LAB-RPT-18-00003 R0

Plutonium Particle Examination by Scanning Electron Microscopy Analysis of Plutonium Finishing Plant Air Filters and Tech Smears

J. S. Page
Washington River Protection Solutions LLC

Date Published
March 2018

Prepared for the U.S. Department of Energy
Office of River Protection

Contract No. DE-AC27-08RV14800

Table of Contents

1 Introduction 4
2 Method 4
3 Analysis Results 6
3.1 B3HLY5 (29) 6
3.2 B3HLY3 (28) 12
3.3 B3HLX5 (10) 15
4 References 19

List of Figures

Figure 1. SEM Image of Several Particles and Their Measured Sizes as Found on Sample S18R000009 . 7
Figure 2. Results Summary of the Automated Runs on Sample S18R000009 7
Figure 3. Image and Spectrum of a Large Plutonium Particle on Sample S18R000009 8
Figure 4. Image and Spectrum of a Plutonium Particle Detected on Sample S18R000009 8
Figure 5. Image and Spectrum of another Larger Plutonium Particle on Sample S18R000009 8
Figure 6. Image and Spectrum of a Smaller Plutonium Particle on Sample S18R000009 9
Figure 7. Image and Spectrum of a Small Plutonium Particle on Top of a Larger Soil Particle on Sample S18R000009 9
Figure 8. Image and Spectrum of a Crushed Plutonium Particle on Sample S18R000009 9
Figure 9. Elemental Mapping Results of a Large Plutonium Particle Showing the Location of Selected Elements in the Images 10
Figure 10. A Plutonium Particle with Elongated Morphology from the 261-Z-9 Crib 11
Figure 11. A Non-Crystalline to Semi-Crystalline Plutonium Particle from the 261-Z-9 Crib 11
Figure 12. Image Showing Particles Typical in Sample SR18000011 with Several Measured for Size... 13
Figure 13. Summary of the Automated Feature Analysis Run on Sample S18R000011 13
Figure 14. Images of a Plutonium Particle on Sample S18R000011 Before and After it Rolled on the Surface 14
Figure 15. Image and Spectra of a Plutonium Particle on Sample S18R000011 14
Figure 16. Typical Particles and Measured Sizes on Sample S18R000029 16
Figure 17. Summary of the Automated Feature Analysis Results for Sample S18R000029 16
Figure 18. Images and Spectra of Plutonium Particles Measured by the Automated Feature Analysis on Sample S18R000029 17
Figure 19. Manual Analysis of a Plutonium Particle in Sample S18R000029 18

List of Terms

Acronyms and Abbreviations

AFA	automated feature analysis
EDS	energy dispersive spectrometry
PAM	portable alpha meter
PFP	Plutonium Finishing Plant
SEM	scanning electron microscopy

Units

dpm	disintegrations per minute
keV	kiloelectron volt
µm	micrometer

1 INTRODUCTION

Under the direction from the Statement of Work titled, "Managed Task Analysis of PFP[1] Air Filters by Scanning Electron Microscopy," 30 samples were received at the 222-S Laboratory for scanning electron microscopy with energy dispersive spectrometry (SEM/EDS) analysis, client sample request 222S20180187. Fifteen of these samples were blanks and were used as a reference to obtain information on the clean media. The analysis results, consisting of images and elemental analysis of particles observed and particle sizes for all 15 field samples and 3 of the blank samples, were reported in LAB-RPT-18-00002 R1, "Scanning Electron Microscopy Energy Dispersive Spectrometry Analysis of Plutonium Finishing Plant Air Filter and Tech Smears." Most of the detected particulate was typical Hanford soil material and demolition debris with trace unique particles such as plutonium, barium sulfate, lead, and cerium-rich phases. Most of the field samples had reported alpha radiation levels of less than one hundred to several hundred decays per minute, but four of the samples had alpha levels over 10,000 dpm. All plutonium particles detected and reported were found on three of these four high-level samples.

This report focuses solely on the plutonium particles detected in this analysis, as requested by the customer, see Attachment A. The results of the three samples where plutonium particles were found by SEM are presented for each sample individually, but the discussion of the plutonium phase and its characteristics is carried throughout as the plutonium particles were similar across all three samples, suggesting the same origination. In addition, the plutonium particles found on these recent samples are compared to plutonium particles from the 216-Z-9 trench to provide more information on the source of origination.

2 METHOD

The samples were received on January 18, 2018. All the samples were adhered to 2-inch metal planchets and were contained in cardboard holders. They were photographed and then analyzed by SEM/EDS; no additional preparation steps were performed prior to analysis. Each sample was loaded individually into the SEM instrument by placing the entire planchet onto the sample stage. The specimens were analyzed according to the laboratory technical procedure, ATS-LT-161-103, "222-S Laboratory Technology Procedure for the ASPEX Explorer Scanning Electron Microscope," and the analysis was documented in the SEM laboratory notebook, HNF-N-832-1, "PSEM Instrument Notebook." The analysis was done at a 25 keV accelerating voltage using the variable pressure mode (0.1 Torr), which allowed the samples to be analyzed without carbon coating. The backscatter electron detector was used for the entire sample set, and the EDS acquisition time was 30 seconds in manual mode.

In addition, the samples were analyzed using the automated feature analysis (AFA) routine on the SEM to specifically look for plutonium-rich particles. This routine automatically progressed through a defined sample area in a continuous step-wise fashion, across the sample surface, measuring particles containing high mass elements. The tabulated particles were then manually evaluated to determine which contained plutonium, and these particles were reimaged manually.

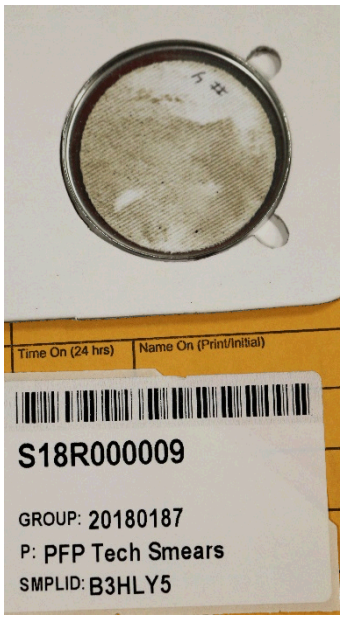
[1] PFP = Plutonium Finishing Plant

The alpha counts were also measured on all the samples at the 222-S Laboratory by radiological personnel using a portable alpha meter (PAM) model 2360. Total counts were recorded for one minute and a disintegrations per minute value was calculated. These results are shown for each sample along with the reported alpha counts (found written on each sample cardboard holder) in the body of this report.

3 ANALYSIS RESULTS

3.1 B3HLY5 (29)

OmniLIMS™[2]: S18R000009
Reported Alpha Counts: 15,830 dpm
PAM Alpha Counts: 7432 dpm



Sample S18R000009 was a tech smear taken from a location on a vehicle. Visually, the smear was nearly covered with a brown residue. The SEM analysis showed the smear to be heavily loaded soil mineral particles with a large range in size from sub-micrometer to up to ~200 µm (Figure 1).

