	98 ± 20	170 ± 34	< 10	50	66	10	< 20
Pb	<0.1	<0.1	< 2	< 2	-	< 3	> 2
Pd	0.31 ± 0.07	0.44 ± 0.10	-	-	-	< 3	-
Pr	0.10 ± 0.03	0.08 ± 0.02	-	-	-	< 50	-
Pt	4.6 ± 0.9	69 ± 14	-	-	13	< 3	-
Sn	0.67 ± 0.16	28 ± 6	< 1	< 1	3	< 3	< 1
Ta	1.5 ± 0.4	0.74 ± 0.15	-	-	3	< 50	< 35
Th	1.4 ± 0.3	0.55 ± 0.11	-	280	5	< 50	< 10
Ti	2.6 ± 0.5	3.5 ± 0.7	-	-	10	< 3	-
V	1.8 ± 0.4	4.1 ± 1.0	-	-	1	< 3	-
W	2.2 ± 0.5	1.1 ± 0.2	-	-	-	-	32
Zn	23 ± 5	47 ± 10	< 10	10	10	< 10	< 10
Zr	2.2 ± 0.2	2.3 ± 0.5	-	-	4	< 1	-

306 Conclusions

307 State-of-the-art nuclear forensic analyses were performed on two plutonium foil samples. Data from
308 these analytical techniques are tied together to find the intended use and the origin of the material.
309 Both samples were produced using super-grade plutonium. Based on $^{239}\text{Pu}/^{235}\text{U}$ and $^{240}\text{Pu}/^{236}\text{U}$
310 chronometers, samples were chemically purified in 1948 and 1955, respectively. The two plutonium
311 metal foils were prepared in different batches using the same general process based on plutonium

isotopic abundances, age of the samples, and trace element analyses. The modelling indicates that the plutonium was produced in a graphite moderator reactor. Combination of age information and reactor modeling indicate that the plutonium metal foils were produced at the Hanford site given the possibility that it was produced in the U.S. The shape of the foils and plutonium isotopic composition indicate that the foils were possibly prepared as ^{239}Pu fission foil targets for physics experiments, such as cross-section measurements, etc.

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