LA-UR- 11-04808

Approved for public release;
distribution is unlimited.

Title:	New methods for actinide characterization using X-ray fluorescence
Author(s):	George J. Havrilla, Michael Collins, Velma Montoya, Zewu Chen, Fuzhong Wei, Matthew Cusack, Tim Elam, Sarvjit Shastri, Ali Mashayekhi
Intended for:	American Chemical Society Denver, CO August 28-September 1, 2011

Los Alamos
NATIONAL LABORATORY
EST. 1943

New methods for actinide characterization using X-ray fluorescence

George J. Havrilla[a], Michael Collins[a], Velma Montoya[a], Zewu Chen[b], Fuzhong Wei[b], Matthew Cusack[b], Tim Elam[c], Sarvjit Shastr[d], Ali Mashayekhi[d]

[a]Los Alamos National Laboratory, [b]X-ray Optical Systems, [c]University of Washington, [d]Argonne National Laboratory

X-ray optics and synchrotron sources offer new opportunities for actinide characterization. X-ray optics provides intense focused x-rays for excitation using low power x-ray tubes. The use of doubly curved crystals (DCC) for monochromatic excitation and collection of emitted x-rays from the specimen has resulted in the development of a new prototype instrument, hiRX, high Resolution X-ray. hiRX is based on monochromatic wavelength dispersive X-ray fluorescence (MWDXRF) technology, which uses DCCs to enable selective and sensitive analyses of selected actinide elements. Synchrotron excitation offers monochromatic excitation with high intensity at high energy. Ultra high energy X-ray fluorescence UHEXRF has been demonstrated to detect uranium through 1.2 mm of Zircaloy shielding. The experiment uses 117 keV excitation and detects the U Ka line at 98.428 keV. Detection sensitivity is below 1 microgram through the 1.2 mm Zircaloy shielding. Both of these new approaches offer direct, sensitive analyses of actinides for safeguards applications.

New methods for actinide characterization using X-ray fluorescence

George J. Havrilla, Michael Collins, Velma Montoya
Los Alamos National Laboratory
Zewu Chen, Fuzhong Wei, Matthew Cusack
X-ray Optical Systems
Tim Elam
University of Washington
Sarvjit Shastri, Ali Mashayeki
Argonne National Laboratory
ACS August 2011

Overview

- Introduction – hiRX and UHEXRF
- Experimental
- hiRX prototype results
- Comparison of hiRX with EDXRF
- UHEXRF results
- Summary
- Future Direction

Objective

- The objective of this work is to improve the accuracy of plutonium assay for nuclear fuel reprocessing
- There are 2 separate projects, one NA22 Global Safeguards concerning advanced concepts Pu characterization and NIS for NGSI Pu assay in spent nuclear fuel.
- Goal is laboratory based methods

Method Description

- hiRX – high resolution X-ray - laboratory-based source for non-destructive direct analysis with high selectivity and high sensitivity
- UHEXRF – ultra high energy X-ray fluorescence - >80 keV currently using synchrotron source, offers through container wall detection and characterization of actinides, for composition, oxidation and coordination state (XANES, EXAFS) and potentially isotopic composition. Ultimate goal - measurements in the laboratory.

Common Features

- XRF based
- Monochromatic excitation
- Sensitive detection
  - sub-ppm
  - Direct
  - Nondestructive

hiRX

- high Resolution X-ray – based on MWDXRF technology developed for direct compositional characterization of nuclear fuel
- MWDXRF – (monochromatic wavelength dispersive XRF) utilizes doubly curved crystals (DCC) to focus and monochromatize the X-rays passing through the optic

