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Chemical Sciences Division

ASSESSMENT OF NEEDS FOR A NEPTUNIUM CERTIFIED REFERENCE MATERIAL

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November 2024

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1. INTRODUCTION

This document describes the results of a detailed assessment of needs within the Nuclear Analytical Chemistry (NAC) section at the US Department of Energy's (DOE's) Oak Ridge National Laboratory (ORNL) for a neptunium certified reference material (CRM) used for instrument calibrations and measurement control. Also included is a summary of input from several other organizations that expressed interest for such a reference material as well as a general needs analysis within the broader nuclear analytical community based on a literature search of publications describing measurements for neptunium.

Because these standards would cover the larger need for the nuclear analytical community performing characterizations for neptunium, this survey only considered reference materials for calibration or measurement control over others the labs would benefit from, such as those that could be used for process control. A traceable primary standard for instrument calibrations for neptunium assays will benefit a multitude of national and international interests in areas such as environmental stewardship, nuclear material accountancy and safeguards, characterization of nuclear materials for research and nuclear forensics, and the production of heavy isotopes.

The predominant analytical methods used for neptunium assays are radioanalytical counting (alpha and gamma spectroscopy) techniques and plasma-based mass spectrometers or optical spectrometers. However, higher precision assays using multicollector mass spectrometers or controlled potential coulometry (CPC), although not as widespread, are of great importance for programs associated with material accountancy and nonproliferation. The benefits of a neptunium CRM specific to each of these methods is discussed further in the following sections. However, instrument calibrations and measurement controls currently use an ad hoc inventory of in-house materials or secondary standards. Moreover, for mass measurements, alternate actinide reference materials are used for instrument calibrations or constraining analytical variables such as mass bias and instrumental drift. Therefore, another important outcome of the development of a neptunium CRM will be the ability for analytical laboratories to validate the methods currently being calibrated or controlled with other neptunium sources.

Finally, this report describes a possible candidate material at ORNL. A portion of this material, currently owned by DOE Isotope Programs, is undergoing purification to remove decay daughters and trace elemental impurities.

2. BENEFITS OF NEPTUNIUM CRM SPECIFIC TO EACH ANALYTICAL TECHNIQUE

2.1 GAMMA SPECTROSCOPY

In general, NAC gamma detectors are calibrated using a multi-nuclide standard to calculate an efficiency curve for the detector's response that covers the range of energies to be measured. The standard used is purchased from a commercial supplier of radiological secondary reference materials. Calibration parameters are set such that the chosen energy peaks generate at least 10,000 raw counts; this value has been evaluated to be the minimum counts required to achieve a response within a 95% confidence level (2σ). Typical 2σ uncertainties for gamma measurements using an efficiency curve are approximately ±10%. A neptunium CRM would allow for the calibration of a region of interest (ROI.)

An ROI is used to calibrate the response of select gamma peaks of an isotope. This calibration can enable improved measurement accuracy and precision. These improvements would particularly benefit NAC gamma measurements used for material accountancy at ORNL. Table 1 shows gamma data and results for the measurement of a 5 mL solution containing 5.7 × 10^6 Bq/mL ^{237}Np (0.537 mg per vial) using a detector with a 19.1% efficiency, sample placement 3 cm above the detector, and counted for 30 min.

Table 1. Gamma results for 0.537 mg per vial ^{237}Np

Gamma energy (KeV)	Branching ratio (%)	Area (counts)	Result (Bq/mL)
86.50	12.6 %	46,241	5.02531 × 10^6
92.38	1.59 %	7,358	5.60951 × 10^6
108.29	0.94 %	5,250	5.72260 × 10^6
143.23	0.39 %	2,330	5.99493 × 10^6
194.87	0.2 %	850	4.90763 × 10^6
212.22	0.15 %	665	5.40992 × 10^6

These data indicate that, for similar NAC gamma systems, a neptunium standard of 0.537 mg total in a 5 mL gamma vial geometry would be the minimum amount of material used. Optimally, a 1 mg ^{237}Np standard in the same geometry would be needed for calibration and measurement control. A 1 mg/g ^{237}Np unit would be sufficient to create a single gamma calibration solution with an expected shelf-life of 6–12 months. The NAC section counting labs' annual consumption is estimated to be two to three 1 mg units.

2.2 ALPHA SPECTROSCOPY

When an isotope-specific alpha calibration standard is not available, the NAC will use a gross alpha measurement on the alpha plate combined with peak ratios from a pulsed height analysis (PHA) of the same plate to quantify the isotope of interest. The gross alpha system is calibrated using a secondary reference material purchased from a commercial supplier. Typical 2σ uncertainties for alpha measurements using this technique are approximately ±10%–20%. Although this method is a convenient way to measure a broad range of alpha emitters, it is not ideal for applications requiring fully quantitative alpha results.

