LA-UR-12-23811
Approved for public release; distribution is unlimited.

Title: Application of Micro-XRF for Nuclear Materials Characterization and Problem Solving

Author(s): Worley, Christopher G.
Tandon, Lav
Martinez, Patrick T.
Decker, Diana L.
Schwartz, Daniel S.

Intended for: Denver X-ray Conference, 2012-08-06/2012-08-10 (Denver, Colorado, United States)

APPLICATION OF MICRO-XRF FOR NUCLEAR MATERIALS CHARACTERIZATION AND PROBLEM SOLVING

Christopher G. Worley, Lav Tandon, Patrick T. Martinez, Diana L. Decker, and Daniel S. Schwartz

Los Alamos National Laboratory

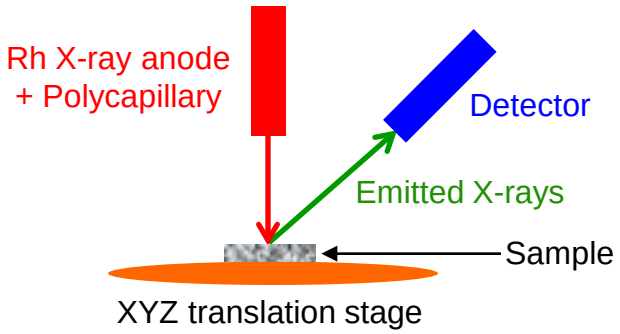
Outline

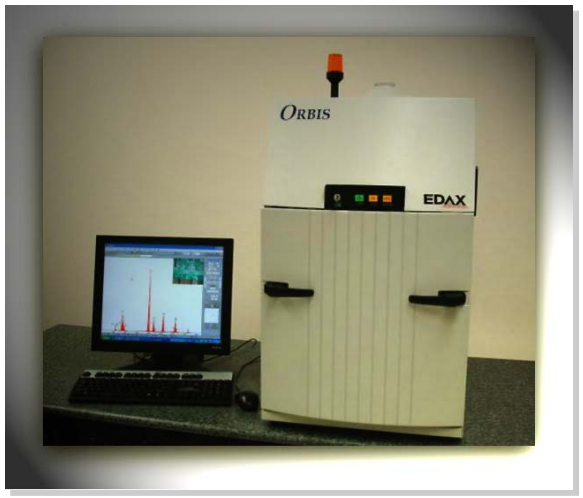
- **Introduction**
- **Instrumentation**
- **Nuclear material studies**
  - Plutonium oxide particle characterization
  - Plutonium particles on HEPA filters
  - Plutonium on surface swipes
  - Plutonium metal
- **Summary**

Introduction

- **Micro-X-ray fluorescence (MXRF) used for >> 20 years**
- **To date MXRF has been underutilized for nuclear materials (NM) spatially-resolved elemental characterization**
- **Scanning electron microscopy (SEM) with EDX much more common for NM characterization at a micro scale**
- **But MXRF fills gap for larger 10's microns to cm^2 scales**
- **Will present four interesting NM applications using MXRF**

Micro-XRF Instrumentation

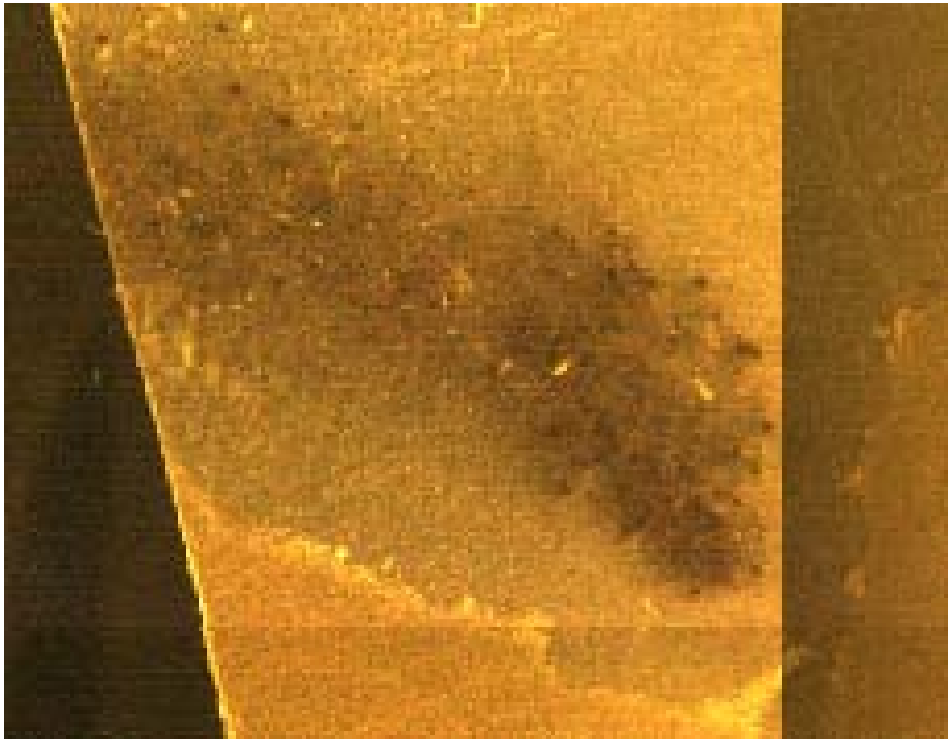




- **EDAX Orbis PC micro-XRF instrument**
- **Polycapillary optic, 30 μm diam. spot (@ Mn Kα)**
- **50 W Rh X-ray anode perpendicular to sample plane**
- **30 mm^2 silicon drift detector (SDD)**
- **1 mm and 2 mm apertures for larger samples**
- **6 source filters: 25 μm Al, 250 μm Al, Ti, Ni, Nb, Rh**
- **Analysis in air or vacuum**
  - Air for radioactive samples

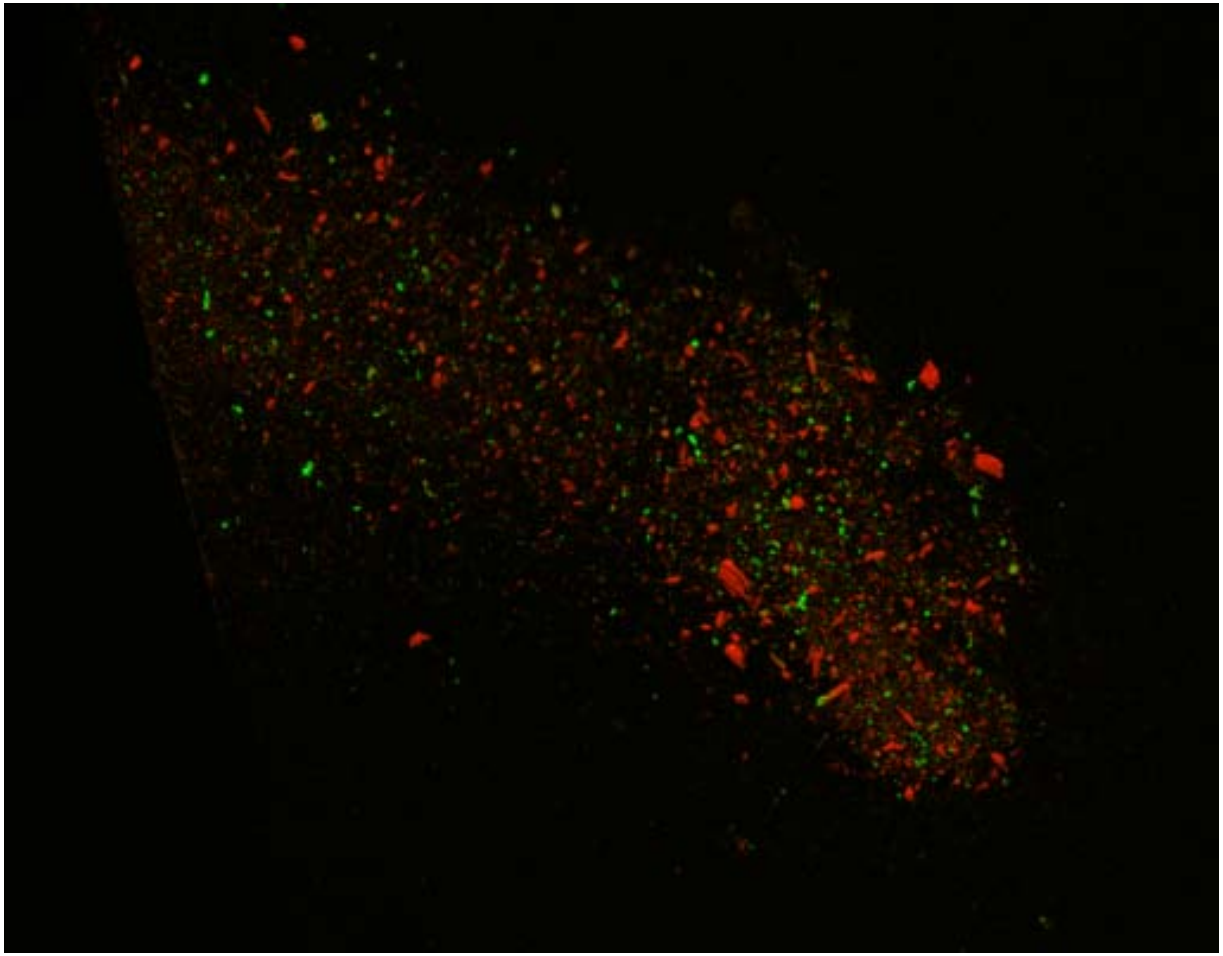
Plutonium / Neptunium Oxide Particle Characterization

- Np/Pu oxide - Some material did not dissolve
- Pu/Np parent oxide placed on Scotch tape and sealed inside cup
- MXRF – Examine particles
  - 30 micron capillary
  - Image spots touching
  - 100 msec dwell time
  - Majors: Pu, Np, W, Ta
- Separate analysis of insoluble fraction
  - Tungsten and residual Plutonium