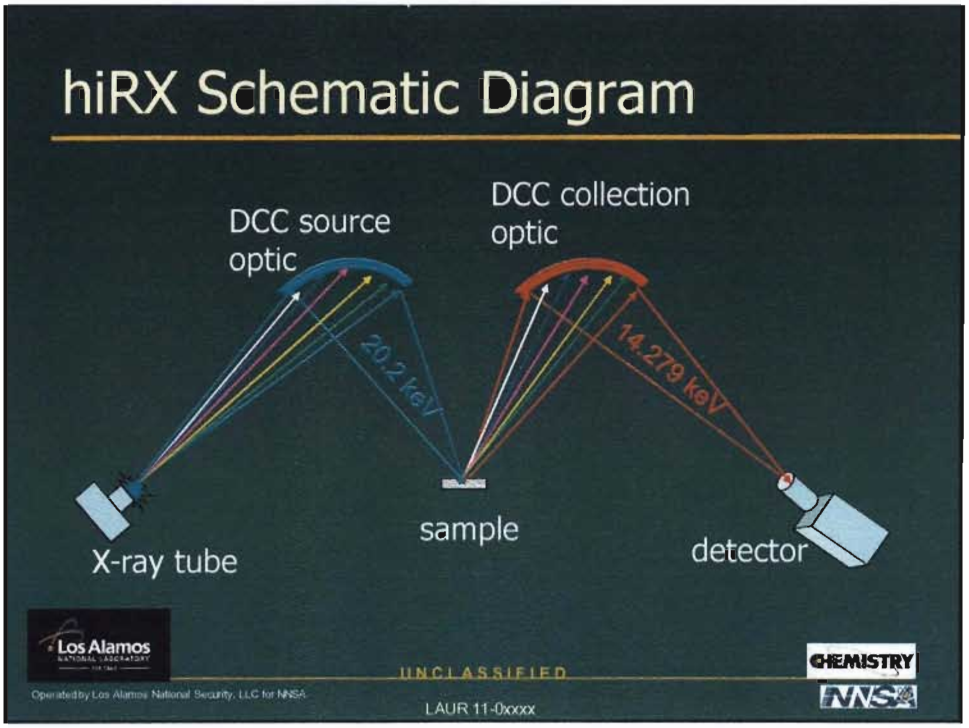
hiRX Technology

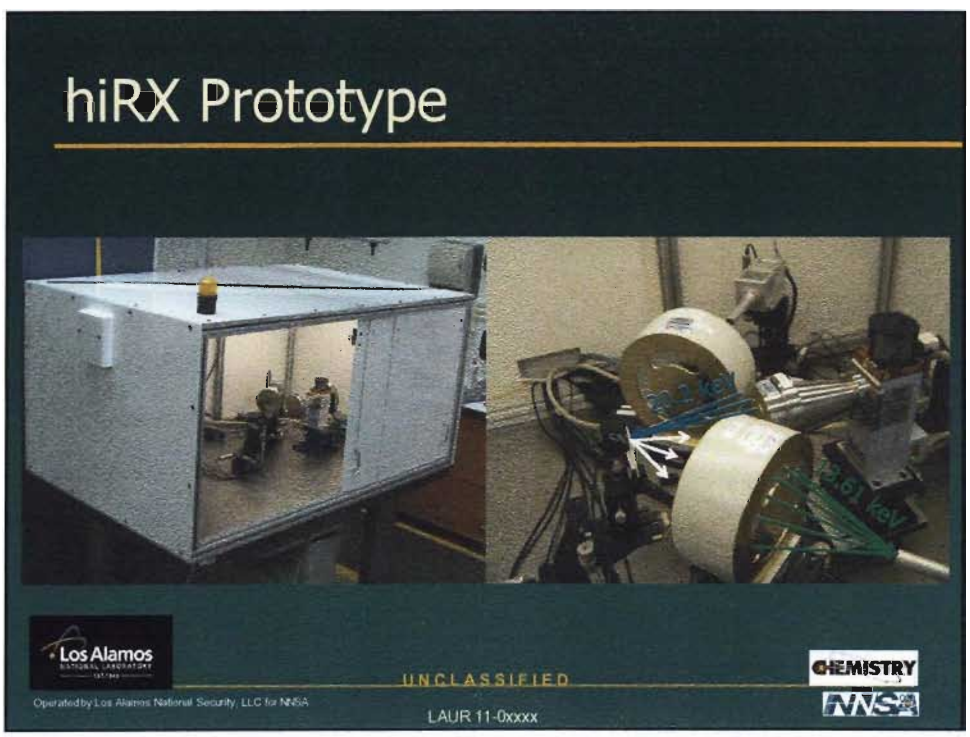
- Doubly curved crystal optics for excitation and collection
- Small spot excitation – several hundred micrometers
- Small sample requirements – 200 microliters or less
- Collection optic to reject background and collect only analyte signal