The AFA run was set up with a defined area on the tech smear that visually exhibited the most particulate, with the brightness and contrast of the backscatter detector adjusted to eliminate lower mass elements. Due to the heavy particulate load of this sample, two separate AFA runs were combined that totaled ~14 hours of analysis and resulted in over 8000 detected and measured particles that were classified as "defined" in a rule file supplied by the vendor (Figure 2). The majority of these particles were iron-rich phases.

The resulting AFA data was manually evaluated by looking at all the collected EDS spectrum of detected particles with a reported potassium level above 5% (potassium was used to mark the presence of plutonium in the EDS spectrum due to the good X-ray overlap of its K-lines with the plutonium M-lines since plutonium X-ray information was not supplied in the instrument's rule file). This data analysis indicated that six particles displayed an EDS spectrum that matched plutonium. These six particles were then found manually on the sample using the reported coordinates from the AFA run, and several images and EDS spectra were acquired confirming the presence of plutonium (Figures 3 through 8). The size measurement of these particles showed that the two larger plutonium particles were ~100 µm and ~50 µm across while the smaller particles were around 5 to 10 µm in size. One of the particles appears to have been crushed during sampling (Figure 8), suggesting this plutonium phase is friable.

It is of interest to note that the EDS analysis shows silicon is associated with all six plutonium particles. It has also been reported that silicon was part of an unwanted material derived from processes at the Plutonium Reclamation Facility where it was observed with plutonium and an organic material to form a crud that would cause difficulties in the facility's reclamation processes, PNNL-25888, "Literature Review: Crud Formation at the Liquid/Liquid Interface during TBP-based Solvent-Extraction Processes."

The elemental composition of the larger plutonium particle was further explored by performing an EDS mapping which produced pseudo-images based upon the detected X-rays of selected elements (Figure 9). The results indicate that the phosphorous observed in the EDS spectra of

[2] OmniLIMS is a trademark of Columbia Energy and Environmental Services, Richland, Washington.

the plutonium particles is solely associated with the plutonium and is not found in the other background particulate (mineral particles).

Figure 1. SEM Image of Several Particles and Their Measured Sizes as Found on Sample S18R000009

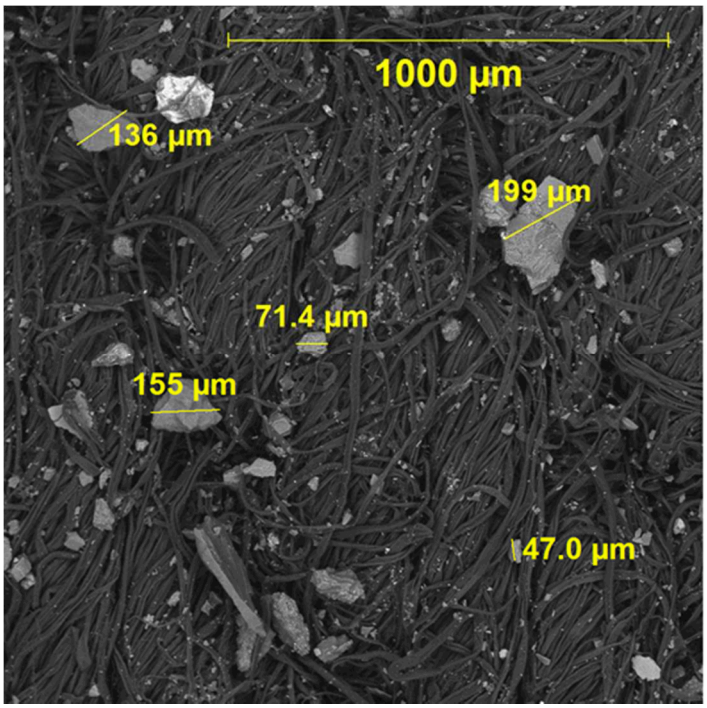
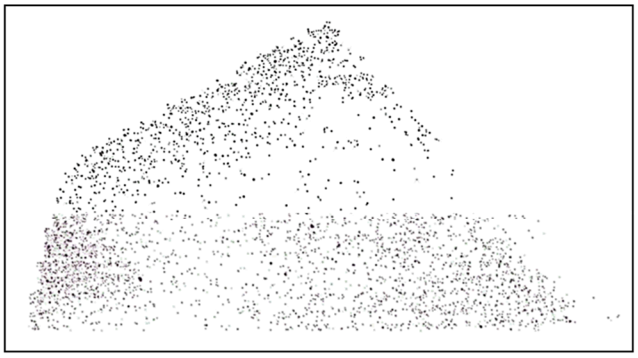


Figure 2. Results Summary of the Automated Runs on Sample S18R000009

All Particles Detected and Measured



Starting 02-13-2018PFP.afa
Results in C:\AFAData\48
Beginning of Analysis
Starting Run_1 with field 1 at 2:56:16 PM on 2/13/2018.
Initial emission: I=33.400 µA [2:56:16 PM]

Result summary:
Data Filename = C:\AFAData\48\Run_1\Run_1.hdz
Beam Energy = 25 kV
'orking Distance = 16.2 mm
Spot = 30%
Detector = BSED
Contrast = 100%
Brightness = -33.9%
Stub = S18R000009
Client name = CH2M Hill
Detail = 15,830 dpm
Description = PFP Smear
Area = 123.721 mm²

Particle count by class:

Rule Name	Count
Iron-Titanium	2943
Iron Rich	2936
Garnet	423
Misc. Silicates	252
Other	166
Barium Sulfate	71
Barium Rich	60
Stainless Steel	57
Cerium Rich	44
Titanium	29
Zircon	26
* Lead Rich	8
Strontium-bearing	3

Figure 3. Image and Spectrum of a Large Plutonium Particle on Sample S18R000009

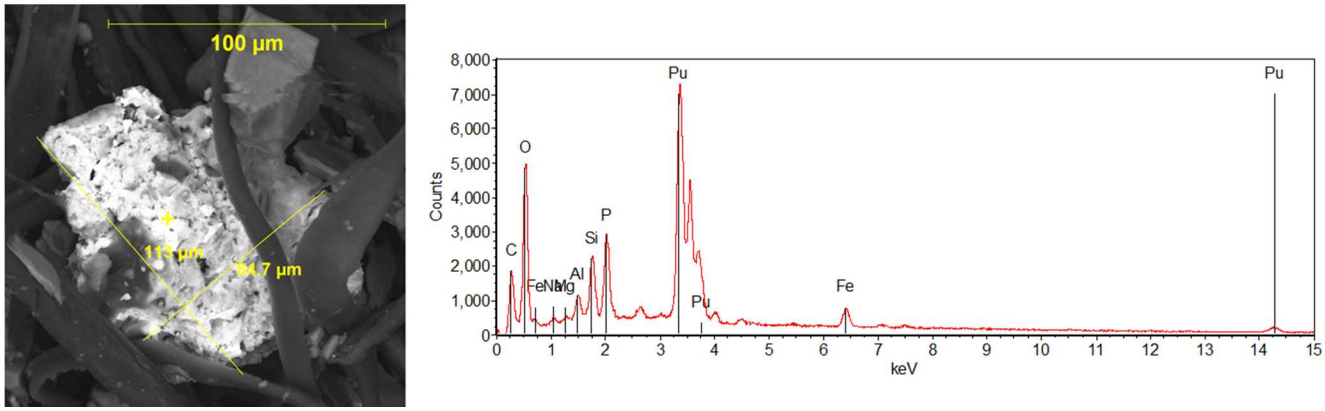


Figure 4. Image and Spectrum of a Plutonium Particle Detected on Sample S18R000009

