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Nuclear forensic analysis of a non-traditional actinide sample



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ABSTRACT

Nuclear forensic publications, performance tests, and research and development efforts typically target the bulk global inventory of intentionally safeguarded materials, such as plutonium (Pu) and uranium (U). Other materials, such as neptunium (Np), pose a nuclear security risk as well. Trafficking leading to recovery of an interdicted Np sample is a realistic concern especially for materials originating in countries that reprocesses fuel. Using complementary forensic methods, potential signatures for an unknown Np oxide sample were investigated. Measurement results were assessed against published Np processes to present hypotheses as to the original intended use, method of production, and origin for this Np oxide.

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1. Introduction

Although the definition of nuclear forensics is inclusive to the investigation of any nuclear material or other radioactive material found outside of regulatory control, nuclear forensics has largely focused on Pu and U materials [1–3]. Most Pu and U materials are a high priority proliferation concern and are regulated by the International Atomic Energy Agency (IAEA) due to associations with the nuclear fuel cycle, defense applications, and trafficking in documented cases of interdicted nuclear material [4–6]. However alternative nuclear materials such as neptunium-237 (^{237}Np) have been put under IAEA control under voluntary agreements, as they too are known to have defense applications [7,8].

Like Pu, Np is a byproduct of nuclear reactor fuel irradiation and therefore is present in significant quantity in spent fuels. Depending on the type of reactor used and conditions applied, the mass of Np produced varies. For example, it is estimated that the amount of Np produced in a pressurized water reactor (PWR) is equivalent to approximately 4–5% by weight of the total Pu generated during irradiation [8]. Due to limited use and limited stocks of separated Np, the likelihood of Np being found in a nuclear forensic case is low. Nevertheless, there are 180 states, 704 facilities, and 563 material balance areas worldwide under safeguard regulations as of 2014. Thus the possibility of an interdicted

alternative nuclear material case involving Np is real [2,4,8,9].

Nuclear forensic investigations use a number analytical methods, both non-destructive and destructive, to evaluate material purity, isotopic composition, trace element content, and morphology [2,10–14]. This measurement information can be assessed to evaluate the date the material was last purified (model age), how effective the separation was, potential processing conditions, intended use, and/or what producers may have generated the material [2,3,15,16].

In this study, a Np oxide sample was subjected to forensic investigation to determine characteristic properties associated with the material's history. Approximately 4 g of Np oxide was processed by the Actinide Analytical Chemistry (AAC) group at Los Alamos National Laboratory (LANL). Validated and qualified analysis methods were applied with appropriate standard and reference materials (RMs) serving as calibration standards and matrix-matched quality control (QC) standards. However, suitable standards are not available for ^{237}Np assay calibration, so multiple techniques were applied and compared to verify accuracy and assess confidence in measurement results. All analyses were completed on duplicate sample cuts to assess sample homogeneity and sample preparation blanks were processed and analyzed.

2. Experimental

The declared Np sample was received as an unknown in a thick-walled Swagelock shipping container and was handled in

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Table 1
Summary of analytical techniques applied.

Technique	Application	Standards/Controls
Gamma Spectrometry ^a	Non Destructive Analysis (NDA), Radionuclide Content, Assay	¹⁵² Eu button source/ ^{166m} Ho button source ^g
Controlled Potential Coulometry (CPC) ^{c,d}	Assay	Well characterized Np oxide/previously characterized Np sample
Alpha Spectrometry/Gas Proportional Counting ^b	Assay	Well characterized and validated Pu and ²⁴¹ Am check standards
Alpha Spectrometry ^b	Americium	Analytics mixed alpha source (SRS 66689–16) ^h
Thermal Ionization Mass Spectrometry (TIMS) ^e	Pu and U Isotopic Characterization, Chronometry	CRM 126a/CRM112a/U 960/IRMM-199 ⁱ
Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) ^f	Assay, Trace Element Content	NIST traceable multi-element calibration standards

^a ORTEC coaxial HPGe with Be window/ DSpec Pro and X-cooler (ORTEC, Oak Ridge, TN, United States).

^b ORTEC Octet Plus Alpha Spectrometer (ORTEC, Oak Ridge, TN, United States).

^c Princeton Applied Research Model 173 potentiostat (PAR, Oak Ridge, TN, United States).

^d EG&G Coulometer (EG&G, Los Angeles, CA, United States).

^e Vacuum Generator (VG) Sector 54 mass spectrometer with multicollector (Faraday) system, Daly detector.