hiRX

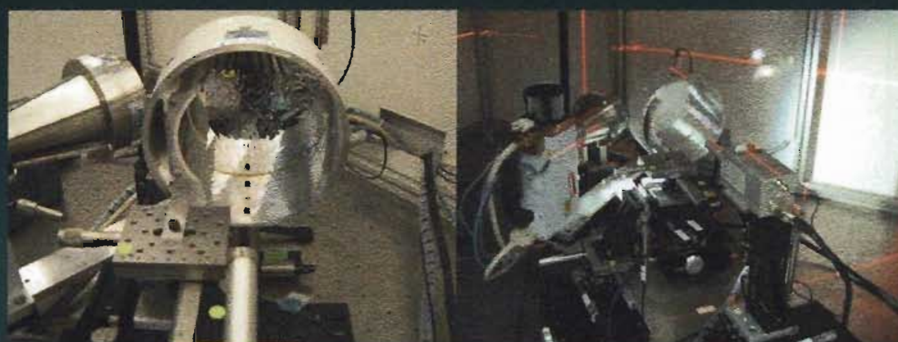
- DCC optics – focus and monochromatize X-rays Based on Bragg diffraction
  - Select both excitation and detection energies
- MWDXRF – monochromatic wavelength dispersive XRF
  - Monochromatic excitation using Rh Ka line 20.2 keV
  - Monochromatic detection – selected analyte target Pu at 14.28 keV
  - Monochromatic detection, U 13.613 keV, Th 12.966 keV, Cm 14.96 keV

Los Alamos NATIONAL LABORATORY
UNCLASSIFIED
Operated by Los Alamos National Security, LLC for NNSA
LAUR 11-0xxxx
CHEMISTRY
NNSA


hiRX Schematic Diagram
DCC source optic
DCC collection optic
20.2 keV
14.279 keV
X-ray tube
sample
detector
Los Alamos
UNCLASSIFIED
Operated by Los Alamos National Security, LLC for NNSA
LAUR 11-0xxxx
CHEMISTRY
NNSA


hiRX Prototype
Los Alamos
UNCLASSIFIED
Operated by Los Alamos National Security, LLC for NNSA
LAUR 11-0xxxx
CHEMISTRY
NNSA

Pu hiRX Prototype



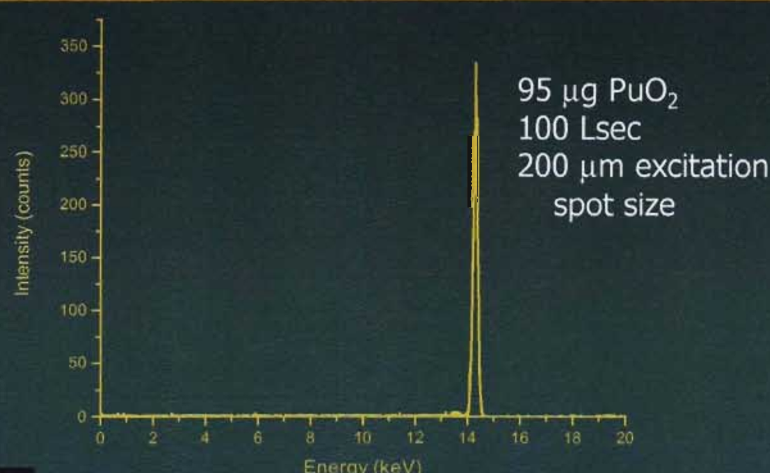
hiRX Prototype Experimental System

- X-ray tube operation – 50 kV and 1 mA
- Detector – SII Vortex EX Si drift 50 mm^2 area
- All optics mounted on Newport stages for x, y and z control

