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Practical Utilization of a Uranium-Containing Particulate Test Samples for SEM/EDS and SIMS Automated Particle Analysis Method Validation

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The detection and characterization of uranium particulates from swipe samples collected by safeguards inspectors from nuclear facilities often relies on automated search algorithms and instrument software for both scanning electron microscopy (SEM) and secondary ionization mass spectrometry (SIMS). Because safeguards samples are inherently cluttered with background environmental material automated particle measurement (APM) methods with correctly tuned instrument parameters are required. Unfortunately no standard or reference specimens are conveniently available for APM method validation or instrument proficiency testing. To meet such challenges the safeguards community has generated and characterized select test specimens over the past decade, but these efforts have been hindered by limited production and challenging characterization.[1-3] Unlike the Gun Shot Residue (GSR) analysis community, where industry-recognized standards are available, no equivalent is commercially available for actinide particulate reference materials at this time.

Laboratories are currently required to generate in-house APM validation test samples if needed. To this end SRNL has developed a rapid method to generate test specimens which are sparsely populated with uranyl oxalate particulates of uniform composition. Our technique utilizes conventional aerosol generation and in-house collection/deposition tools to simultaneously create multiple substrates with micro to nanograms of total uranium mass loading.[4] Characterization of individual particles by micro-Raman spectroscopy and TEM of lamella (post FIB processing) have verified the uranyl oxalate species as anhydrous by both vibrational modes and lattice spacing, respectively, as shown in Figure 1. Sample generation parameters may be tuned to produce multiple specimens simultaneously with a desired mass/particle loading. A prototypical specimen contains approximately ~1000 spherical uranium particulates (~5 particles/mm^2), a monomodal particle size distribution with average diameter of 1.8 microns (σ = 0.4 microns), and approximately 10^{-11} grams uranium per particle. The sparse particulate density and low U mass make these samples ideal for method validation for trace detection/characterization of actinides by automated SEM/EDS or SIMS.

Typical SEM/EDS APM methods employ a validation specimen as the initial and terminal analysis for a series of unknowns processed by automated technique. Metrics assessed include particle count, position, and size distributions. Coupling the known uranyl oxalate test sample with carbon stub blanks, in an end-to-end serial analysis similar to standard GSR procedures, monitors instrument stability and operator efficacy. Figure 2 demonstrates an evaluation of particle measurement accuracy for a given test specimen where particle count and area histograms are compared on two different day of instrument operation. A shift in overall particle count typically coincides with stage or backscatter detector electronics drift. In practice, these failures often coincide with a decrease in detection of the smaller diameter particles. Figure 2 also shows an example SIMS APM for a validation sample comparing ionization yield and 235/238 uranium isotopic concentrations and used as an instrumentation efficacy

diagnostic. Correlation microscopy can be employed between SEM and SIMS to analyse particle size and ionization yields relationships. Consistent use of this type of validation sample provides increased analysis confidence, provides quality assurance diagnostics, and allows easier interlaboratory assessments in both SEM/EDS and SIMS APM methods.

References:

(1) Kraiem, M.; Richter, S.; Erdmann, N.; Kuhn, H.; Hedberg, M.; Aregbe, Y. *Anal. Chim. Acta* **2012**, *748*, 37.

(2) Simons, D. S. *J. Trace Microprobe Tech.* **1986**, *4*, 185.

(3) Sharp, N.; Fassett, J. D.; Simons, D. S. *J. Vac. Sci. Technol., B: Nanotechnol. Microelectron.: Mater., Process., Meas., Phenom.* **2016**, *34*, 03H115/1.

(4) Bridges, N. J.; Fugate, G. A.; Kriz, M. R.; Pittman, J. J.; Siegfried, M. J.; Wellons, M. S.; 2013 Savannah River National Laboratory LDRD Annual Report #SRNL-STI-2014-00096, SRNL: Aiken SC, 2013, p 6.

