Contract No:

This document was prepared in conjunction with work accomplished under Contract No. 89303321CEM000080 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

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Doc# SRNL-STI-2023-00169
R&R Date: April xxx, 2023

Development of an Aerosol-Based Method for the Manufacture of Surrogate Environmental Test Swipes

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Abstract

The analysis of environmental test swipes laden with actinide-bearing particles is a key component of treaty verification activities and nuclear safeguards inspections. The frequency and importance of these analyses has resulted in the need for high-quality reference materials with known particle loadings and compositions for use in proficiency testing, interlaboratory comparisons, and method development. Recent advancements towards the manufacture of actinide-bearing microparticulates including the THermally Evaporated Spray for Engineered Uniform particulateS (THESEUS) production platform, developed at Savannah River National Laboratory (SRNL), have resulted in the availability of highly uniform uranium-bearing particulate reference materials with tailored isotopic compositions in quantities ranging from nanograms to milligrams. However, the availability of suitable particle-laden test swipes has lagged. To expand this particulate generation capability to include particle-laden test swipes, the settling behavior of aerosolized particles within a static volume of air was leveraged to develop a capability for the manufacture of swipes with tailorable and uniform particle loading in conjunction with the THESEUS particle production platform. The developed method was tested using depleted uranium oxide particles, with 1-micron equivalent circular diameter, to produce batches of particle-laden swipes with varying particulate loadings. Total uranium content of the generated swipes was measured using kinetic phosphorescence analysis (KPA), and the preservation of the particulate qualities through the manufacturing process was assessed using scanning electron microscopy (SEM) as well as large geometry secondary ion mass spectrometry (LG-SIMS). Assessments of inter-swipe uniformity suggest good agreement of particle loading both within and between batches, with variation between swipes below 15% in most scenarios, as measured by KPA. Furthermore, the developed capability displays a high degree of tailorability in the particle dosing on a per-swipe basis, with a linear relationship including demonstrated loadings ranging from tens of nanograms to tens of micrograms of uranium per-swipe. The developed method for the generation of particle-laden test swipes displays promise for the future manufacture of reference surrogate environmental swipe specimens, and is expected to enable both future proficiency tests, as well as development and evaluation of particle extraction techniques.

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Introduction

The analysis of environmental samples, often in the form of swipes laden with actinide-bearing particles, is a key component of both treaty verification activities and nuclear safeguards inspections.[1] The IAEA routinely uses the analysis of environmental swipes to verify the absence of undeclared nuclear activities within a facility and/or country.[2, 3] The frequency and importance of these analyses has resulted in a critical need for high-quality reference materials consisting of swipe materials with known particle loadings and compositions for use in proficiency testing, interlaboratory comparisons, and method development

The nonproliferation community has benefitted from recent advancements towards the manufacture of actinide-bearing microparticulate reference materials, including hydrothermal[4, 5] and aerosol-based methods,[6, 7] resulting in the in the availability of highly uniform actinide-bearing particulates with tailored isotopic and elemental compositions in sample quantities ranging from nanograms to milligrams. While prior efforts have resulted in the generation of quality control swipe materials for bulk analysis,[8] there is still a gap in the availability of surrogate environmental swipe test materials with known loadings of these tailored actinide-bearing particulates.

This work seeks to leverage recent advancements in the manufacture of actinide-bearing microparticulates, specifically the THermally Evaporated Spray for Engineered Uniform particulateS (THESEUS) production platform, developed at Savannah River National Laboratory (SRNL), to enable the production of surrogate environmental test swipes with uniform and tailorable particulate loadings. The developed method exploits the predictable settling behavior of aerosolized particles within a static volume of air to generate batches of swipes with known particle loadings, which when coupled with the tailored physical parameters and composition achievable using the THESEUS production platform offers a powerful method for the generation of surrogate environmental test swipes. The availability of high-quality surrogate environmental swipe materials with known particle loadings and particulate compositions is expected to meet the quality control needs of ongoing swipe analysis activities and further enable comprehensive studies of swipe processing and analysis techniques by providing critical test materials.