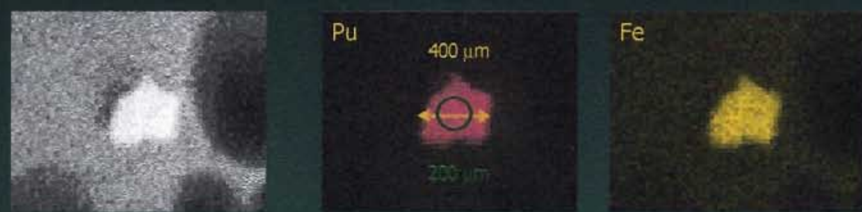
hiRX Prototype DCC Optics

- X-ray source – XOS X-beam X-ray tube with DCC selecting Rh Ka at 20.21 keV, Si<220>, Johann geometry, solid angle of 1.2° x 51.2°, focal distance 200.3 mm, spot size 190 x 250 μm on sample
- Pu collection optic – DCC log spiral geometry, Si<400>, 14.28 keV, focal distance 144.4 mm, solid angle 0.22 sr

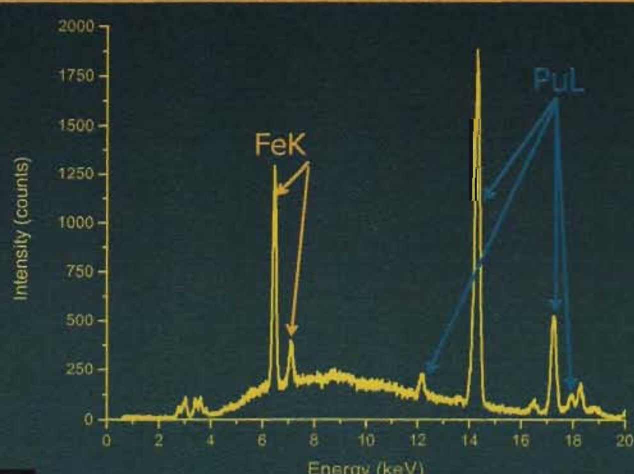
hiRX Pu Spectrum



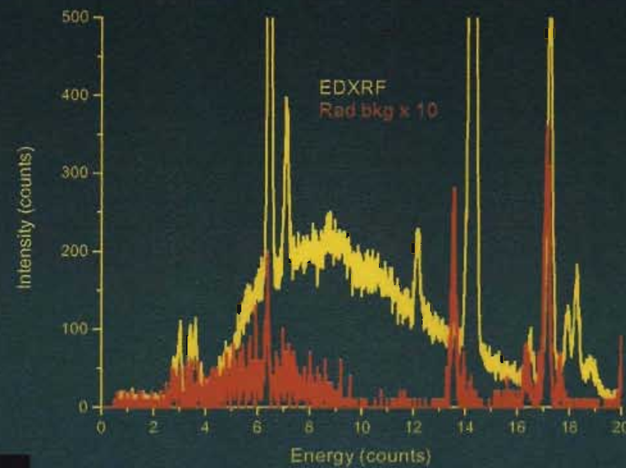
EDXRF Elemental Maps



EDXRF Pu Spectrum



EDXRF Pu Spectrum with Rad Background



Los Alamos NATIONAL LABORATORY

UNCLASSIFIED

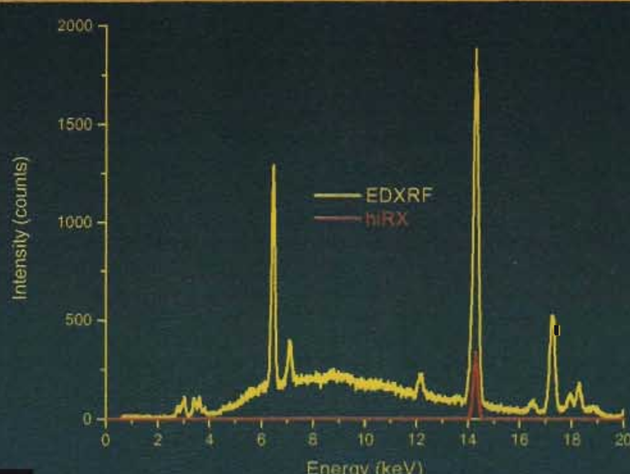
Operated by Los Alamos National Security, LLC for NNSA