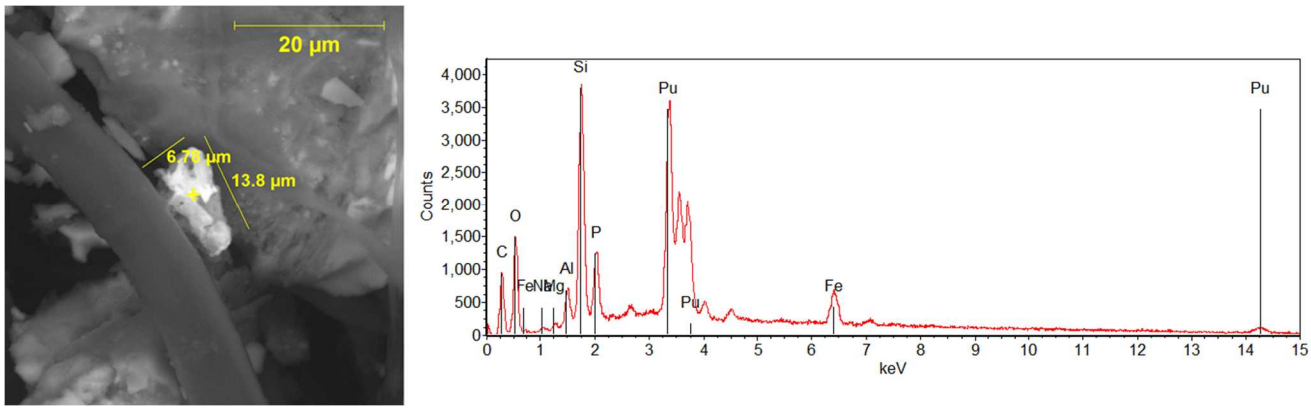


Figure 5. Image and Spectrum of another Larger Plutonium Particle on Sample S18R000009

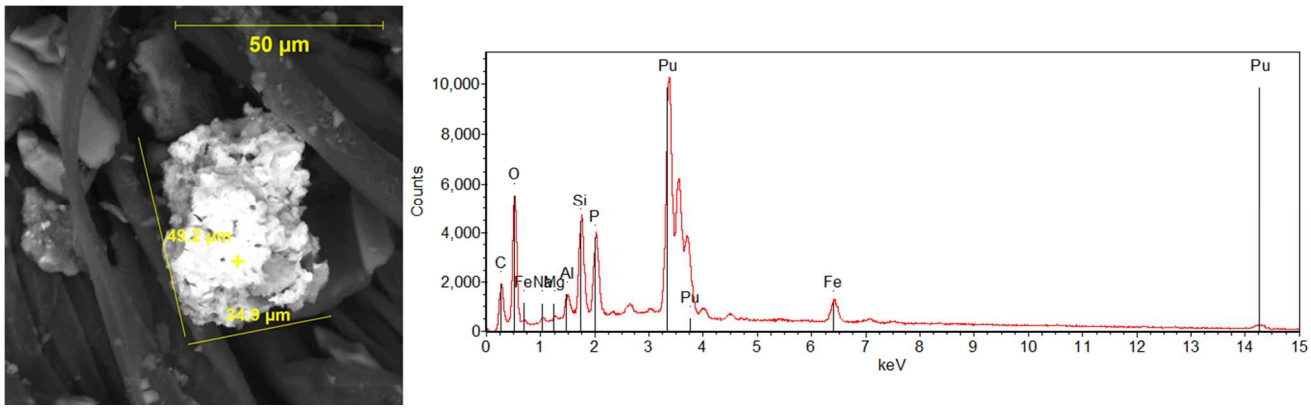


Figure 6. Image and Spectrum of a Smaller Plutonium Particle on Sample S18R000009

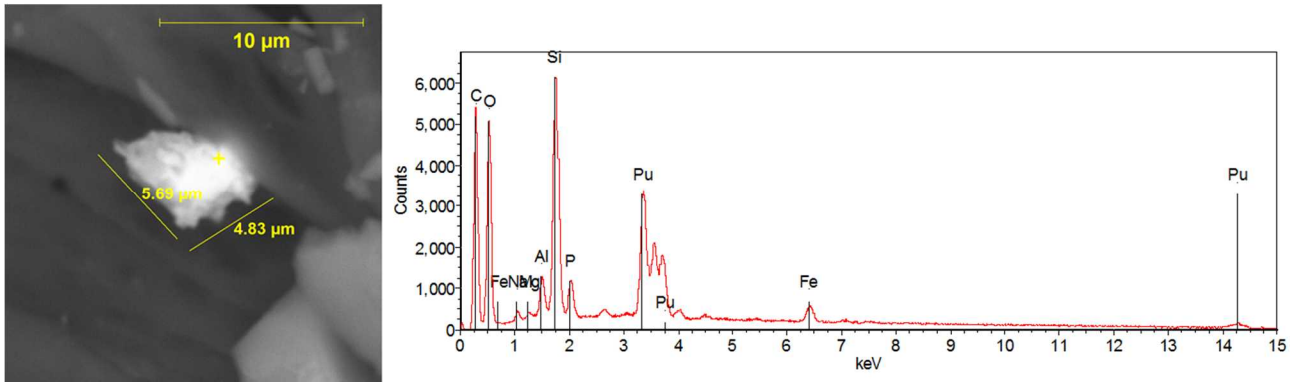


Figure 7. Image and Spectrum of a Small Plutonium Particle on Top of a Larger Soil Particle on Sample S18R000009