Experimental Methods

Particle generation and swipe manufacturing

Uniform particulates of depleted (0.17% ^{235}U) uranium oxide, U_3O_8, with a target equivalent circular diameter of 1-µm were generated from a uranyl oxalate feedstock using the (THESEUS

production platform, as described in in earlier literature (

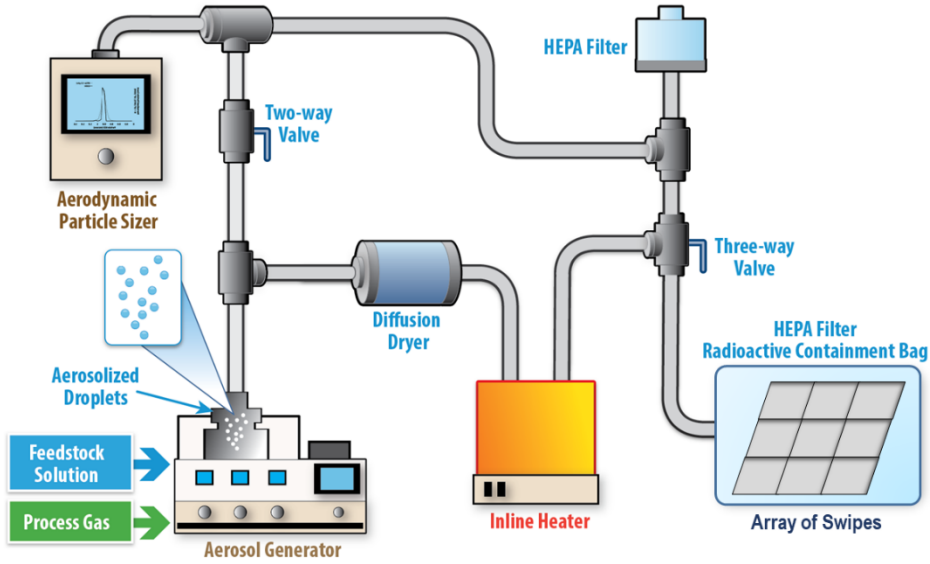

Figure **1**).[6, 9] Droplets of the uranyl oxalate feedstock material were converted to U_3O_8 via inline heating at 1000°C using a tube furnace (Lindberg/Blue M Mini-Mite tube furnace, equipped with a 1" Inconel 625 tube). Modifications to the particle collection backend of the THESEUS production platform were carried out to facilitate the manufacture of particle-laden swipes, including removal of the of the electrostatic precipitator (ESP) from the filtered radiological containment housing, as well as the installation of an alternative ceramic core heater which was used in the conversion of uranyl oxalate to U_3O_8 at 600°C.

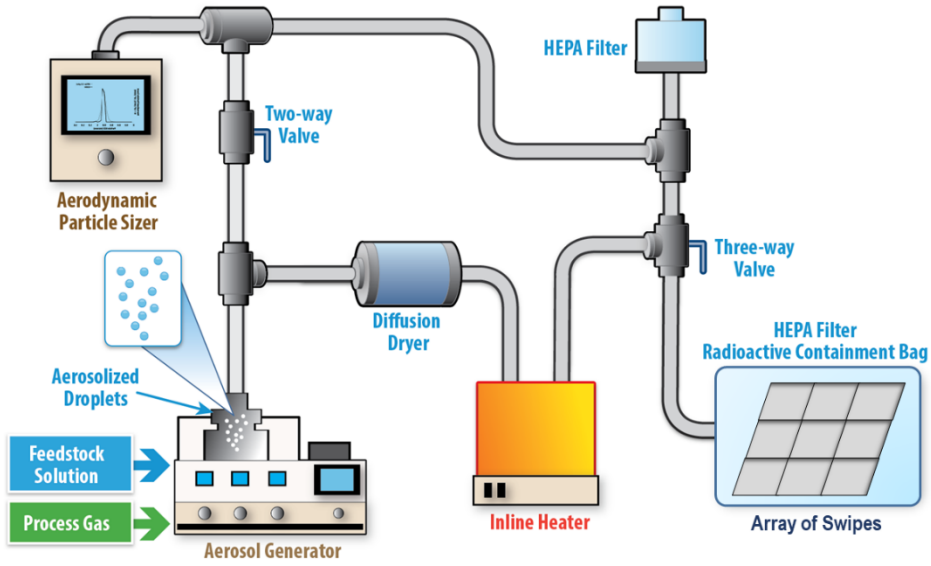

Figure 1 *Diagram of the THESEUS particle production platform.*

Whereas prior efforts involving the manufacture of uniform uranium particulates utilized electrostatic precipitation for the collection of the generated particles on conductive substrates, particle-laden swipes were prepared by removing the electrostatic precipitator from the filtered