LAUR 11-0xxxx

CHEMISTRY

NNSA

Comparison hiRX and EDXRF



Los Alamos NATIONAL LABORATORY

UNCLASSIFIED

Operated by Los Alamos National Security, LLC for NNSA

LAUR 11-0xxxx

CHEMISTRY

NNSA

hiRX Summary

- Demonstrated prototype hiRX Pu instrumentation
- Detection limit with one segment optic, less than 1 microgram Pu
- Good selectivity

hiRX Next Steps

- Run known mass dried spot deposits to determine linearity and detection limits
- Run maps of PuO2 particle and dried spots to estimate particle size detection limit
- Preliminary study of spectroscopic interferences, Sr, Rb, Cm
- Compare high U composition with low Pu

Los Alamos NATIONAL LABORATORY
UNCLASSIFIED
Operated by Los Alamos National Security, LLC for NNSA
LAUR 11-0xxxx
CHEMISTRY
NNSA

UHEXRF

- Ultra High Energy X-ray Fluorescence – energy range above 80 keV
- Utilize the high energy K lines of the actinides for characterization and quantification

Advantages/Disadvantages

- Kα and Kβ lines for actinides
- Simple spectra, less likelihood of spectral interferences
- Deep critical depth of penetration
- High energy – commercial sources not common
- No tube line to provide monochromatic energy using DCCs

Experimental

- Monochromatic excitation at ~117 keV – synchrotron radiation, Advanced Photon Source, beam line 1-ID-C, 50-150 keV, $\Delta E/E = 1.4 \times 10^{-4}$, photon flux 7×10^{9} photons per second

APS 1-ID-C Beam Line

Experimental Setup

Los Alamos NATIONAL LABORATORY

Operated by Los Alamos National Security, LLC for NNSA

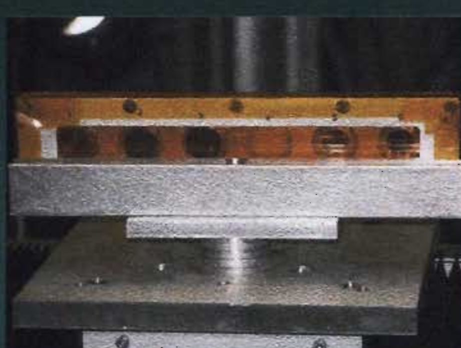
LAUR 11-0xxxx

MISTRY

NNSA

Sample Holder and Shielding

Sample holder



Zircaloy shield in place

Los Alamos NATIONAL LABORATORY

UNCLASSIFIED

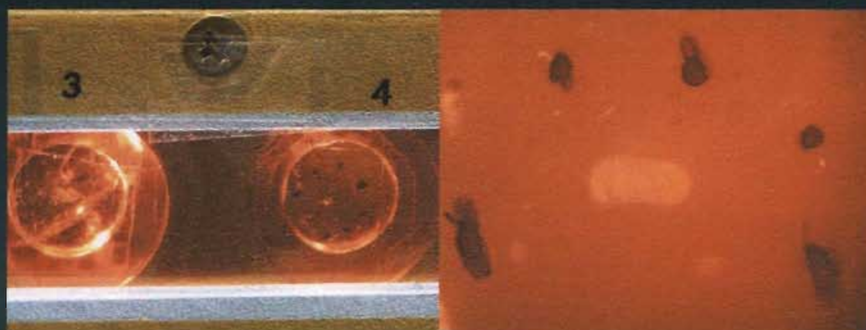
Operated by Los Alamos National Security, LLC for NNSA