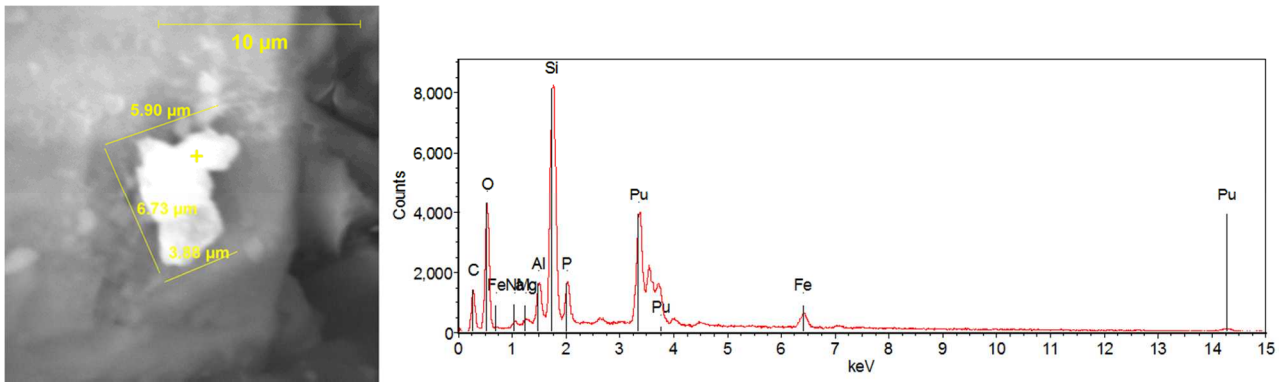


Figure 8. Image and Spectrum of a Crushed Plutonium Particle on Sample S18R000009

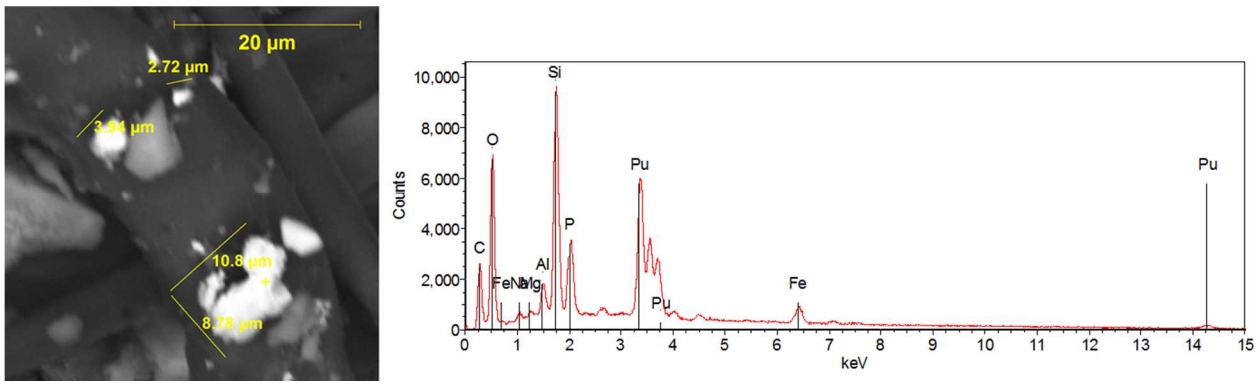
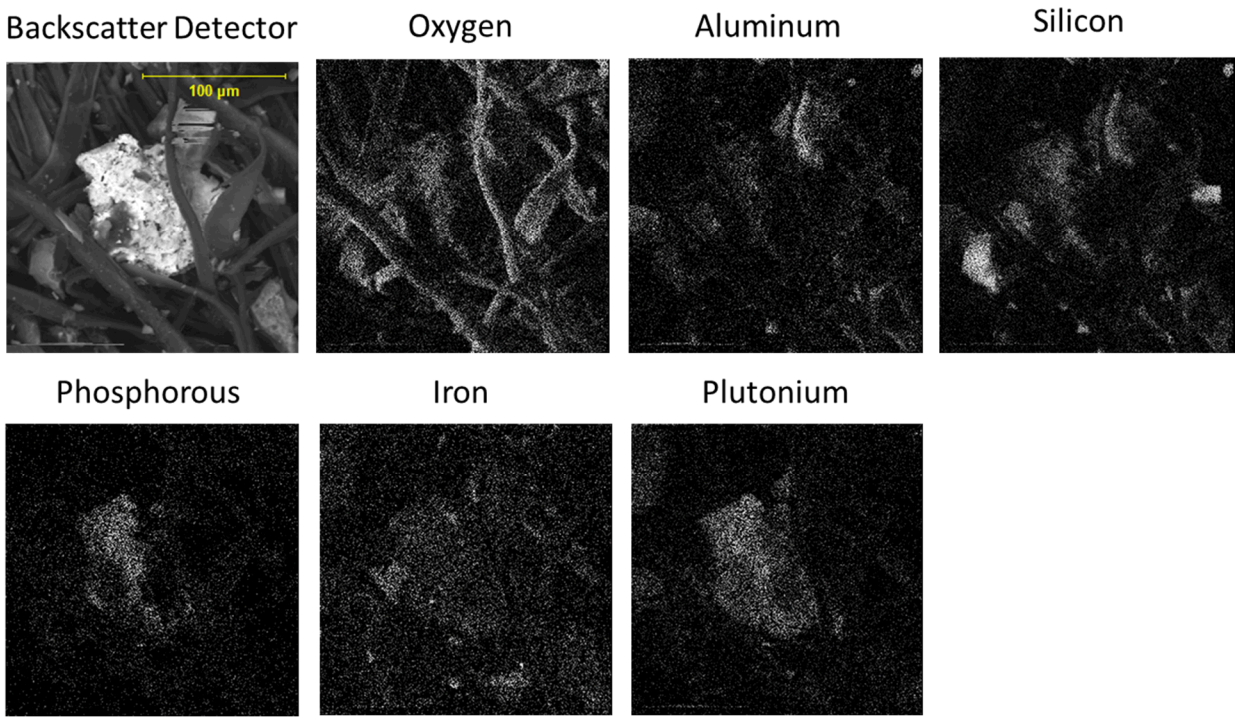


Figure 9. Elemental Mapping Results of a Large Plutonium Particle Showing the Location of Selected Elements in the Images



A previous report characterized plutonium-bearing particles from the 261-Z-9 crib located near PFP (LAB-RPT-12-00006, "Characterization of Plutonium-Bearing Waste in the High-Level Waste Storage Tanks 241-SY-102, 241-TX-118, and 241-AZ-101 and the Plutonium Finishing Plant Z-9 Crib"). That document reports the observed plutonium particles from the crib had a size range of 5 to 26 µm and consisted of either a plutonium oxide phase or an undetermined plutonium-rich phase (Figures 10 and 11). There was evidence of trace to only moderate levels of phosphate and silicon in the plutonium particles from the 261-Z-9 crib, compared to the higher levels detected in all the plutonium particles on the PFP smear sample. This suggests likely different plutonium sources between the crib and smear samples.