radiological containment housing and lining the floor of the containment housing with a 3x3 array of 4x4-inch cotton swipes (TexWipe® TX304 Dry Cotton Cleanroom Wipers). Throughout the experiment the position of the generated swipes within the 3x3 array were tracked, with the positions labeled A through I, to enable assessments of swipe positioning of particulate loadings. The U_3O_8 particles were introduced to the containment housing with a known and constant mass injection rate (28.8 µg U_3O_8/min) for a set period of time (injection time). The flow to the containment housing was then stopped, and the particles were allowed to settle for a fixed period of time (settling time). The total particle loading was controlled by varying the duration of the aerosol injection and the settling times (Figure 2). Once the target settling time for a given operation was reached, the particle-laden swipes were removed from the containment housing and individually packaged within plastic zip-lock bags (the swipes each underwent a single, inward, fold during packaging). The containment housing was cleaned, including the replacement of the foil lining the floor of the housing. Batches of particle-laden swipes were generated in triplicate, across three days of replicate operation in order to assess operational variability in the developed surrogate swipe manufacturing process.

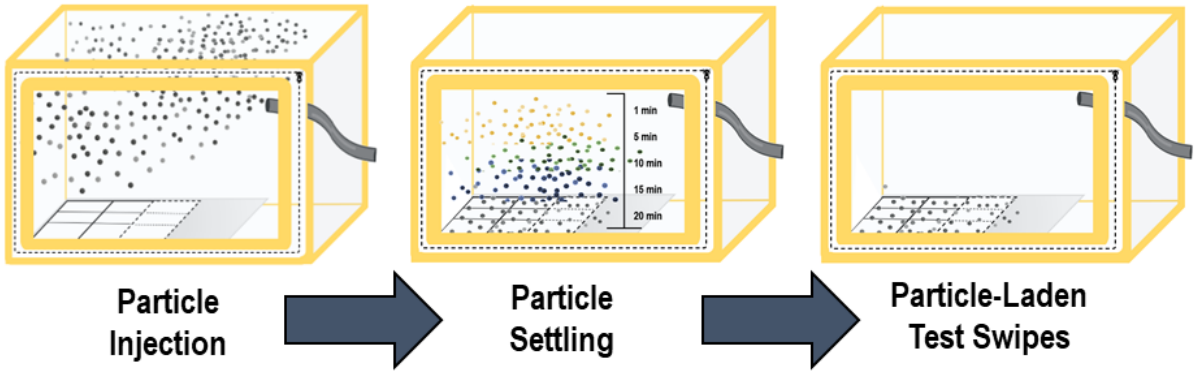

Figure 2 *Diagram of the particle-laden swipe manufacturing process, displaying particle injection, particle settling, and particle-laden swipes within the filtered radiological containment housing.*

The aerosolized particles injected into the containment housing were expected to settle onto the swipes lining the floor of the containment housing uniformly based on a simplified version of the settling velocity equation of particles in static air (Equation 1)[10]:

$$v_s = \frac{g * d^2 * \rho_p}{18\mu} \qquad \text{(Equation 1)}$$

where v_s is the settling velocity of the aerosolized particles (m-s^{-1}), g is gravitational acceleration (m-s^{-2}), ρ_g is the material density of the particulates (kg-m^{-3}), and μ is the viscosity of air (kg-m^{-1}-s^{-1}). The settling velocity equation was used to approximate the required settling time of the generated particles within the containment housing; while the effect of variable settling times was investigated, a standard settling time of 10-minutes was utilized for experiments with variable particle injection times.

Characterization

The prepared particle-laden swipes were characterized for total uranium content via Kinetic Phosphorescence Analysis (KPA)[11]. To facilitate the measurement by KPA, swipes were processed by ashing and subsequent leaching in nitric acid. During this process, individually packaged swipes were transferred to new, acid-leached 100 mL PYREX beakers. The folded swipes were carefully pushed out of the sealed incasement from the outside and into the respective beaker, where care was taken not to touch the swipes which were opened directly above the beaker to catch any loose particles that may be present during transfer. Uranium laden swipes were slowly ashed in a muffle furnace of up to 525°C before they were serially leached and evaporated down with nitric acid solutions ranging from 8 M nitric acid and a final dissolution of U particles in 0.1 M nitric acid for final storage in acid-leached glass Supelco vials with caps containing a conical Teflon liner. Swipe masses before and after ashing and the masses of the final stored solutions were recorded. At least one blank swipe and at least one matrix-matched standard, a blank swipe with a small (<0.5 mL) aliquot of the uranyl oxalate feedstock used during particle generation, were included in the ashed sample set to serve as comparisons of the uranium background in the swipe material and the uranium analyte with known concentration.