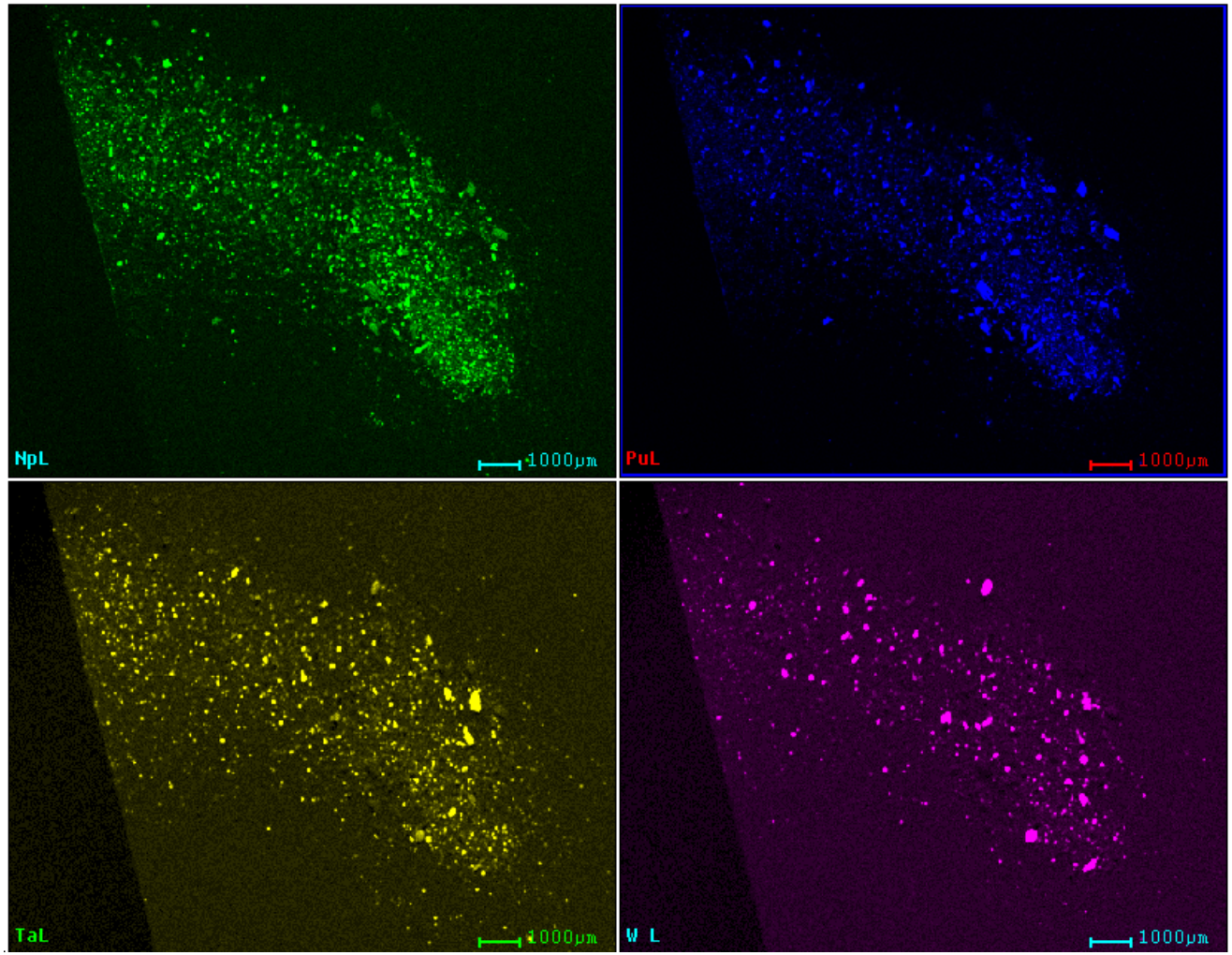
Area of tape specimen imaged by MXRF
(~15 mm W x 9 mm H)