Figure 10. A Plutonium Particle with Elongated Morphology from the 261-Z-9 Crib

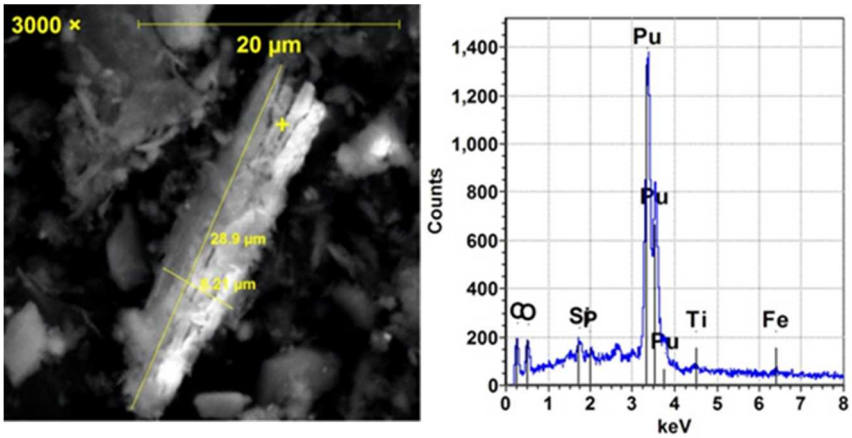
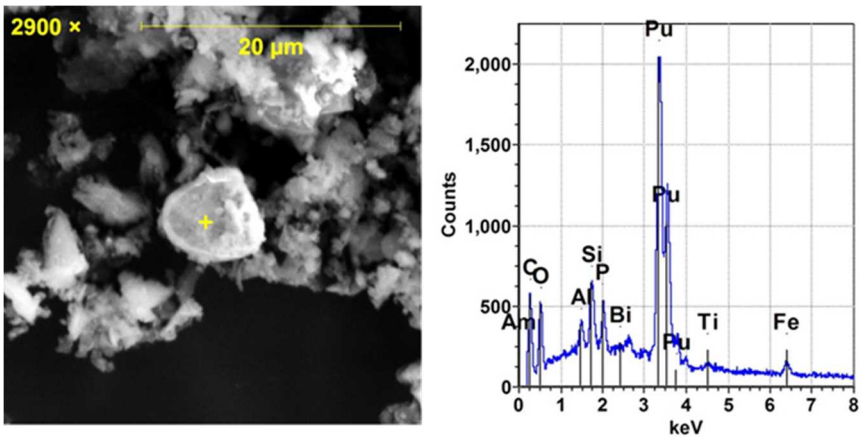
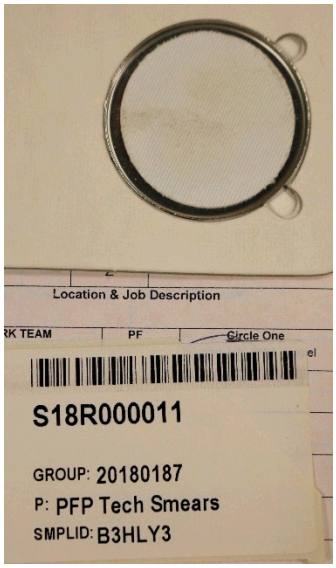


Figure 11. A Non-Crystalline to Semi-Crystalline Plutonium Particle from the 261-Z-9 Crib



3.2 B3HLY3 (28)
OmniLIMS: S18R000011
Reported Alpha Counts: 13,600 dpm
PAM Alpha Counts: 3766 dpm



Similar to sample S18R000009, sample S18R000011 was a tech smear taken from a location on a vehicle. Visually, the smear had a slight, dark discoloration across the surface. The SEM analysis showed mineral particles embedded in the fibers ranging in size from sub-micrometer up to ~30 µm (Figure 12). An AFA run was performed to search for plutonium particles. The run was set up with a defined area on the tech smear that visually exhibited the most particulate, with the brightness and contrast of the backscatter detector adjusted to eliminate lower mass elements. The 6.5-hour automated run resulted in over 150 detected and measured particles which were classified as "defined" in a rule file supplied by the vendor (Figure 13). The majority of these particles were classified as iron-rich mineral phases.

The resulting AFA data was manually evaluated by looking at all the collected EDS spectrum of detected particles with a reported potassium level above 5% (potassium was used to mark the presence of plutonium). This data analysis indicated that only one particle had an EDS spectrum that matched plutonium. This particle was then found manually on the sample using the reported coordinates from the AFA run, and several images and EDS spectra were taken. During the manual analysis, the plutonium particle rolled on the sample. Figure 14 shows two images of the same particle before and after a roll. The dark material on the particle in the left image was not analyzed by EDS because the particle rolled before this could be performed, but it appears to be a carbon-rich material adhered to the surface. Figure 15 contains the results of the EDS analysis at three different locations on the particle. Spot #2 shows a mineral phase on or adhered to the surface, and spots #1 and #3 are from a bare location on the particle. Both of these bare locations indicate that the phase is a plutonium oxide with trace phosphorous and silicon in or on the particle. The elemental content of this plutonium particle is more consistent with the 261-Z-9 crib plutonium particles.

Figure 12. Image Showing Particles Typical in Sample SR18000011 with Several Measured for Size

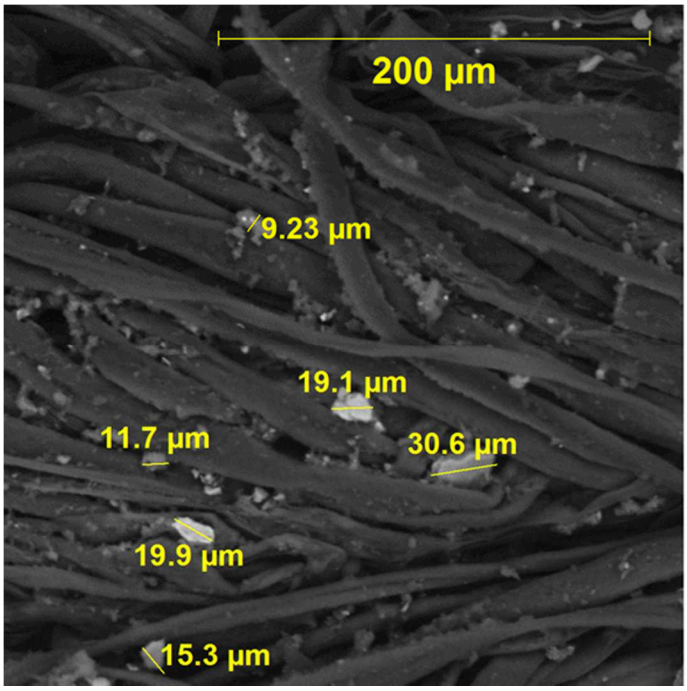
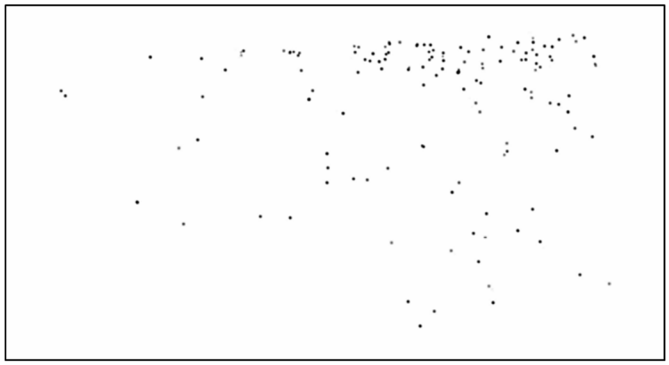