The final digestions, or bulk solutions, were primarily characterized for total uranium content by a ChemChek^{TM} KPA. Pulse height analysis (α-PHA) measurements were additionally performed on a full batch of test swipes to support analytical reconciliation and validation of the data refinement during characterization. Bulk solutions were measured for total uranium content by KPA using up to 1 mL of sample mixed with 1.5 mL of Uraplex or 1 M phosphoric acid. Sample concentrations on the order of ng-mL^{-1} were extracted by KPA using a corresponding intercept fitted to a calibration curve prepared prior to each set of samples to be analyzed. Calibrations were performed using a matrix-matched NIST-traceable natural uranium standard (NIST traceable uranyl nitrate prepared at Eckert and Ziegler Analytics, Physikalisch-Technische Bundesanstalt (PTB) a calibrated, solid U_3O_8 from NIST) at up to four concentrations. Additionally, recovery yields of the chemical digestions, bulk solutions, were determined by measured feedstock solutions, in water and dilutions prepared in uranyl nitrate form (0.1 M nitric acid), in addition to NIST-traceable uranium standard solutions. Recovery yields and recorded masses were applied to each sample to determine the total uranium content per swipe. The swipes used in this analysis were sourced from a single lot, with a measured background of 2.4 ± 0.8 ng U, as obtained by analyzing 20 swipes by KPA. By comparison, reported values for natural uranium backgrounds in cotton swipes are approximately 2 ng.[12]

A small fraction (up to 2%) of the bulk solutions from select specimens were further used to prepare samples for alpha spectrometry to further validate the KPA measurements. The alpha spectrometry samples were prepared via electrodeposition onto a 1.9 cm diameter stainless steel disk. The electroplated samples were measured ~1 mm distance from passivated implanted planar silicon (PIPS) detectors with an active area of 450 mm^2 (efficiency 33 ± 3%) within the Ultra Low-level Counting Facility at SRNL[13] for up to three days. A comparison of total uranium content measurement for the analyzed swipes suggested agreement between KPA (1.05 ± 0.13 μg U) and alpha spectrometry (1.30 ± 0.22 μg U) using alpha pulse height analysis (α-PHA).

Results

Initial estimates of the required particle settling time, based on 1-µm spherical particles of U_3O_8 (ρ= 8.30 g-cm^{-3}) with a settling distance of 15-cm, indicated a required particle settling time of 10 minutes to achieve complete settling. The validity of the calculated particle settling time needed was assessed by preparing a series of swipes with variable settling times of 1, 5, 10, 15, and 20 minutes and a fixed (10-minute) particle injection time. A comparison of the average uranium loading per swipe for each of the settling times (Figure 3) suggests an incomplete settling of the particles at 10 minutes (0.534 ± 0.053 µg U per swipe), with near complete settling of the particles occurring near 20 minutes, as indicated by the negligible increase in the average mass of U per swipe between 15 and 20 minutes (0.610 ±0.040 vs. 0.625 ±0.011 µg U per swipe, respectively).

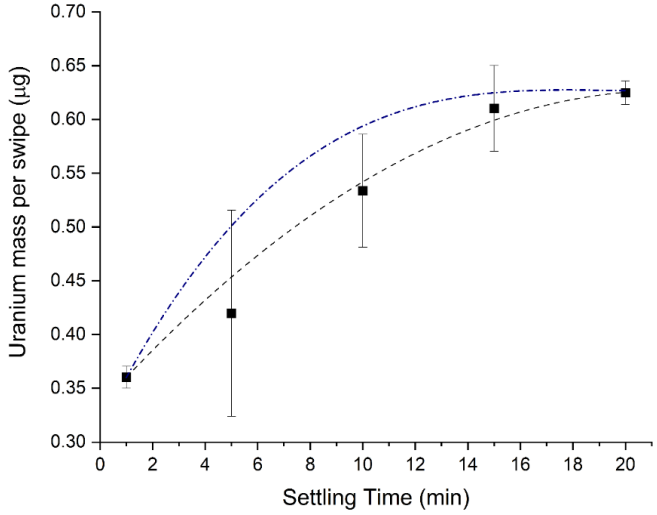

Figure 3 *Average mass of uranium per swipe as a function of particle settling time, as compared to the anticipated particle settling behavior for ideally smooth particles (blue line). Error bars represent the propagated 1σ counting statistics uncertainty for the averaged batch values.*