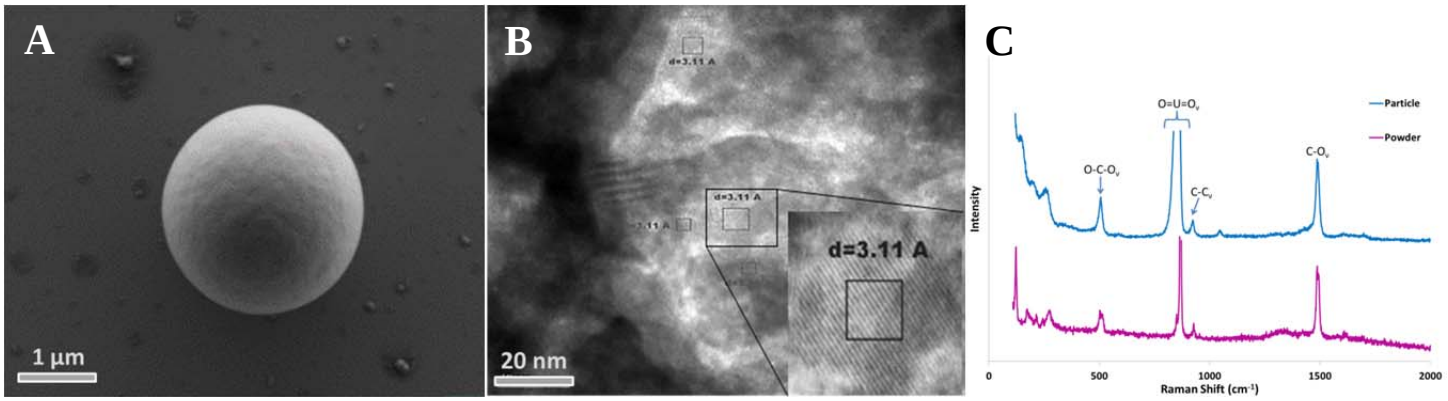

Figure 1. (A) Typical micron-sized uranyl oxalate particulate, (B) Post FIB lamella characterized by TEM and demonstrating lattice fringes consistent with anhydrous $UO_2(C_2O_4)$; (C) Raman spectra of anhydrous uranyl oxalate commercial powder and a generated particulate.

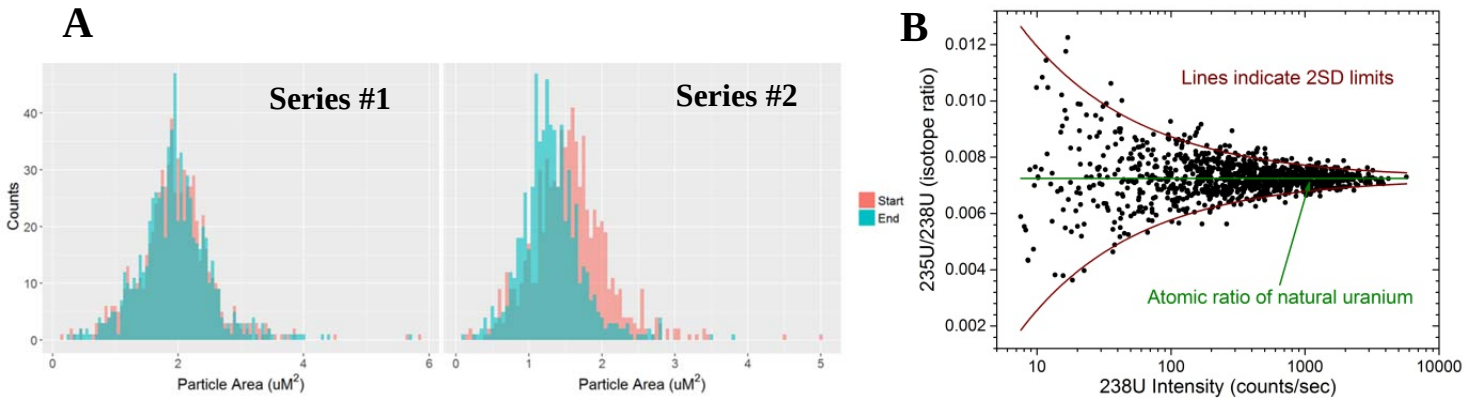

Figure 2. (A) Histograms of a validation sample analyzed twice for two different sample analysis queues. The first validation measurements demonstrate consistent histograms for the standard from sample queue beginning to end. The second demonstrates a shift in overall measured particle area consistent with working distance drift between APM measurements; overall particle count remains high but average particle area decreases. (B) Plot of the 235/238 U isotope ratio per 238 U counts per sec collected on a Cameca IMS 1280 LG-SIMS (n=1134).