^f VG Elemental PlasmaQuad PQ2+.

^g Analytics, Atlanta, GA, United States.

^h New Brunswick Laboratory, Chicago, IL, United States.

ⁱ IRMM, Geel, Belgium.

accordance with the conduct of operations typically enacted upon receipt of a forensic sample [17]. Table 1 provides a summary of the techniques used and their applications specific to the Np sample.

Further details of characterization are as follows.

2.1. Non-destructive analysis (NDA)

Non-destructive analysis of the solid sample was performed by gamma spectrometry. The packaged sample was placed approximately 53" from the detector end cap within its original packaging (Swagelock container), producing a 23% dead time (DT). Gamma spectra were collected over the course of 5 hours in energy ranges of 0–1 MeV, 0–2 MeV, and 0–5 MeV using the ORTEC GammaVision Software (Oak Ridge, TN, Version 7.02.01). The spectra were analyzed after collection using the Spectral Nondestructive Assay Platform (SNAP) software (Eberline Services, NM) and the Fixed energy Response function Analysis with Multiple efficiencies (FRAM) code (Los Alamos National Laboratory, NM, Version 5.1) [18]. This NDA analysis by gamma was completed first on the solid sample in the original packaging container and then again as a liquid after the sample was sub-sampled and dissolved. Photographs of the solid sample were taken upon opening the container for physical evaluation followed by sub-sampling and dissolution. The sample container was opened inside a glove-bag inside a cleaned glove-box to reduce potential contamination, which was monitored throughout the process by swiping the work areas with IAEA style swipes (10 × 10 cm clean cotton squares).

2.2. Loss-on-ignition (LOI)

Loss-on-ignition analysis was performed to quantify the mass of volatile substances in the sample. For the LOI determination, 0.7g of the sample was weighed into a tared Pt crucible, covered, and placed into a CM 1608 FL furnace (CM Furnaces, Bloomfield, NJ) to heat the sample at 200 °C for one hour. Upon completion, the sample was stored in a desiccator to cool to room temperature before the final weighing following stabilization.

2.3. Dissolution

The sample was dissolved using 12 M HNO₃ in pressurized acid digestion vessels [19]. Upon transferring the sample to a

perfluoroalkoxy (PFA) digestion vessel (Saville, Eden Prairie, MN), 12 M HNO₃ was added and the sealed vessels were loaded onto an electronically controlled hot block and allowed to digest for 16 hours until dissolution was complete.

2.4. Neptunium assay

Neptunium assay of the digested sample was performed by multiple methods since no NIST traceable matrix-matched standard currently exists for controlled potential coulometry (CPC) Np assay. In brief, gamma spectrometry, CPC, and alpha spectrometry/gas proportional counting were run to obtain multiple independent Np values [19]. Controlled potential coulometry was chosen as the primary method for assay analysis as the technique provides the highest accuracy and precision and lowest uncertainty when properly calibrated [20,21]. The dissolved sample was fumed multiple times before being re-dissolved in sulfuric acid. A 0.5 M ceric sulfate solution (H₄Ce(SO₄)₄) in 1 M sulfuric acid was added to the sample and the working electrode was inserted. An aliquot of Ce(IV) was added to the Np solution in order to oxidize the Np(V) to Np(VI). A volume of sulfuric acid sufficient to completely cover the working electrode was added and the cell was inserted into the coulometry assembly which included an Ar stream, stirrer, platinum auxiliary electrode, and calomel reference electrode. The Np(VI) was reduced to Np(V) along with Ce(III) at the working electrode.

Controlled potential coulometry utilizes the redox chemistry of Np in sulfuric acid solution to measure the amount of Np in the sample, so the final coulometric measurement was made when the Np(V) was re-oxidized to Np(VI) at the working electrode. The total current can determine the amount of Np in the sample according to Faraday's Law [20]. The precision of the technique is quite good, with the main uncertainty contributors being instrumental calibration, coulomb measurements for the sample, and blanks. In this case a well characterized Np material was run to calibrate the system, while a previously characterized Np sample was run as a control/check. Overall, accuracy and precision of CPC is very high at 0.1 wt% or better in samples containing 60–90 wt% Np [22–24]. Thus, this is an excellent technique for assay of metals and oxides.

From historical Np assay measurements the factor used in Faraday's Law to account for the electrons transferred per mole was recorded as nearly identical to that for Pu. Thus, the coulometer could be calibrated with the standard typically used for Pu,

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