The observed difference between the idealized particle settling behavior and the observed response to settling time is most likely driven by increased drag effects on the particles due to surface roughness. The calculated value to estimate settling time assumes smooth, spherical particles, however surface roughness and/or irregularity in the shape of the particles would result in increased aerodynamic drag which would lead to longer settling times. Further reduction in the variability of particle-loading would be expected by increasing the settling time beyond the 20 minutes investigated in this study and would be recommended to operationalize the developed method.

The tailorability of particle loading per swipe in the developed method was assessed by varying the particle injection times across a dynamic range (1, 5, 10, 30, 60, and 120 minutes), with a constant settling time (10 minutes). The resultant uranium mass loading per swipe displayed a high degree of linearity (slope of 0.04 µg/min, R^2 = 0.999), suggesting particle loading per swipe may be directly controlled through the variation of the particle injection time (Figure 4). Additional

assessments of the tailorability of the particle loading on a per swipe basis included the assessment of an alternative ceramic core heater within the THESEUS platform (Tutco Farnham Heat Torch 050). The use of the ceramic core heater, with a demonstrated reduced transmission efficiency as compared to the tube heater used in the other tests in this study, enabled the assessment of the lower bounds of particle loading with the developed method. The swipes prepared using the ceramic core heater displayed similar linearity (slope of 0.02 µg/min, $R^2 = 0.994$) as those prepared using the tube heater. The pair of the heater configurations tested resulted in the production of swipes with per-swipe uranium mass loadings spanning tens of nanograms up to tens of micrograms, and further suggests the application of filtration and/or dilution-based techniques may be suitable for the preparation of particle-laden swipes at lower mass loadings.

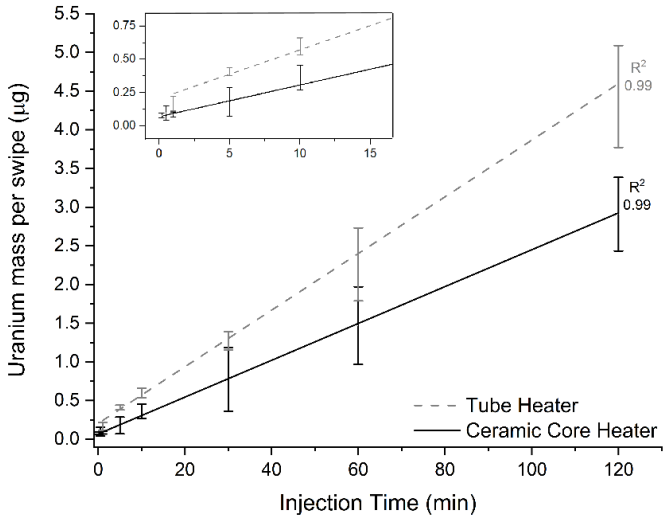

Figure 4 *Average mass of uranium per swipe as a function of particle injection time for both a ceramic core and tube heater (inset: magnified for injection time 0 to 15 minutes). Error bars represent the propagated 1σ counting statistics uncertainty for the averaged batch values.*

Assessments of reproducibility and variability in the particulate loading of the swipes were conducted on both an inter- and intra-batch basis. To assess the extent of inter-batch (operational) variability, swipes produced with varying particle injection times (1, 5, 10, 30, 60, and 120 minutes) were generated across 3 production batches occurring on discrete days of operation and were subsequently analyzed for their total uranium content using KPA (Figure 5A). The generated swipes displayed good agreement in their uranium loadings between batches, with operational variability < 15% for particle injection times of 10 minutes or greater. Notably, higher variabilities, up to 28%, were observed for low particle injection times (Table 1). This trend in increasing operational variability is explained in part by the counting statistical error associated with lower uranium loadings, however additional contributions to operational variability are hypothesized to include a greater sensitivity to time measurements (for both the particle injection and settling times), as well as the transients associated with reconfiguration of the production system during the manufacturing process, at the lower particle injection times.