Figure 13. Summary of the Automated Feature Analysis Run on Sample S18R000011

All Particles Detected and Measured



Starting 02-12-2018PFP.afa
Results in C:\AFAData\47
Beginning of Analysis
Starting Run_1 with field 1 at
2:41:49 PM on 2/12/2018.
Initial emission: I=33.500 µA
[2:41:49 PM]

Result summary:
Data Filename =
C:\AFAData\47\Run_1\Run_1.hdz
Beam Energy = 25 kV
Working Distance = 14.6 mm
Spot = 30%
Detector = BSED
Contrast = 100%
Brightness = -34.4%
Stub = S18R000011
Client name = CH2M Hill
Detail = 13,600 dpm
Description = PFP Smear
Area = 534.210 mm²

Particle count by class:

Rule Name	Count
Iron-Titanium	44
Iron Rich	47
Barium Rich	15
Stainless Steel	12
Cerium Rich	11
Other	5
Brass	4
Lead Rich	4
Barium Sulfate	4
Misc. Silicates	3
Zinc	2
Misc. salts	2

Figure 14. Images of a Plutonium Particle on Sample S18R000011 Before and After it Rolled on the Surface

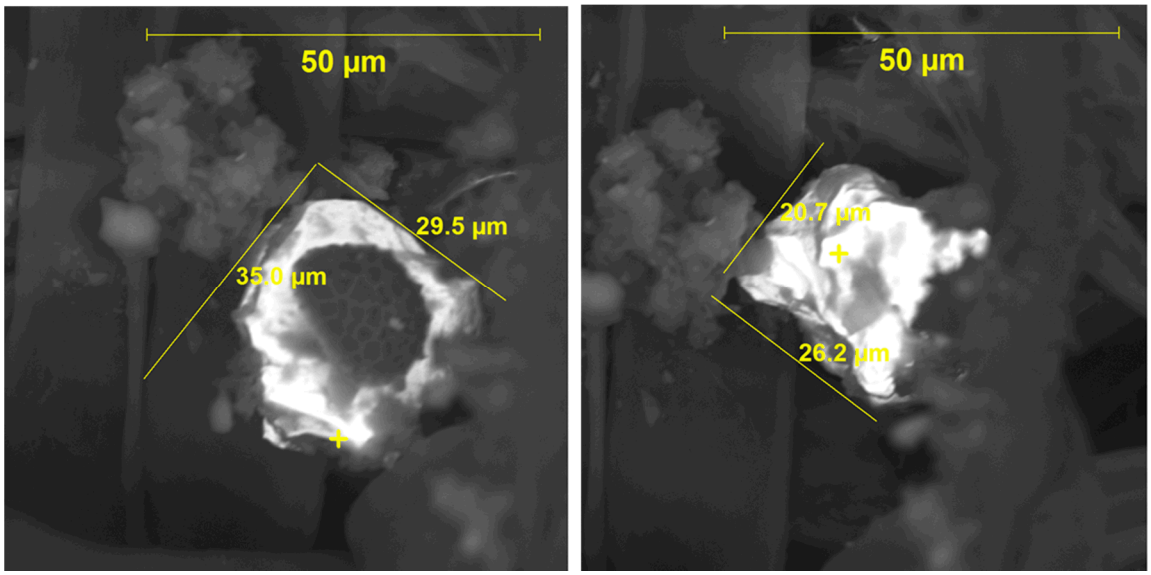
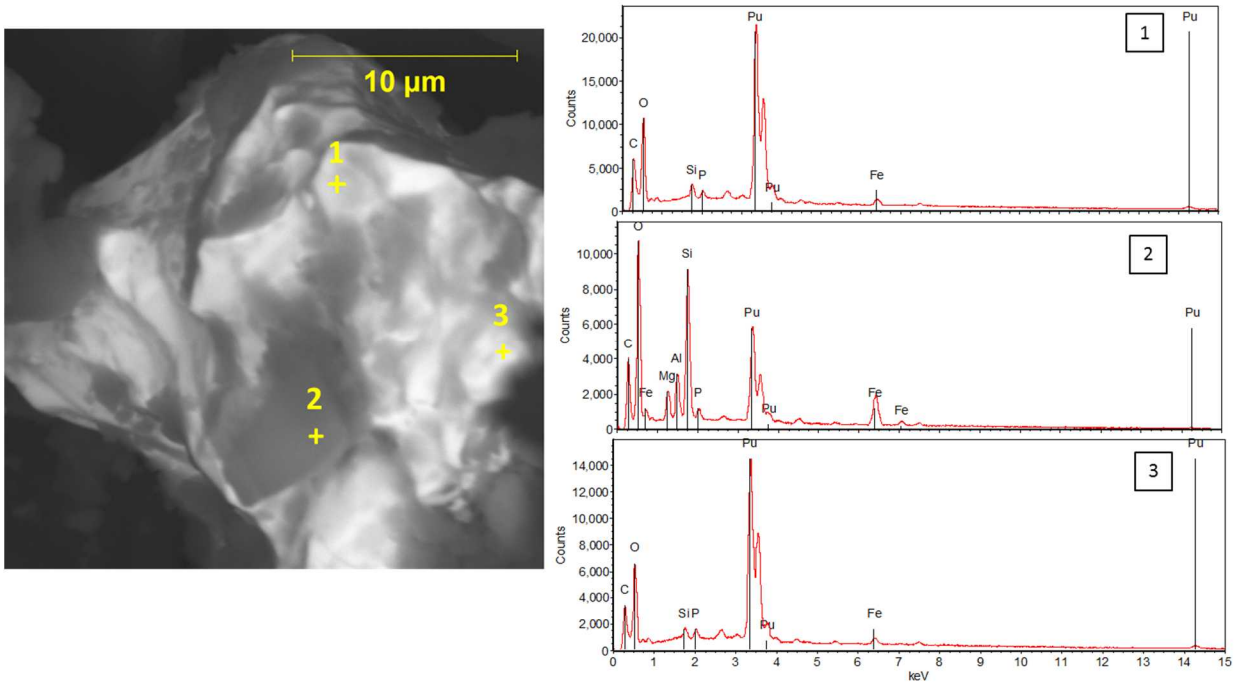
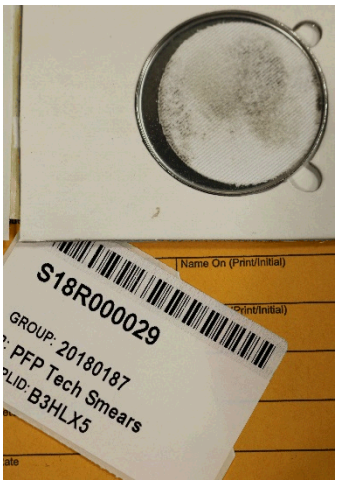


Figure 15. Image and Spectra of a Plutonium Particle on Sample S18R000011



3.3 B3HLX5 (10)
OmniLIMS: S18R000029
Reported Alpha Counts: 11,570 dpm
PAM Alpha Counts: 469 dpm



Sample S18R000029 was a tech smear with a darkened smudge across the surface. The SEM analysis showed mostly mineral matter on, and embedded in, the fibers of the sample. The majority of these particles were mineral phases sub-micrometer to ~20 µm in size with some larger particles scattered throughout (Figure 16).