As with gamma spectroscopy, an ROI can be calibrated for measurements using alpha PHA, leading to improved measurement accuracy and precision. Again, these improvements would particularly benefit NAC alpha measurements used for material accountancy at ORNL. A National Institute of Standards and Technology (NIST)-traceable ^{237}Np source was used to determine that an alpha count rate of 10,000 counts/min provided optimal counting statistics for the measurements while avoiding self-attenuation owing to too much mass loaded on the alpha plates. Table 2 lists the alpha energies, which make up about 96% of the emitted alpha energies of ^{237}Np.

Overlaps on a typical resolved alpha PHA cause these energies to show two broad peaks at 4.65 MeV and 4.80 MeV. Normally, alpha spectroscopy would be considered accurate if the full width at half maximum of a peak was less than 100 KeV, but that rule does not necessarily apply to neptunium because of these overlaps. Instead, when a clear delineation between the 4.65 and 4.80 MeV groups (i.e., the curve goes to near baseline between the two groups) self-attenuation on the plate is minimal, and thus the sample count is accurate. At 10,000 counts/min (~50% eff) of ^{237}Np, this count rate equates to 333 Bq total (12.8 µg.) A 1 mg/g ^{237}Np unit would be sufficient to create 78 alpha plates, which would be expected to be more than enough for a year's use among the NAC section's counting labs. Annual consumption is estimated to be one 1 mg unit.

Table 2. Branching ratios

Alpha energy (MeV)	Branching ratio (%)
4.5984	0.34
4.6395	6.18
4.6592	0.6
4.6646	3.32
4.6971	0.48
4.7071	1.0
4.7661	8
4.7715	25
4.7884	47
4.8040	1.6
4.8173	2.5

2.3 INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY/OPTICAL EMISSION SPECTROMETRY

Inductively coupled plasma mass spectrometry (ICP-MS) and optical emission spectrometry (OES) are quantitative measurement techniques based on a relative relationship between a detected response and quantity of the analyte. Because of the lack of a ^{237}Np calibration standard, the NAC performs semiquantitative measurements based on a calibration curve built using other actinides. This method relies on the assumptions that (1) neptunium ionizes in a manner identical to the other actinide(s) and (2) the response at the detector is similar. Therefore, these techniques are especially susceptible to issues that arise from the lack of a neptunium CRM. Furthermore, the NAC performs characterization of trace ^{237}Np in complex matrices such as irradiated fuels using in-house matrix-matched calibration solutions as well gravimetric standard addition. An available neptunium CRM certified to a higher precision than what is available with the NIST counting standard (i.e., approximately ±3%) would greatly improve neptunium assay by these techniques. Moreover, chemically removing or minimizing the impurities within the neptunium CRM would benefit the creation of the matrix-matched multielement in-house calibration solutions: impurities in the single-element calibration solutions would complicate the mixture owing to the overlap of impurities with the analytes or contribution to isobaric interferences.

For the NAC mass spectrometers, calibration standards are typically used at low parts-per-billion concentrations, and those used for the optical emission instruments are used at low parts-per-million concentrations. A 1 mg/g ^{237}Np unit would be sufficient to create a single working solution for use in serial dilutions to establish the calibration curves. Such a working solution would be expected to have a shelf-life of 6–12 months. Four instrument labs in the NAC section would benefit from a ^{237}Np calibration standard. Annual consumption for all four labs is estimated to be four to five 1 mg units.

2.4 MULTICOLLECTOR ICP-MS AND THERMAL IONIZATION MASS SPECTROMETRY FOR ISOTOPE RATIO MEASUREMENT

If the neptunium CRM isotopic composition is well quantified, then it could be used to support high-precision isotope ratio measurements as a mass bias control standard during a neptunium analytical session. Currently, other actinide CRMs are used for this purpose, but this method requires an extrapolation of the mass bias behavior between the element being used and the observed neptunium isotope ratios. A neptunium CRM with a certified ^{236}Np/^{237}Np ratio would be used as a quality control to verify corrected ratios using the other actinide CRMs. Consumption for all the NAC section's isotope ratio mass spectrometers is estimated to be one 1 mg unit every 3–5 years for use as a mass bias quality control.

2.5 CONTROLLED POTENTIAL COULOMETRY

CPC is generally recognized as being able to provide the highest precision neptunium assay data compared with ICP-MS and counting techniques.[1] However, CPC requires considerable radiochemistry expertise to perform correctly and requires more material than many of the other techniques. For example, at Savannah River National Laboratory (SRNL) each CPC analysis requires approximately 40 mg of material. Although CPC does not require a CRM to be used during each measurement cycle of the unknowns, a laboratory performing this technique routinely would perform an annual quality control analysis on the CRM for measurement control.