Plutonium / Neptunium Oxide Particle Characterization



Plutonium Neptunium

Plutonium / Neptunium Oxide Particle Characterization

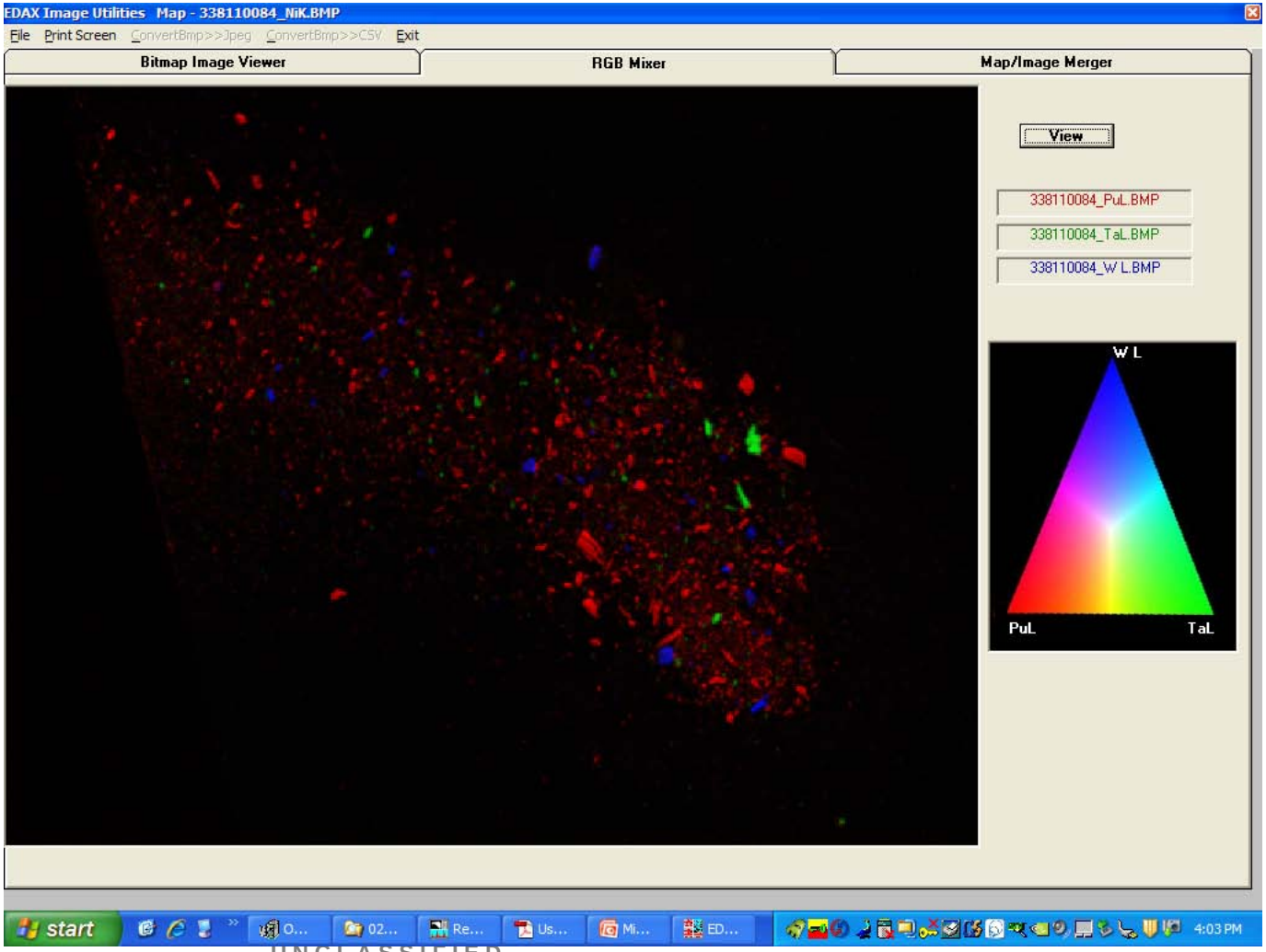


Plutonium / Neptunium Oxide Particle Characterization

Tungsten
Plutonium
Tantalum

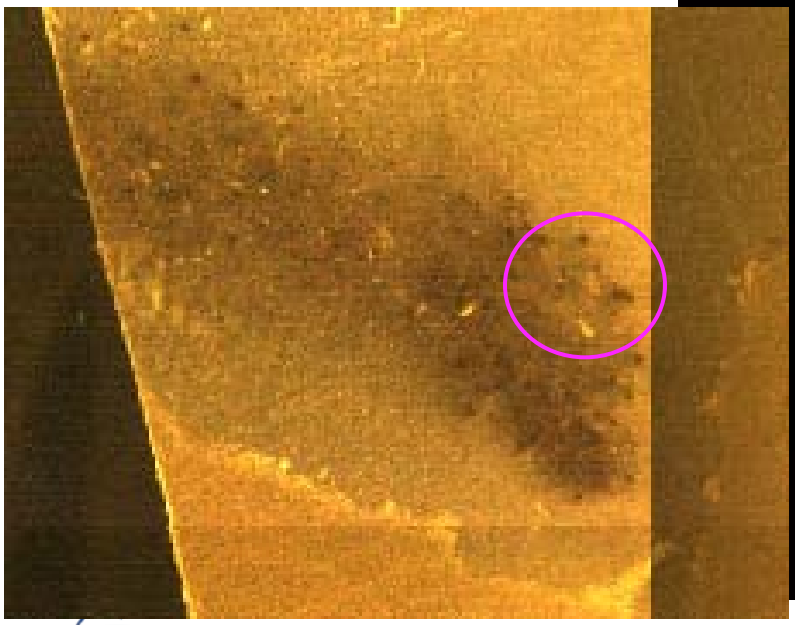
--Distinct phases

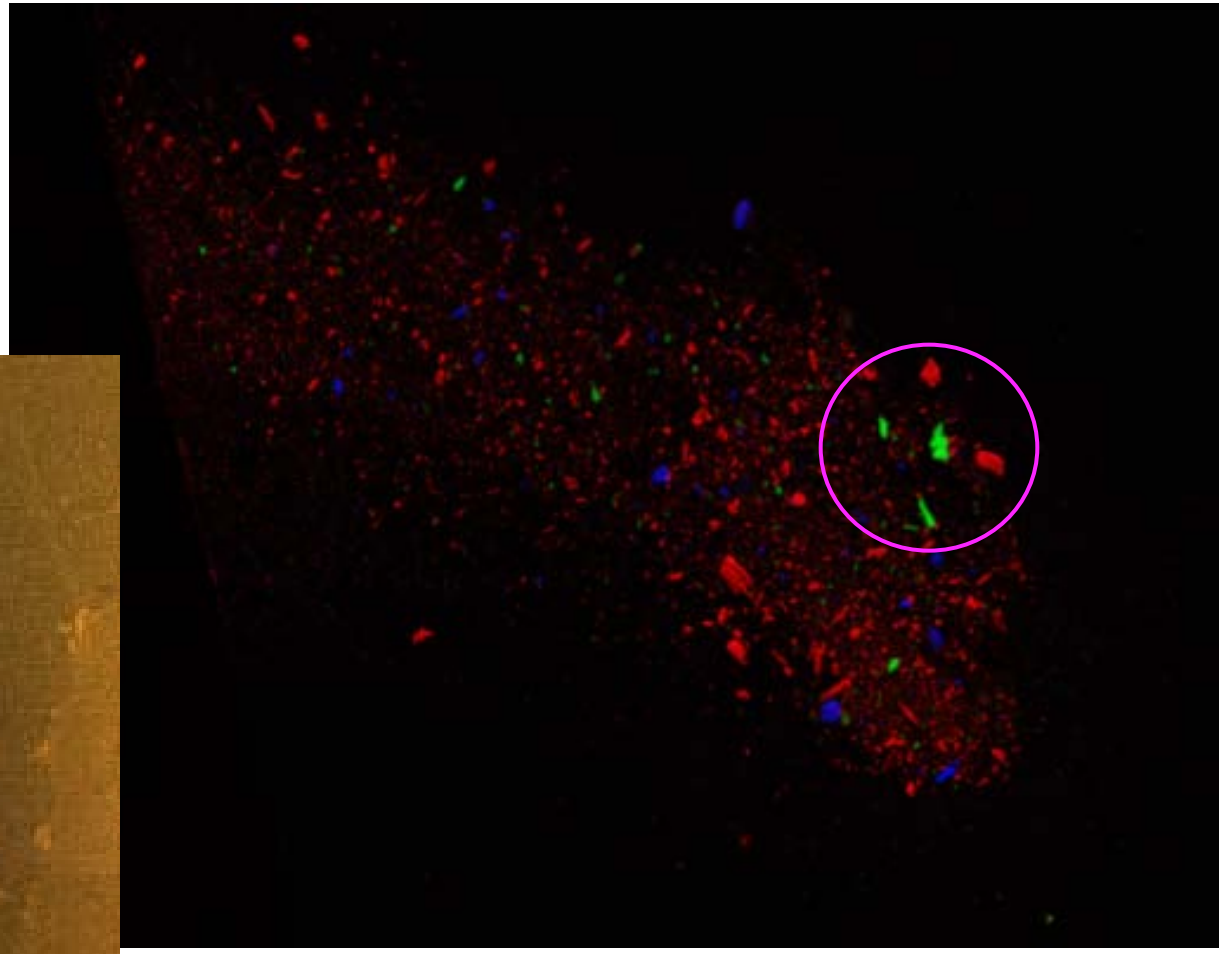
--No component overlap



Plutonium / Neptunium Oxide Particle Characterization

- **Potential to extract specific particle types for analysis by other methods**
  - Use distinct visible features as frame of reference
  - Single stage impactor to extract
    - More on this later





Plutonium Tantalum Tungsten

Plutonium Facility HEPA Filter

- Goal: Extraction of trace Plutonium particles from HEPA filters for particle characterization by SEM
- MXRF imaging
  - Advantages
    - Nondestructive
    - Large surface area coverage
    - Better Plutonium detection limits than SEM
    - Non-conducting surfaces
    - Analysis through radioactive containment film (impossible with SEM electron beam)
  - Limitations
    - Detection limits – Very low levels of Pu present
    - Lateral resolution (~30 microns) – Some particles submicron in size
    - Substrate impurity energy overlaps with Pu L and M
- IAEA type micro-vacuum to extract located Pu particles
  - Deposited particles onto Carbon adhesive tape for SEM characterization

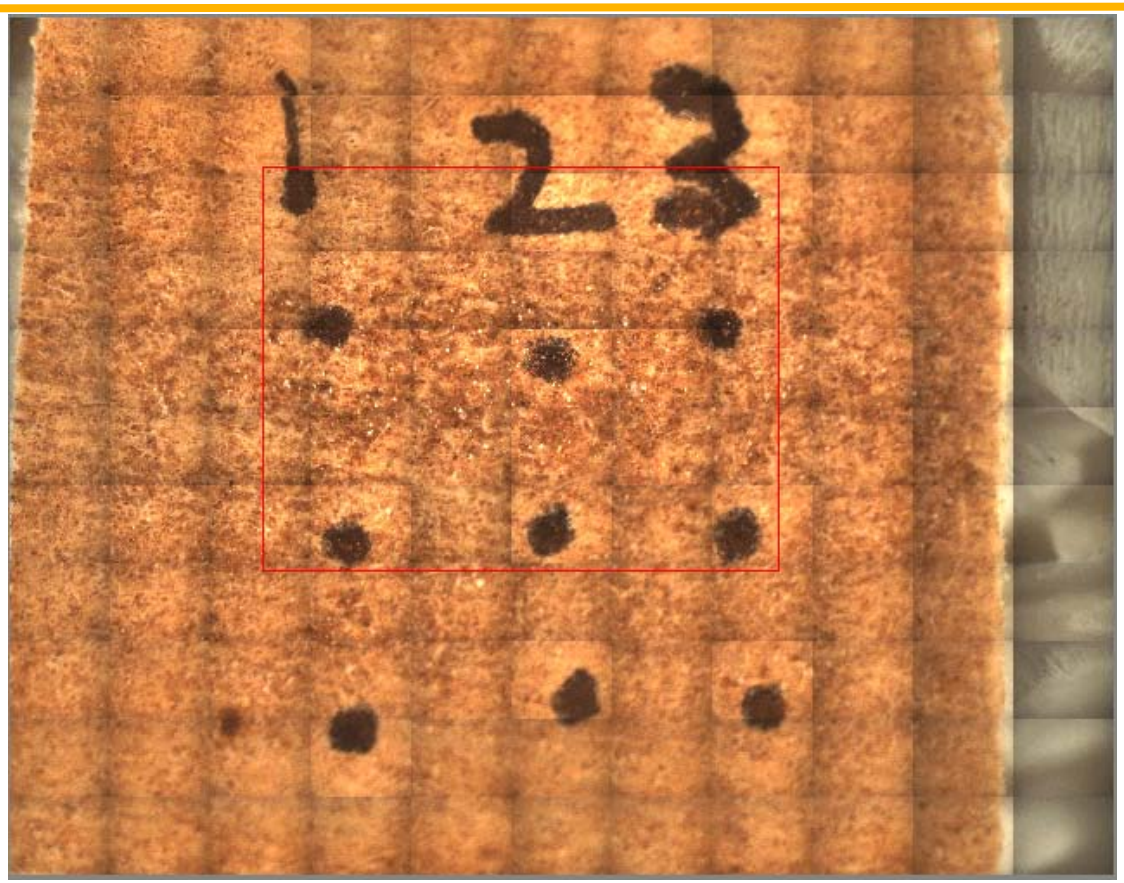
Plutonium Facility HEPA Filter

- Facility HEPA filters collected downstream of Pu work area
- Samples obtained with 1.5” diameter, 4” long coring tool
- ~2 cm x 2 cm pieces cut from each core for MXRF imaging
- Added reference marks to sample for guiding particle extraction
- Radioactive contamination - Samples sealed in cups with Mylar film
- Instrumental parameters
  - 30 micron polycapillary optic
  - 48 kV, 950 micrA
  - 25 micron Nickel source filter
    - Best compromise between signal-to-noise and image time
  - 256 x 200 points
    - Compromise between spot overlap and image time
    - No beam overlap → ~1.5 beam width spacing between points
  - 2 sec / pixel dwell time → ~29 hr image time
  - Background-subtracted net intensity imaging

Plutonium Facility HEPA Filter

- **Trace Pu on filters**
  - Avg 7.2 μg/cm^2 Pu239
  - ~51 pg Pu in beam analysis area (IF were completely homogeneously distributed)
  - Reality – Small very isolated Pu particle aggregates present

- **XRF challenges**
  - 30 μm XRF beam – Submicron particles too small to resolve
  - Strontium and potassium in filter fibers
    - Pu La and Sr Ka peaks substantially overlap
  - Pu Ma and Potassium Ka peaks severely overlap
  - Pu La 14.3 keV – Less than ideal Pu sensitivity using polycapillary and SDD
  - Dwell time vs. image area compromise