LAUR 11-0xxxx

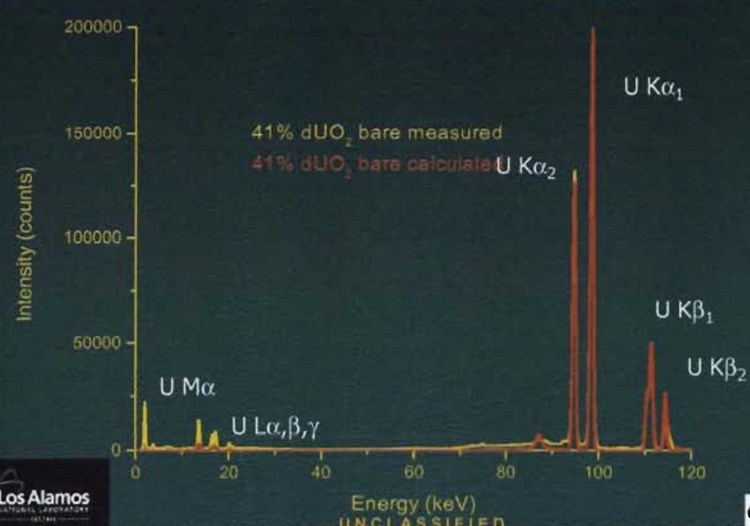
CHEMISTRY

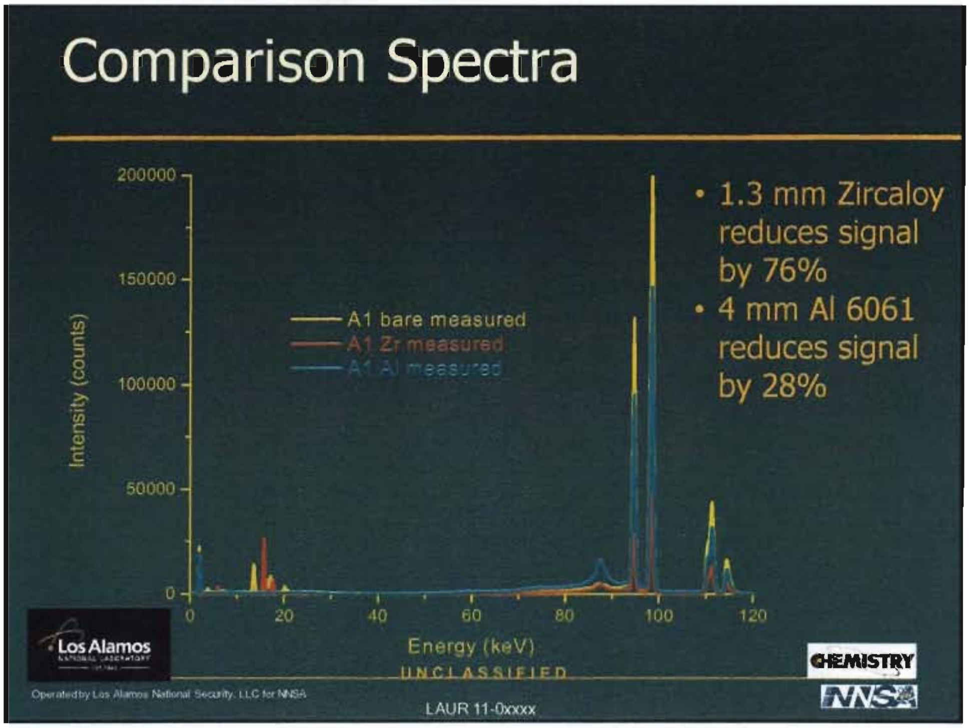
NNSA

Dried Spot Specimens

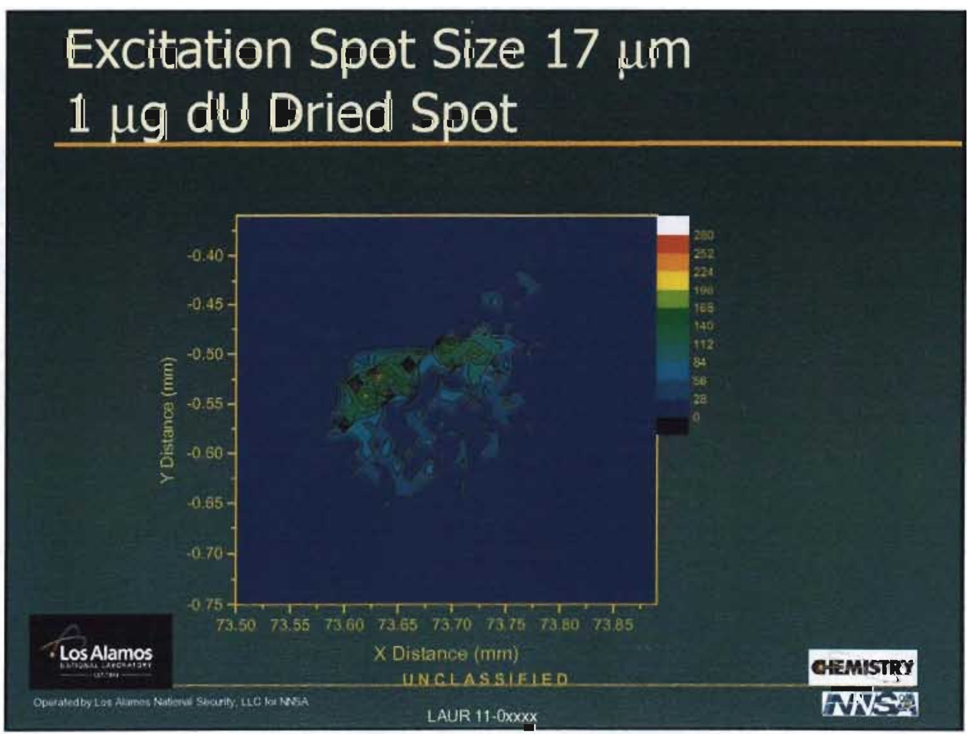


Comparison of measured and calculated spectra

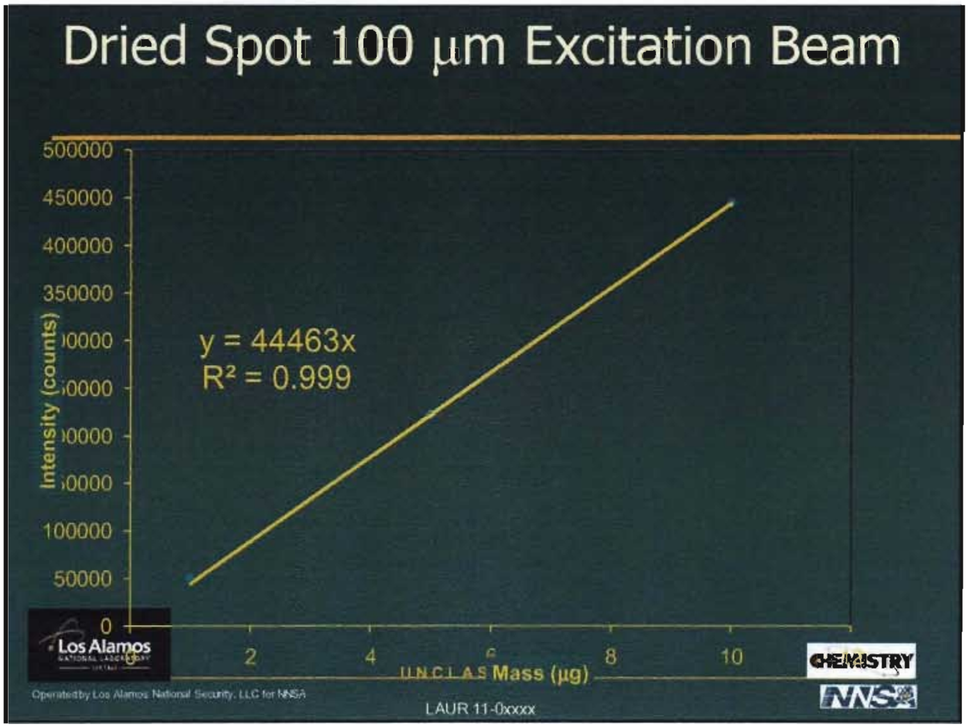


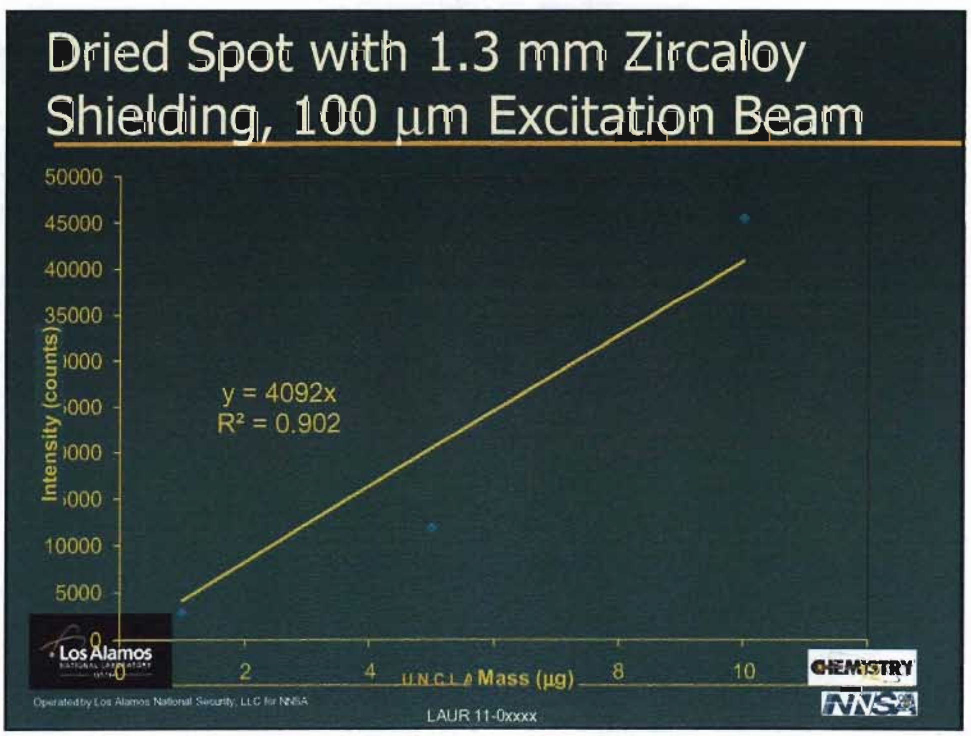


Comparison Spectra
200000
150000
100000
50000
0
Intensity (counts)
A1 bare measured
A1 Zr measured
A1 Al measured
0
20
40
60
80
100
120
Energy (keV)
• 1.3 mm Zircaloy reduces signal by 76%
• 4 mm Al 6061 reduces signal by 28%
Los Alamos
UNCLASSIFIED
Operated by Los Alamos National Security, LLC for NNSA
LAUR 11-0xxxx
CHEMISTRY
NNSA



Excitation Spot Size 17 µm
1 µg dU Dried Spot
-0.40
-0.45
-0.50
-0.55
-0.60
-0.65
-0.70
-0.75
Y Distance (mm)
73.50
73.55
73.60
73.65
73.70
73.75
73.80
73.85
X Distance (mm)
280
252
224
196
168
140
112
84