3. CHEMICAL FORM

Actinide reference materials are available in a variety of chemical and physical forms (e.g., oxides, metals, liquids, nitrates), and no single form would satisfy all the nuances of the myriad analytical methods in existence. However, certain factors, including the material's stability during storage conditions and ease of preparation of the material for use in measurements, are universally important.

Oxides are typically considered to be the most stable chemical forms of an element. However, neptunium oxides are produced using high temperatures, readily adsorb moisture, and are not as stable as uranium oxides. Consequently, they can require more aggressive and lengthy digestion methods and a heating or ignition process before use to ensure stoichiometry and negate possible adsorption of moisture. Failure to properly prepare an oxide would introduce a bias into any measurement that subsequently relied on the inferred concentration of the stock solution created.

Although a metallic form of neptunium would likely be readily digestible, it would also likely experience oxidation under atmospheric conditions, thus changing the stoichiometric abundance of neptunium and requiring chemical removal of the oxide layer before dissolution. Furthermore, a metal would have special safeguards and security controls for storage and handling associated with it because of its fissile properties with potential for use in a weapons program.

A liquid form would be easy to use. Aliquots could be drawn directly from the stock solution with minimal preparations. However, liquids are prone to evaporation, and once the aliquot is opened, the correctness of the certified assay would become less reliable over time without subsequent verification.

A dried nitrate form would be expected to remain stable over time and could be readily dissolved in dilute HNO_3 at room temperature. Consequently, this form would provide a simple avenue to prepare the standard for use while retaining an adequate level of resistance to environmental degradation during storage. Moreover, the container used for the units can be a simple screw top such as a Savillex capsule. This container would further the ease of effort to prepare each unit for use. Therefore, based on NAC end-user input, this form would be preferred for a neptunium CRM.

Producing a CRM as a dried $NpNO_3$ that is isotopically and elementally homogeneous will be considerably simpler than producing an oxide with similar characteristics. The candidate NpO_2 material has a relatively unknown purity and stoichiometric makeup. To prepare it so that its chemical and physical form meets the requirements of a calibration CRM will require the material be digested,

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[1] Xu et al. 2013. *J. Radioanal. Nucl. Chem.* 296, 245–249.

chemically purified, and recalcined to a stoichiometrically pure oxide. However, producing gravimetric units of dried nitrates from a purified homogeneous master solution should be relatively straightforward. A drying step in an inert atmosphere should stabilize the $NpNO_3$ without changing the material's structure (and thus stoichiometry) or causing significant environmental interaction. By contrast, the high-temperature calcination step that would be required to produce the desired oxide can easily induce physical and chemical changes in the material and thus require substantially more effort to characterize during the certification process. For these reasons, production of the $NpNO_3$ is likely to be much simpler and more cost effective.

4. QUANTITY AND PACKAGING FOR INDIVIDUAL ALIQUOTS

Based on this assessment, smaller and more manageable 1 mg units of dried $NpNO_3$ would satisfy the needs of most users. Other nuclear labs performing the same types of measurements on similar instruments described in this document likely would also be satisfied with that unit size. However, some end users, such as SRNL's CPC lab, would require large unit sizes, closer to 40 mg. Across the DOE complex, neptunium content greater than 50 mg is subject to the Nuclear Material Control and Accounting program. Therefore, to simplify handling, individual units should remain smaller than 50 mg (e.g., 40 mg). Additionally, aliquots packaged within clean (e.g., leached) Savillex (or similar) vessels would be amenable to quantitative removal after digestion using low-molarity acid.

Without input from other potential users, a consumption rate is difficult to predict. To accurately predict consumption, a detailed user survey should be conducted among the potential end users at environmental and nuclear labs that perform measurements for neptunium. Annual NAC consumption is estimated to be 9–11 1 mg units.

5. SPECIFIC PROJECTS CURRENTLY REQUIRING NEPTUNIUM ANALYSIS

The NAC leads a multitude of analytical projects requiring neptunium analyses for multiple sponsors. These sponsors and regulators listed would directly benefit from the creation of a neptunium calibration CRM.

1. DOE Isotope Programs and NASA for the production of ^{238}Pu
2. Office of Nuclear Forensics (NA-83) for the National Nuclear Material Archive
3. Office of Defense Nuclear Nonproliferation Research and Development (NA-22) for research and development in the field of nonproliferation
4. Office of Nonproliferation and International Security (NA-24) for safeguarding nuclear materials
5. DOE Office of Nuclear Energy for research and development in the nuclear fuel cycle
6. Nuclear Regulatory Commission for safeguards of nuclear fuels and licensing of nuclear power plants
7. US and Tennessee Environmental Protection Agencies for the National Pollutant Discharge Elimination System permit program