25.3 mm x 19.8 mm Red boxed MXRF imaged area = 11.8 mm x 9.2 mm

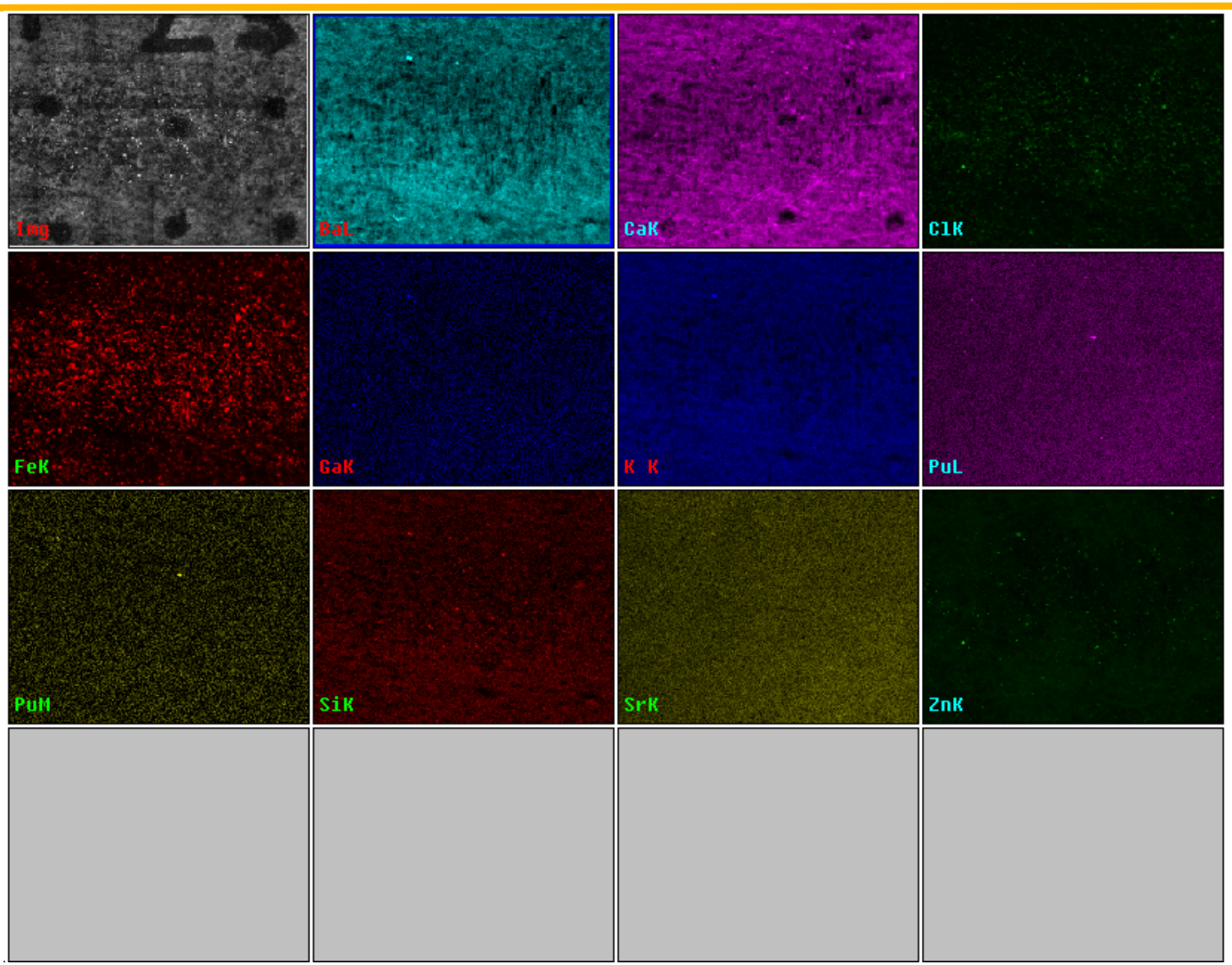
Plutonium Facility HEPA Filter

HEPA impurities:
Majors:
K, Ca, Ba, Zn
Minors:
Si, Sr, Cu

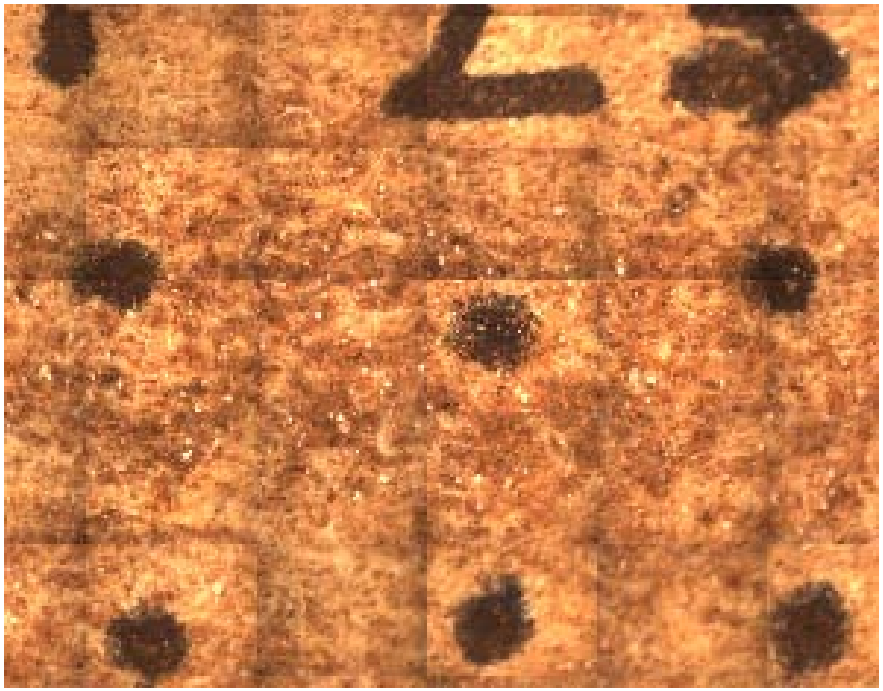
Substantial rust coating

Difficult to detect Pu on 2 of 3 samples; few minor spots. Counts slightly > background

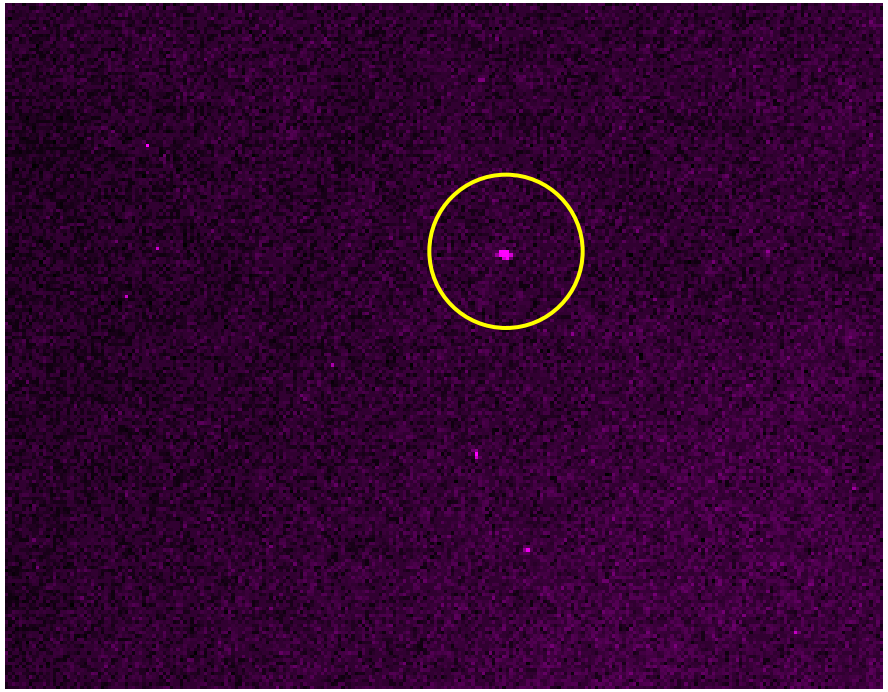
Pu spot also confirmed in Mα map. Indicated, probably located near surface.