An AFA run was performed to search for plutonium particles. The run was set up with a defined area on the tech smear that exhibited the most particulate, with the brightness and contrast of the backscatter detector adjusted to eliminate lower mass elements. The 8-hour automated run resulted in over 3600 detected and measured particles which were classified as "defined" in a rule file supplied by the vendor (Figure 17).

The resulting data was manually evaluated by focusing on all detected particles with a reported potassium level above 5% (potassium was used to mark the presence of plutonium). This data analysis showed that a total of two plutonium particles were found (Figure 18). Manual analysis of these two plutonium particles was attempted by returning to the reported particle locations on the sample, but only one of the two particles was found manually. The images and EDS spectrum in Figure 19 show this particle. Many of the detected elements in the spectrum are probably associated with neighboring particles due to the relatively small size of the plutonium particle, but the phosphorous seems to be associated with the plutonium as it was seen in both particles in the AFA run.

Figure 16. Typical Particles and Measured Sizes on Sample S18R000029

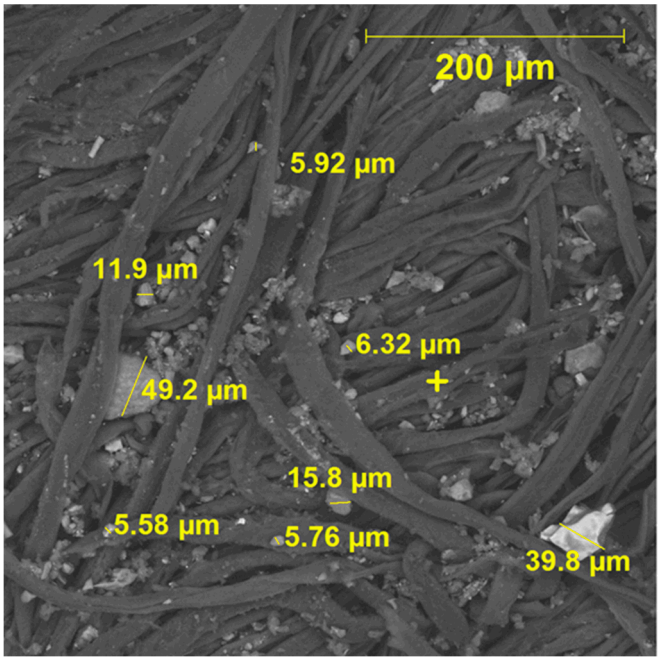
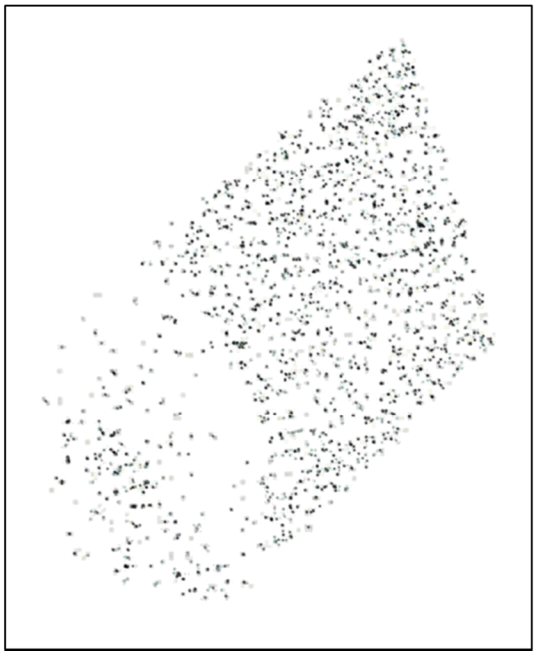


Figure 17. Summary of the Automated Feature Analysis Results for Sample S18R000029

All Particles Detected and Measured



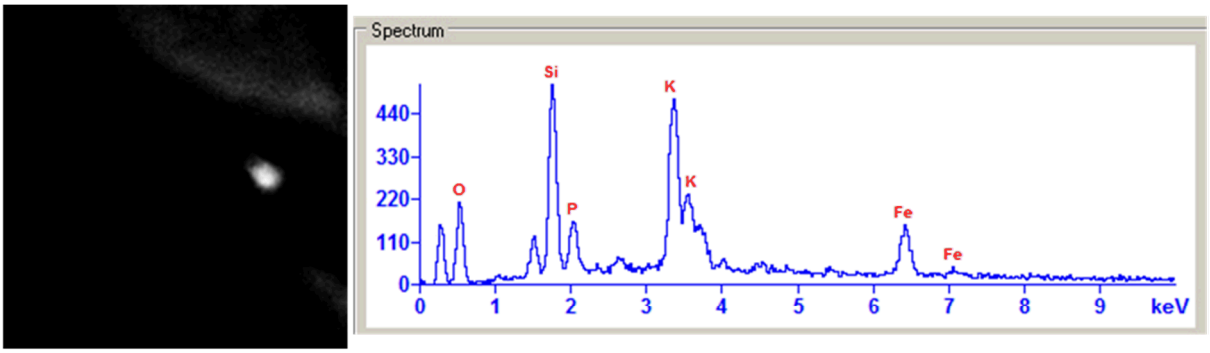
Starting 02-06-2018PFP.afa
Results in C:\AFAData\41
Beginning of Analysis
Starting Run_1 with field 1 at 3:08:16 PM on 2/6/2018.
Initial emission: I=33.500 µA [3:08:16 PM]

Result summary:
Data Filename = C:\AFAData\41\Run_1\Run_1.hdz
Beam Energy = 25 kV
Working Distance = 15.9 mm
Spot = 30%
Detector = BSED
Contrast = 100%
Brightness = -24.6%
Stub = S18R000029
Client name = CH2M Hill
Detail = 11,570 dpm
Description = PFP Smear
Area = 263.416 mm²