The evaluation of intra-batch (positional) variability involved a comparison of uranium particle loading per swipe for each location within a batch of swipes. Each swipe from five of the nine positions (locations B, D, E, F, and I) were analyzed by KPA for total uranium content in each of 3 batches generated across the range of particle injection times (1, 5, 10, 30, 60, and 120 minutes) (Figure 5B). The generated swipes displayed minimal positional variability (< 5%) for particle injection times of 10 minutes or greater, with the greatest variability (43%) observed at the lowest injection time of 1 minute (Table 1). Notably, this difference in positional variability as compared to operational variability reinforces the hypothesized contributions of timing sensitivity to the operational variability, as the uniformity of particle settling within the containment housing, which drives the positional variability in the swipes, would be largely unaffected by such factors. This suggests that future refinements of the developed method should emphasize increased attention to the time measurements to reduce operational variability between batches of swipes.

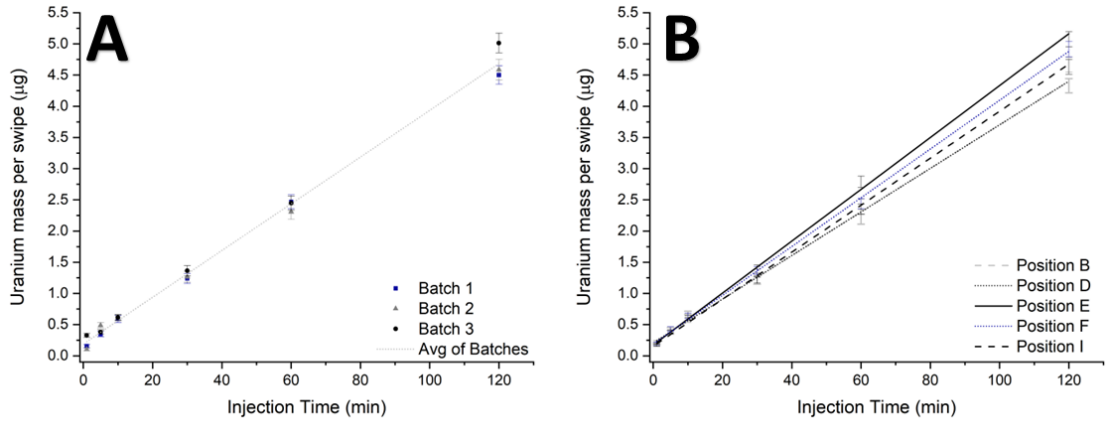

Figure 5 *(A) Inter-batch (operational) variation, and (B) intra-batch (positional) variation for particle-laden swipes generated across a range of particle injection times with a uniform (10 minute) settling time. Error bars represent the propagated 1σ counting statistics.*

Table 1 *Inter-batch (operational) variation, and (B) intra-batch (positional) variation for particle-laden swipes generated via tube-furnace equipped THESEUS across a range of particle injection times with a uniform (10 minute) settling time.*

Particle Injection Time (min)	Average Uranium Mass Loading per Swipe (µg)	Intra-Batch (Positional) Variance (µg)	Relative Intra-Batch (Positional) Variance (RSD)	Inter-Batch (Operational) Variance (µg)	Relative Inter-Batch (Operational) Variance (RSD)
1	0.17	0.084	43 %	0.047	28 %
5	0.41	0.051	13 %	0.070	17 %
10	0.60	0.0099	2 %	0.085	14 %
30	1.3	0.046	4 %	0.14	11 %
60	2.3	0.062	3 %	0.20	8 %
120	4.6	0.19	4 %	0.27	6 %

Conclusions

The aerosol-based method for the manufacture of surrogate environmental test swipes discussed in this work displays promise as a means to generate test materials in support of treaty verification and nuclear safeguards activities. The developed method enables the deposition of engineered particulates with tailored properties onto swipe substrate with controlled particulate loadings and reproducibility on a per-swipe basis (< 15% variability in uranium mass for injection times of 10 minutes or greater). Further refinement of the developed surrogate environmental test swipe manufacturing method is expected to include: improvements in the reproducibility and tailorability of the particle loadings using filtration and/or dilution-based techniques, ability to generate swipes with multiple particulate species, including diluent particulates resembling environmental matrices (i.e. dirt or dust), and the development of techniques to restrict particle deposition to target areas of the generated test swipes.

Acknowledgements

This work was conducted as a part of the National Nuclear Security Administration Defense Nuclear Nonproliferation Research and Development (NNSA DNN R&D) project "Nuclear Test Material Development for Arms Control and Treaty Monitoring".

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