Plutonium Facility HEPA Filter

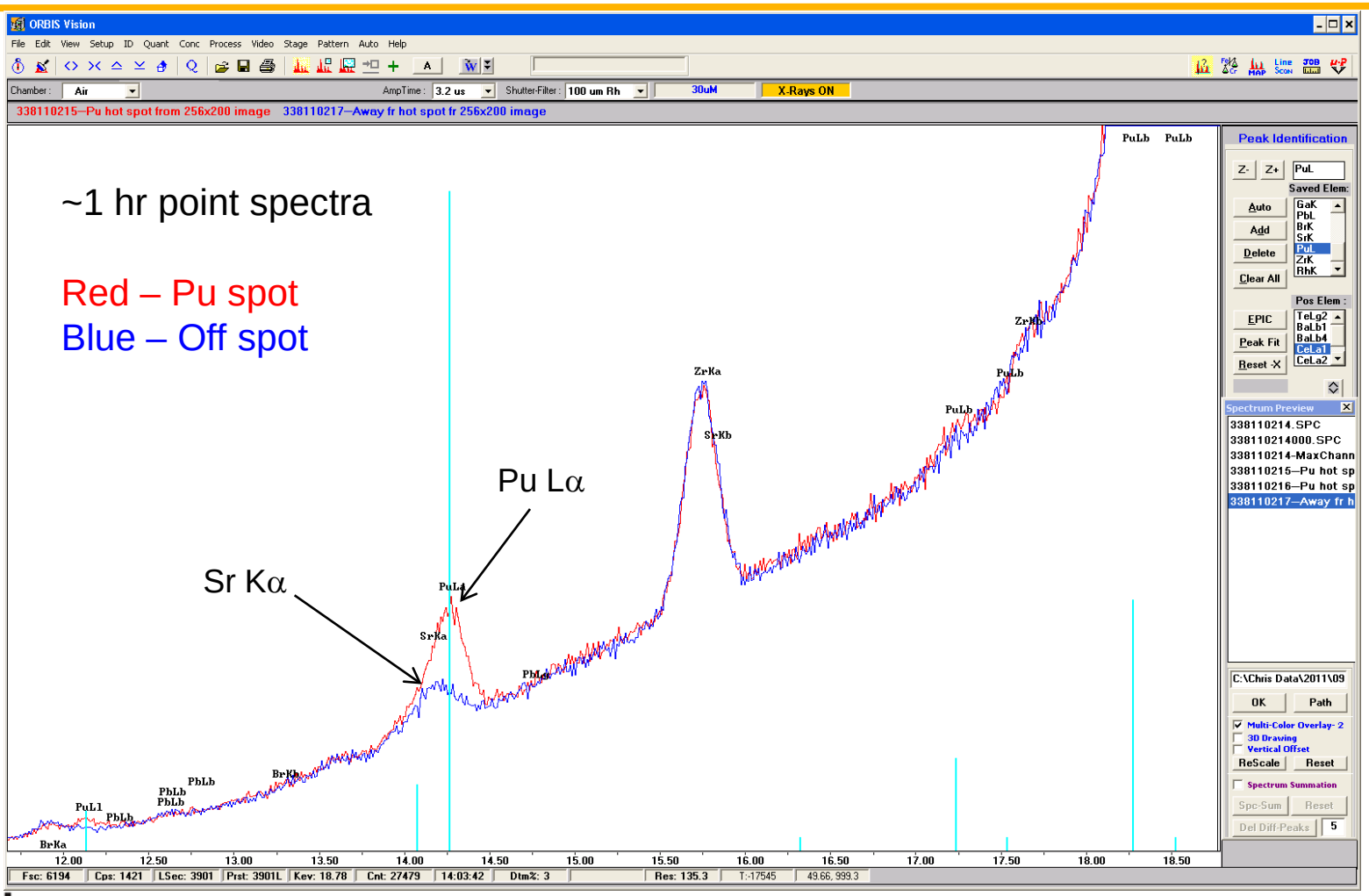


11.8 mm x 9.2 mm



Pu Lα map

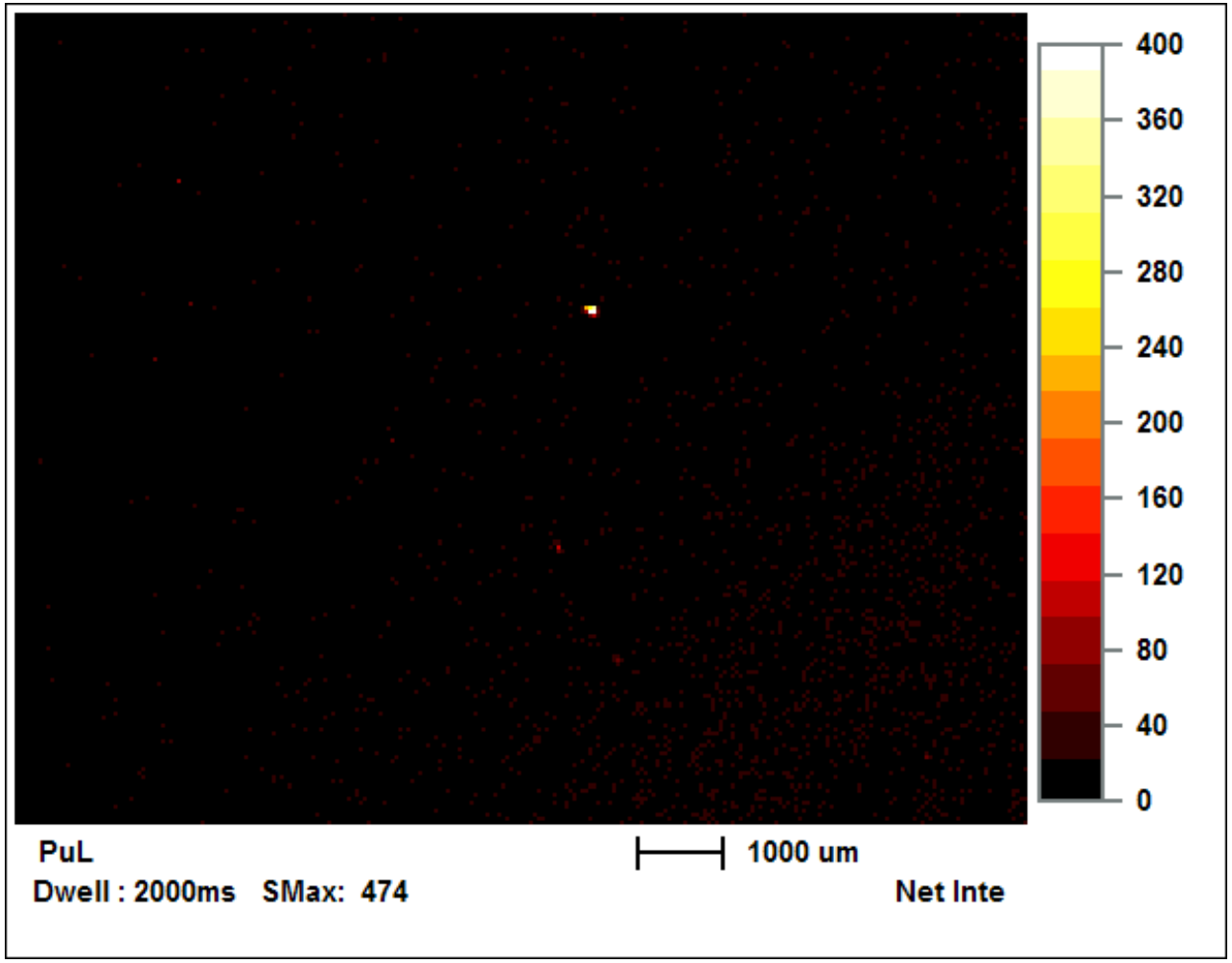
Plutonium Facility HEPA Filter



Plutonium Facility HEPA Filter

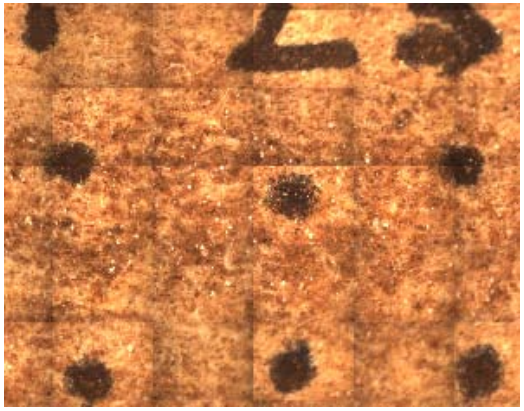
Largest Pu particle intensity ~20x greater than background

Extracted particle on carbon tape using micro-vacuum for SEM characterization

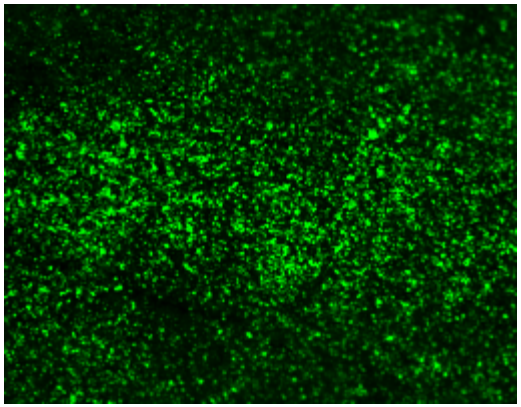


Plutonium Facility HEPA Filter

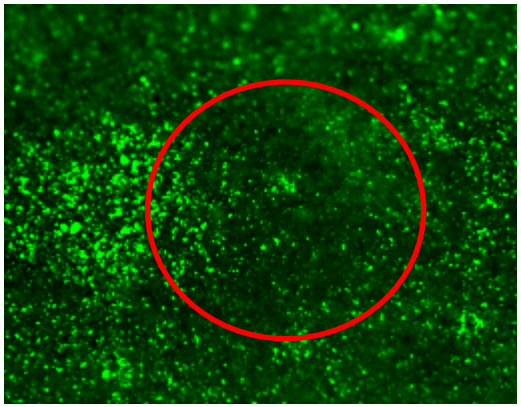
- Removed material from approximate location of Pu spot using micro-vacuum
- Residue collected on carbon tape on planchet for SEM analysis
- Iron (rust) visibly removed after vacuum extraction of region



Filter Image

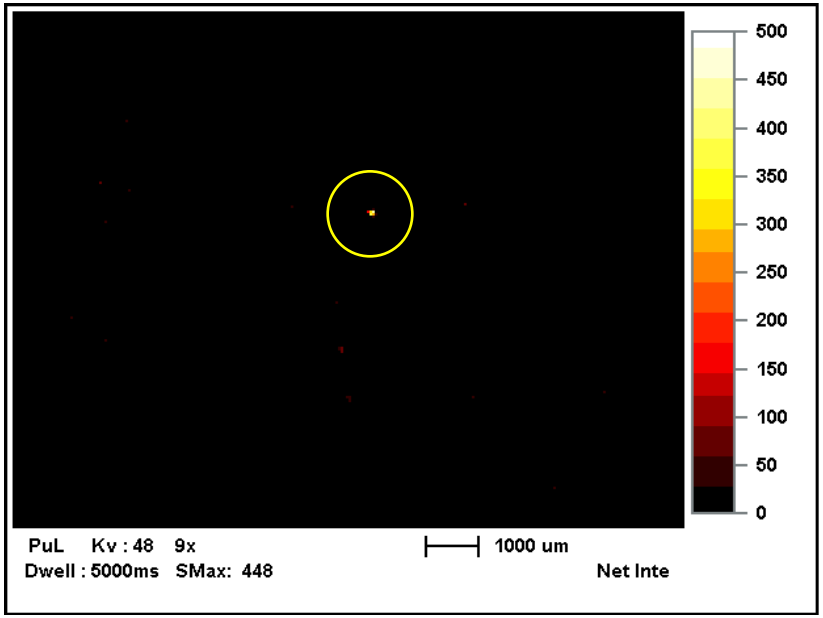


Iron Before Extraction

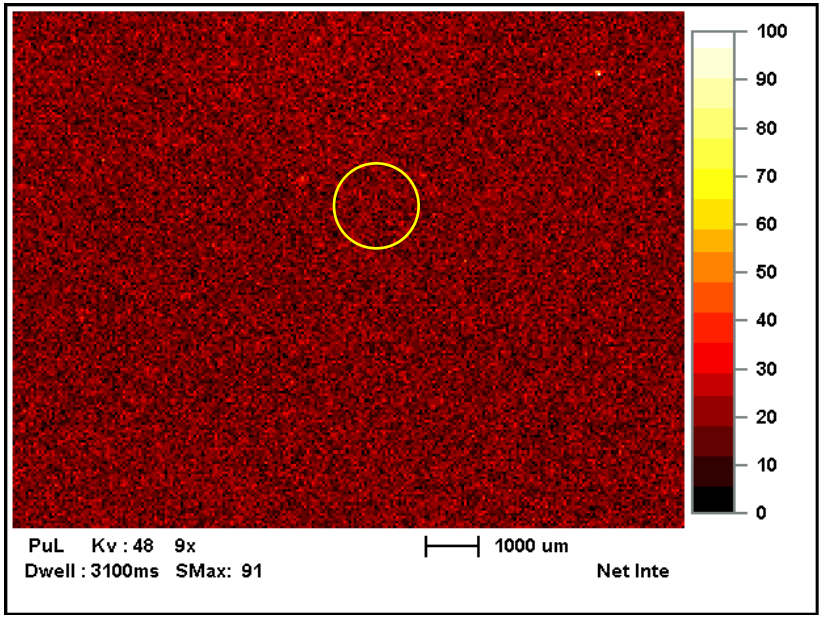


Iron After Extraction

Plutonium Facility HEPA Filter



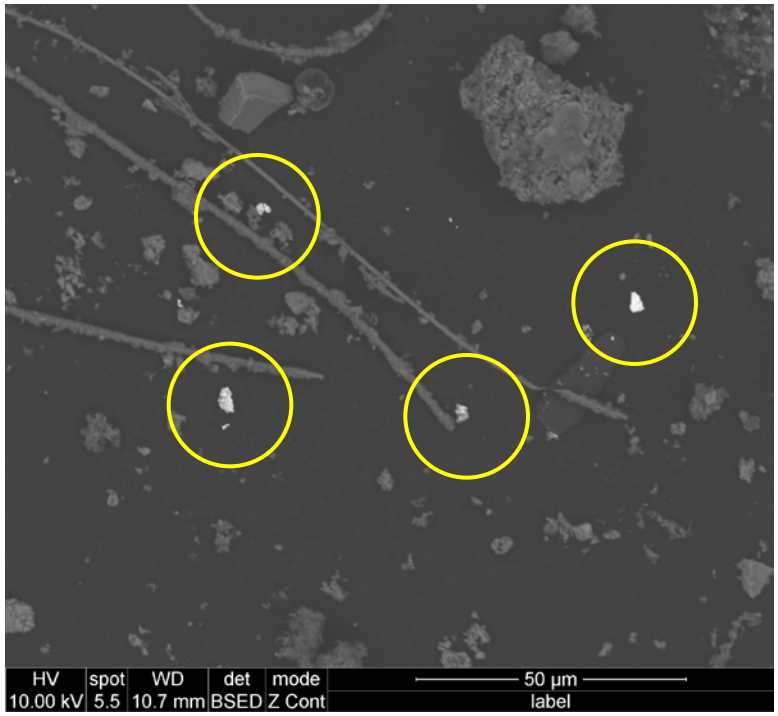
Pu Lα MXRF Image
Before Vacuum Extraction