5.1 NEPTUNIUM CRM NEEDS FOR OTHER USERS AND PROGRAMS

In 2015, Richard Essex of NIST led a survey of needs for neptunium reference materials for the DOE labs and international nuclear labs participating in predetonation nuclear forensics sponsored by the Department of Homeland Security. That survey indicated considerable interest in having a certified ^{236}Np tracer for high-precision isotope dilution mass spectrometry characterizations of low levels of neptunium in bulk matrices and showed a level of interest for a neptunium assay standard. Particularly, Los Alamos National Laboratory expressed an interest for a neptunium assay standard for coulometry and estimated an annual consumption rate of 250 mg. Lawrence Livermore National Laboratory and the Swedish Defense Research Agency also expressed interest in a neptunium assay standard. Phone conversations with Essex confirmed that, in his opinion, a bulk neptunium assay standard of purified units of dried nitrate salts that can be easily dissolved and aliquoted for use in mass spectrometry, atomic emission spectrometry, or counting calibrations would be advantageous for Bulk Special Nuclear Material Analysis Program labs and labs performing predetonation nuclear forensics analyses.

Phone conversations with Maria Morales-Arteaga confirmed an interest at SRNL for 40 mg assay standards for CPC measurements. In these discussions, Morales-Arteaga also expressed an interest in supporting the production of small pieces of a pure metal to be used to conduct a small-scale study to verify the CPC electrical calibration method, which has been a recent subject of discussion in the CPC user community.

The broader nuclear analytical community recognizes that the general lack of a neptunium CRM is a recognized issue. For example, the International Atomic Energy Agency has recently highlighted the need for both a ^{236}Np isotopic tracer and a neptunium assay CRM. A surveying the scientific literature on neptunium measurement shows that a ^{236}Np tracer was used by several researchers more than a decade ago.[2,3] However, this material is not widely available, so, for high-precision mass spectrometric neptunium assay, other researchers[4,5] have been utilizing ^{242}Pu and[6] even ^{239}Np as the isotopic tracers. Furthermore, a preliminary survey of the neptunium measurement literature (represented by about 30 publications spanning various measurement types, study goals, sample materials, and other facets) reveals that the lack of a suitable neptunium CRM is often mentioned by the paper's authors as an impediment to attaining more precise and accurate measurements. Although a bulk neptunium assay standard would not satisfy needs for an enriched tracer, certifying the ^{236}Np/^{237}Np ratio would benefit users performing isotopic ratio measurements for neptunium.

6. CANDIDATE MATERIAL

A 150 g batch of NpO_2 is currently being purified to remove decay daughters and elemental impurities for DOE Isotope Programs by ORNL's Emerging Isotopes Research (EIR) group. The material is part of a larger batch of oxide that was sent to ORNL from the Savannah River Site (SRS) in March 2009. Exact processing details are not known at this time but could be easily obtained from SRS historical records if desired. However, an analytical report characterizing the bulk and trace elemental and isotopic content of the material from July 2008 is on file with EIR. A small portion of the purified oxide would be a good candidate for the neptunium CRM production campaign.

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[2] Beasly et al. 1998. *J. Environ. Radioactivity* 38, 133–146.
[3] Cooper et al. 2000. *Marine Chemistry* 69, 253–276.
[4] Quiao et al. 2011. *Talanta* 84, 494–500.
[5] Chen et al. 2002. *J. Radioanal. Nucl. Chem.* 253, 451–458.
[6] Joe et al. 2012. *Nucl. Eng. Technol.* 45, 415–420.

7. CONCLUSION

Production of a certified bulk neptunium assay CRM for use primarily for analytical instrument calibration, quality control, and validation of the measurement processes would benefit nuclear labs performing neptunium measurements and the sponsors who fund their work. Such a standard would allow improvement over current instrument calibration methods by generating calibration profiles directly based on the mass or energy response to neptunium, thereby improving the traceability of the measurement as well as its accuracy and precision. Measurements conducted for nuclear material accountancy and trace neptunium characterizations in nuclear materials would particularly benefit from this capability.

A CRM with certified chemical assay value for neptunium and ^{236}Np/^{237}Np atom ratio on a purified master stock would satisfy the greatest needs. A documented separation date with informational values for any remaining decay daughters and metallic impurities would also be beneficial.

Units of 1 mg or 40 mg neptunium in the form of dried nitrate salts packaged in screw-top Savillex or other trace clean vessel that is easy to handle and open and amenable to quantitative removal of the material when reconstituted with low-molarity acid are preferred.

Production of a small portion of high-purity neptunium metal to conduct a small-scale study to validate CPC as a primary method is also of interest.

A candidate material has been identified at ORNL. The EIR group is currently chemically purifying the material to remove trace impurities. Transfer of ownership for a small portion of the final purified oxide for neptunium CRM production would have to be negotiated with DOE Isotope Programs.