56
28
0
Los Alamos
UNCLASSIFIED
Operated by Los Alamos National Security, LLC for NNSA
LAUR 11-0xxxx
CHEMISTRY
NNSA


Dried Spot 100 μm Excitation Beam
Intensity (counts)
500000
450000
400000
350000
100000
50000
0
y = 44463x
R² = 0.999
2
4
8
10
Mass (μg)
Los Alamos
CHEMISTRY
Operated by Los Alamos National Security, LLC for NNSA
LAUR 11-0xxxx


Dried Spot with 1.3 mm Zircaloy Shielding, 100 μm Excitation Beam
Intensity (counts)
50000
45000
40000
35000
10000
5000
0
y = 4092x
R² = 0.902
2
4
8
10
Mass (μg)
Los Alamos
CHEMISTRY
Operated by Los Alamos National Security, LLC for NNSA
LAUR 11-0xxxx

UHEXRF Summary

- Achieved sensitive detection of uranium (10's of nanogram level) through container walls two times thicker than typical nuclear fuel cladding
- Demonstrated preliminary direct quantitative capabilities. Could cover at least 4-5 orders of magnitude, sub-microgram to weight percent
- Applicable to actinide elements of interest, Pu, Cm
- Demonstrated UHEXRF to justify development of x-ray optics for laboratory instrumentation development

Overall Summary

- hiRX mid-level energy L line, lab-based characterization method, potential for in-line and person-portable instrumentation
- UHEXRF – ultra high energy K line, SR currently, through container walls, goal is laboratory-based instrumentation
- Both sensitive, selective and direct detection of actinides - Pu

Acknowledgements

- DOE Office of Nonproliferation and International Security (NIS) and the Next Generation Safeguards Initiative program for financial support for hiRX
- Support for Advanced Concepts UHEXRF project provided by DOE NA22 Global Safeguards

Shop Support

Ron Martinez
Leon Lopez
Chris Martinez
George Ortiz