Pu Lα image After Extraction
Pu particle clearly removed

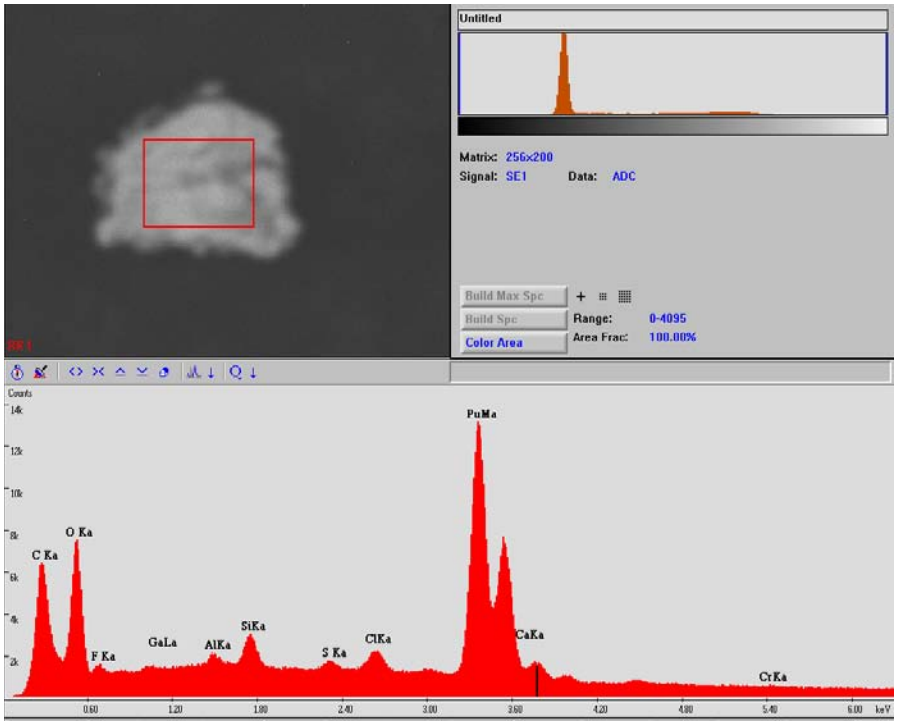
Plutonium Facility HEPA Filter

Scanning Electron Microscopy (SEM)
Backscatter Image



Bright particles contain Pu

SEM EDS of a Typical Pu Particle



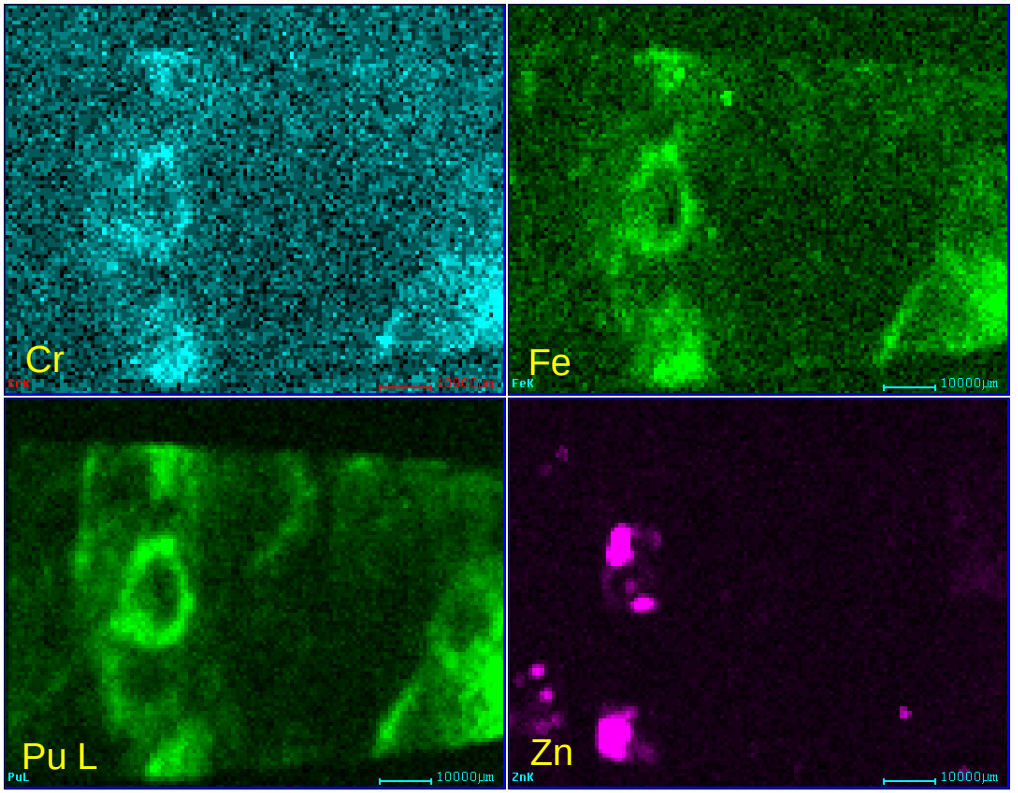
Pu M peaks confirmed

Plutonium Surface Swipes

- Large cotton swipes (~10 cm Wide)
- Wiped surfaces in Plutonium glove boxes
- MXRF imaging
  - Nondestructively examine residue composition
  - Locate regions of interest for removing residue with micro-vacuum
  - Residue collected on tape for SEM
  - 2 mm aperture used to allow beam overlap over such a large area

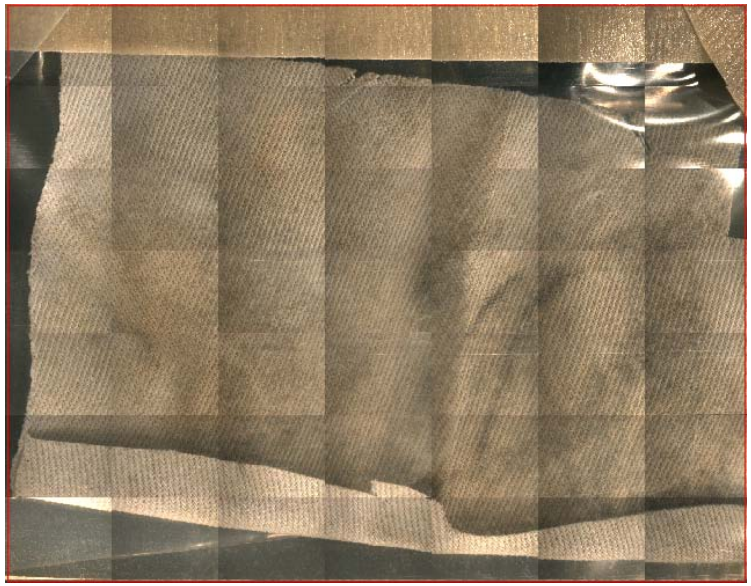
Plutonium Surface Swipes

- Swipe example #1
- Plutonium easily detected
  - Correlates with dark deposits
- Other significant elements detected: Fe, Cr, Zn, Ga