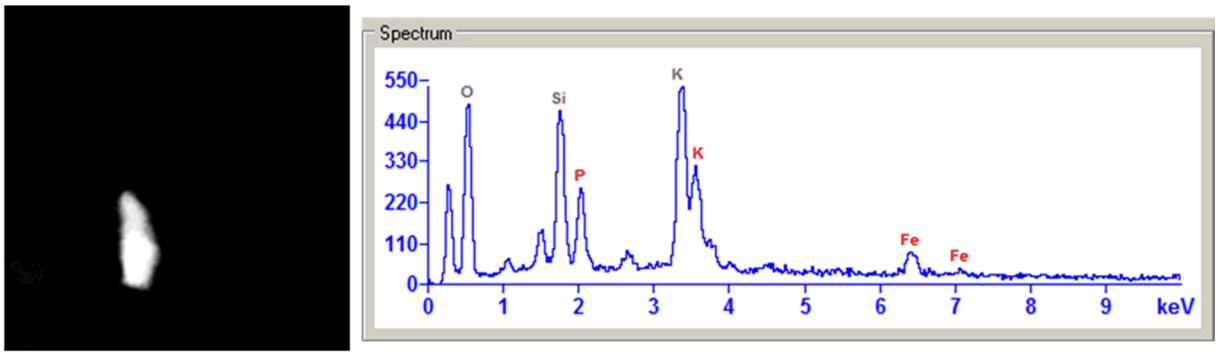
Particle count by class:

Rule Name	Count
Other	958
Iron Rich	890
Misc Metal	544
Iron-Titanium	231
Barium Rich	95
Stainless Steel	53
Lead Rich	44
Misc. Silicates	12
Strontium-bearing	20
Cerium Rich	7
Titanium	6
Manganese	6
Garnet	5
Titanium	4
Stainless Steel	3
Barium Sulfate	3

Figure 18. Images and Spectra of Plutonium Particles Measured by the Automated Feature Analysis on Sample S18R000029

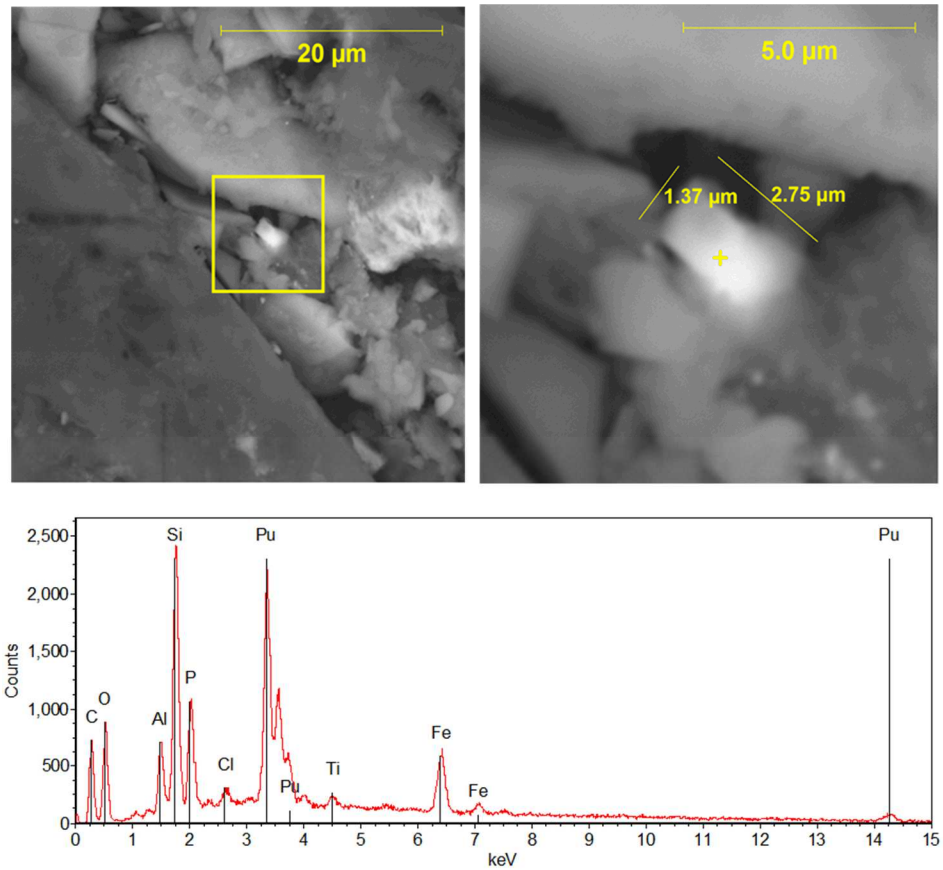


Size: Max = 1.7 µm Min = 1.3 µm Area = 2.2 µm^2



Size: Max = 6.0 µm Min = 2.3 µm Area = 11.3 µm^2

Figure 19. Manual Analysis of a Plutonium Particle in Sample S18R000029



4 References

ATS-LT-161-103, "222-S Laboratory Technology Procedure for the ASPEX Explorer Scanning Electron Microscope," as revised, Washington River Protection Solutions LLC, Richland, Washington.

HNF-N-832-1, "PSEM Instrument Notebook," Laboratory Notebook, 222-S Laboratory, Washington River Protection Solutions LLC, Richland, Washington.

LAB-RPT-18-00002, 2018, "Scanning Electron Microscopy Energy Dispersive Spectrometry Analysis of Plutonium Finishing Plant Air Filter and Tech Smears," Rev. 1, Washington River Protection Solutions LLC, Richland, Washington.

LAB-RPT-12-00006, 2013, "Characterization of Plutonium-Bearing Waste in the High-Level Waste Storage Tanks 241-SY-102, 241-TX-118, and 241-AZ-101 and the Plutonium Finishing Plant Z-9 Crib," Washington River Protection Solutions LLC, Richland, Washington.

PNNL-25888, 2016, "Literature Review: Crud Formation at the Liquid/Liquid Interface during TBP-based Solvent-Extraction Processes," Pacific Northwest National Laboratory, Richland, Washington.

Attachment A

PROBLEM AND DISCREPANCY (P&D) REPORT	**P&D Number:** PD18-0150 **Rev. Number:** 0 222-S 222S20180187 03/08/2018

SAMPLE EVENT INFORMATION

SAF NUM(S): F18-017

SAMPLING INFORMATION

NUMBER OF SAMPLES: 30

SAMPLE MATRIX: OTHER SOLID

ISSUE BACKGROUND

CLASS: Miscellaneous Issues

TYPE: Other

DESCRIPTION: The narrative discussion for the samples listed above should be restricted to alpha and plutonium observations only.

RESOLUTION

PROPOSED RESOLUTION: Please correct the issue and resubmit the hard copy and data package.

FINAL RESOLUTION:

SUBMITTED BY:

HEY, BE 03/08/2018

Electronically Approved by:

UserName: Page, Jason (h2841343)
Title:
Date: Wednesday, 21 March 2018, 12:02 PM Pacific Time
Meaning: Approved by the author or delegate
==========

UserName: Cooke, Gary (h0410221)
Title: APD Chemist
Date: Wednesday, 21 March 2018, 12:32 PM Pacific Time
Meaning: Approved by the customer or delegate
==========

UserName: Moser, Dave (h0008068)
Title:
Date: Wednesday, 21 March 2018, 07:02 PM Pacific Time
Meaning: Approved by the Facility Manager or delegate
==========

UserName: Cooke, Gary (h0410221)
Title: APD Chemist
Date: Thursday, 22 March 2018, 05:47 AM Pacific Time
Meaning: Approved by the Group Manager or delegate
==========