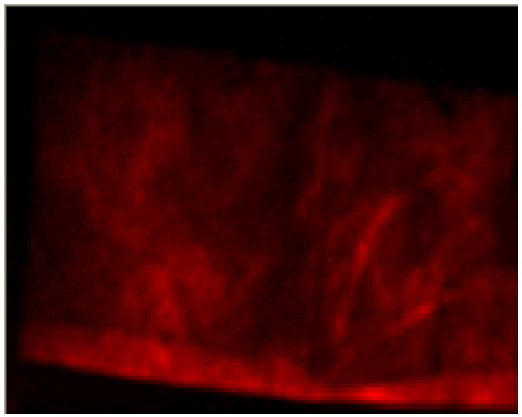


Plutonium Surface Swipes

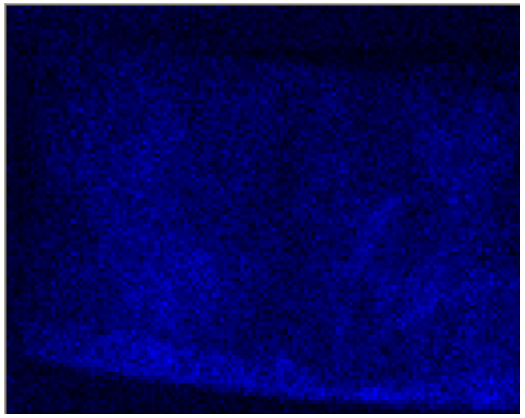
Swipe example #2



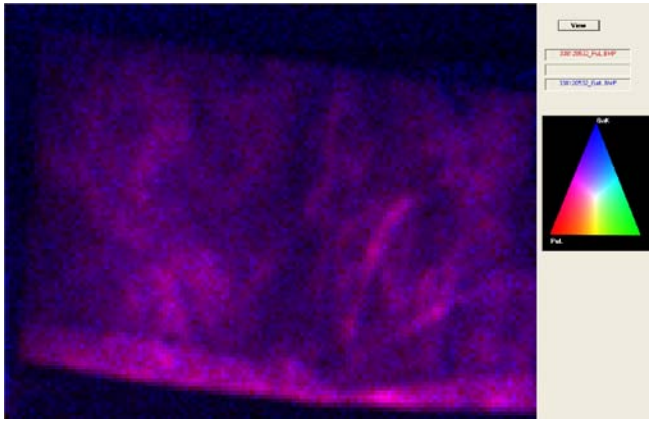
9.8 cm x 6 cm



Plutonium

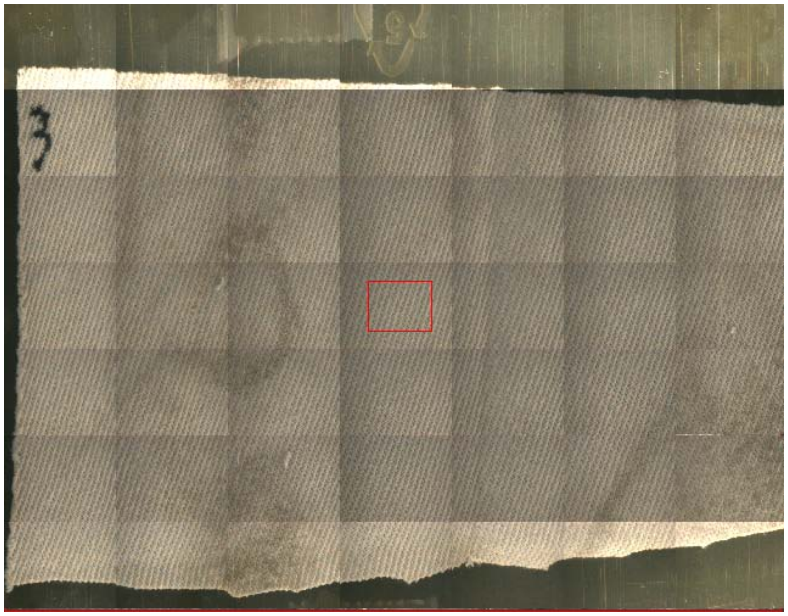


Gallium

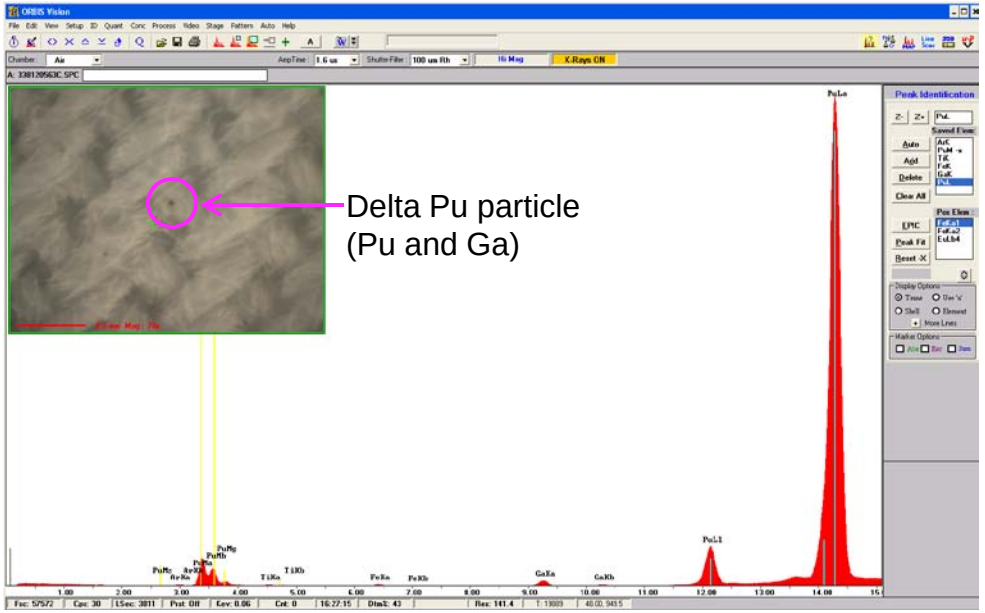


Pu & Ga Overlap
(Delta phase Pu)

Plutonium Surface Swipes

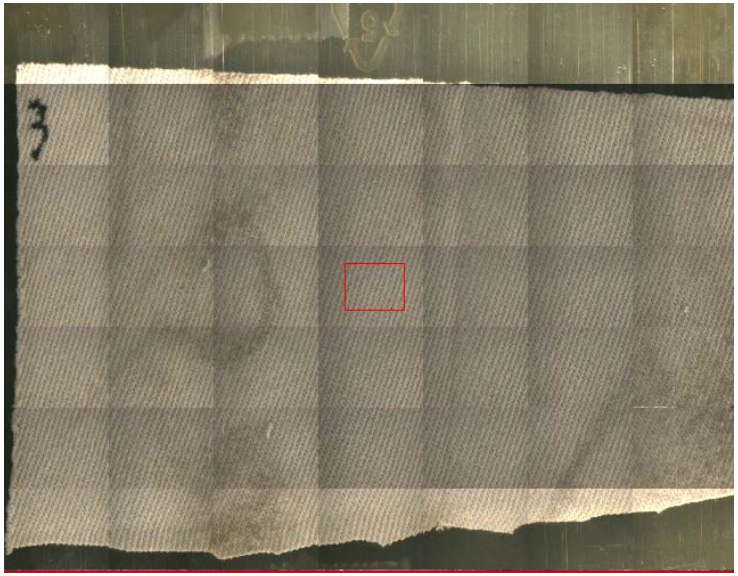


~10 cm wide cotton swipe

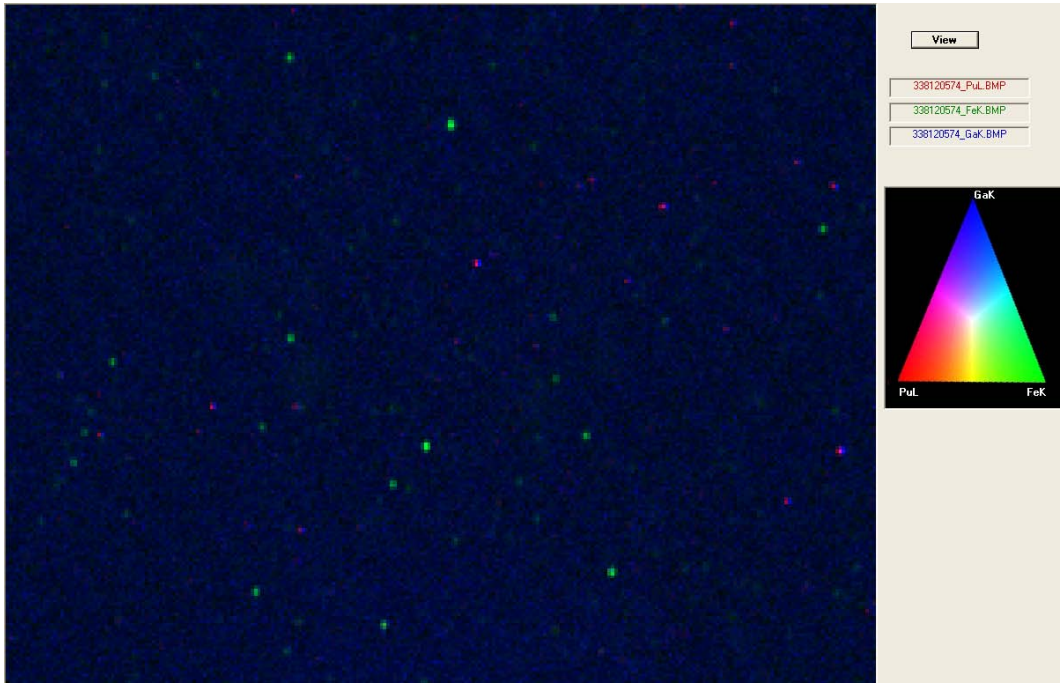


Identified delta Pu particle from within red boxed area on cotton swipe

Plutonium Surface Swipes



Capillary optic high resolution image of red box area (8 mm x 5 mm)

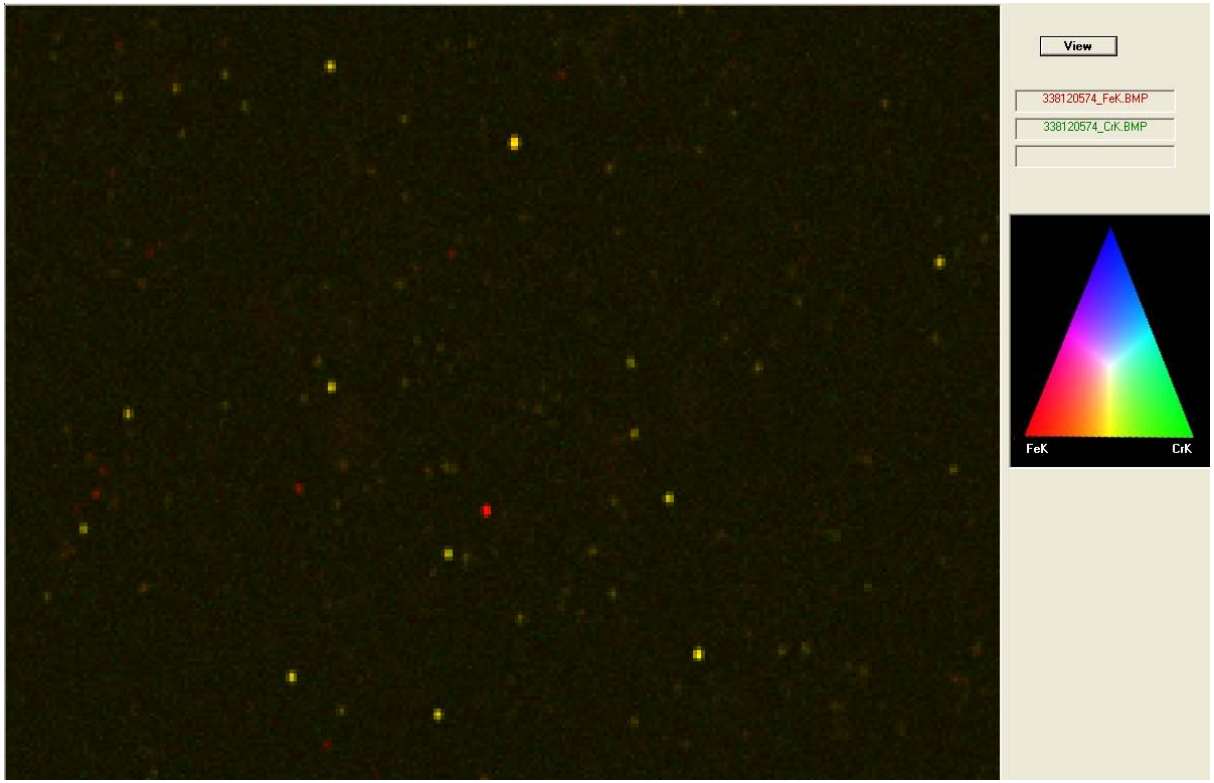


Pu Ga Fe

- Pink particles - Delta Plutonium
  - Ga and Pu overlap
- Iron particles not correlated with Pu or Ga
  - Fe probably from rust and/or particles steel

Plutonium Surface Swipes

- Iron and Chromium overlay
- Strong correlation (orange/yellow particles)
  - Probably steel
- Few isolated (red) Fe particles
  - Probably rust



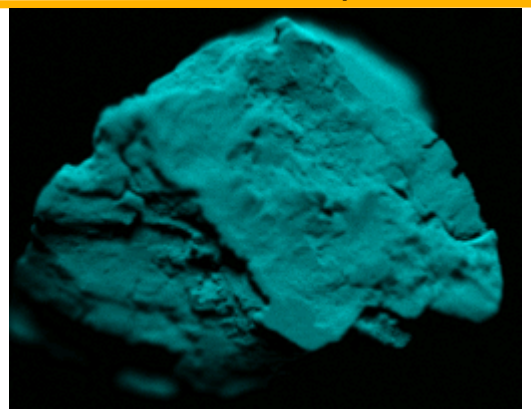
Fe - red Cr - green

Electrorefined (ER) Plutonium Metal

- Plutonium metal electrorefined to remove impurties
- Samples submitted for analytical chemistry elemental analysis
- Metal pieces are cut for each analysis team
- Sometimes trace analysis results are not reproducible
- Possible that sample is not homogeneous
- MXRF – Direct imaging of elemental lateral distribution
- 350 mg piece of ER Pu metal from parent sample imaged by MXRF
  - Sample Pu assay results were inconsistent between multiple analyses
  - Trace tungsten results (by ICP) varied by 0.2% relative

Electrorefined Plutonium Metal

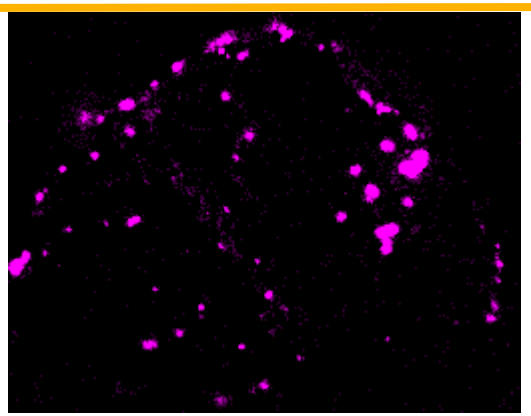
Pu Lα map



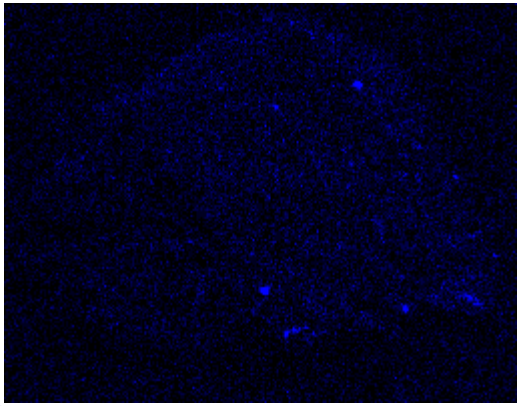
~350 mg Pu metal piece

~3.5 mm

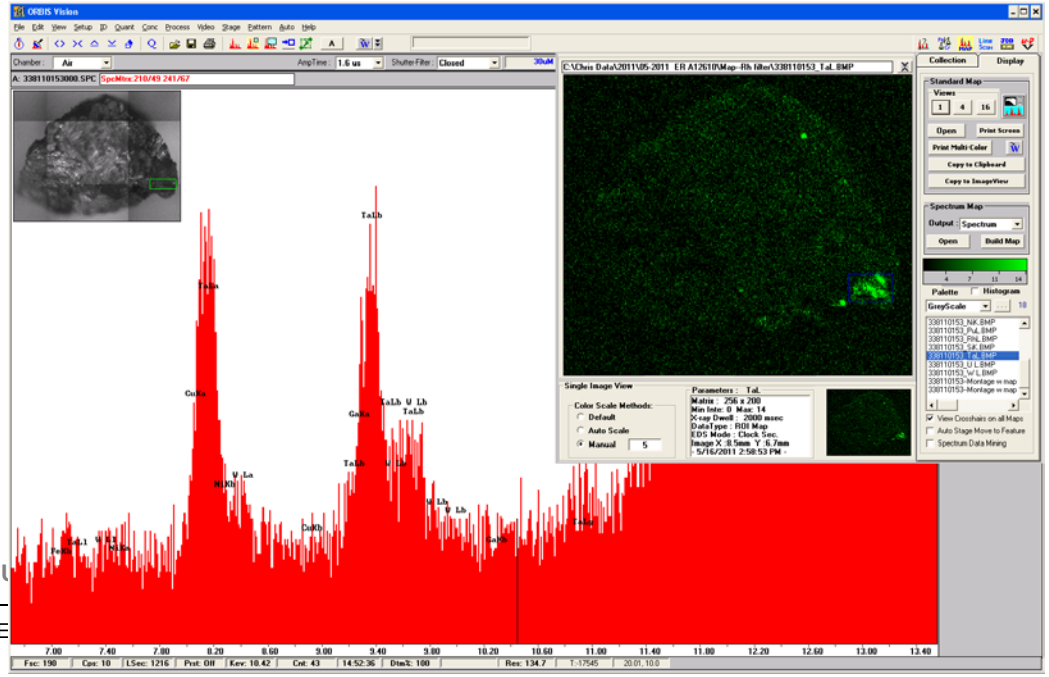
Iron Kα map – From wire brushing?



Tungsten Lα map



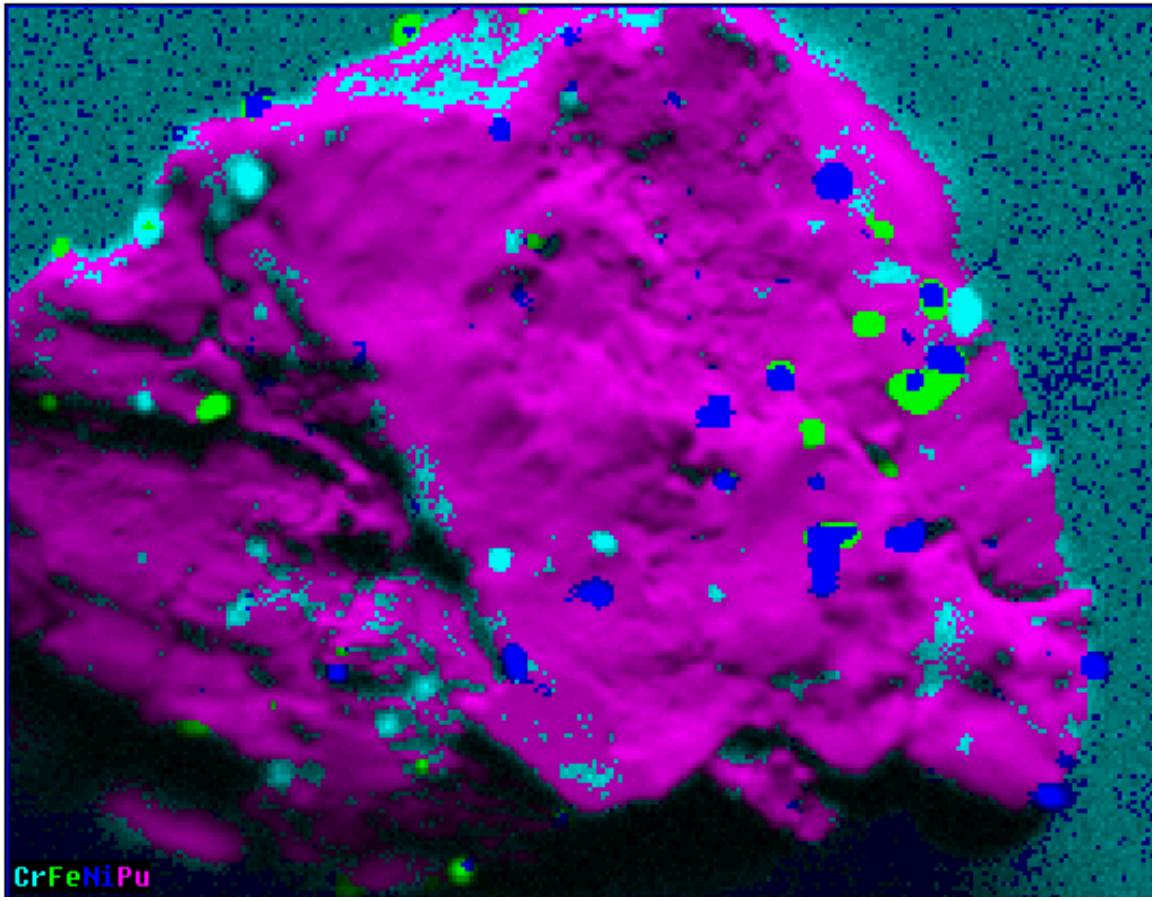
Tantalum Lα map and spectrum from boxed area



Los Alamos NATIONAL LABORATORY EST.1943

Electrorefined Plutonium Metal

- Fe, Ni, Cr spots
- Steel wire brush used to remove Pu surface oxide prior to cutting pieces
- However, no strong correlation between these components
- Could be (at least partially) due to sample heterogeneity



Summary

- Demonstrated unique value of MXRF for various plutonium applications
- Although SEM has much higher resolution, MXRF clearly better for these larger scale samples (especially non-conducting samples)
- MXRF useful to quickly identify insoluble particles in Pu/Np oxide
- MXRF vital to locating HEPA filter Pu particles over cm^2 areas which were then extracted for SEM morphology and particle size distribution analysis
- MXRF perfect for surface swipes which are far too large for practical SEM imaging, and loose residue would contaminate SEM vacuum chamber
- MXRF imaging of ER Plutonium metal warrants further studies to explore metal elemental heterogeneity

Acknowledgements

- ER metal cutting
  - Fran Martin

- Pu/Np oxide
  - Elmer Lujan
  - Kathy Garduno
  - Lisa Colletti