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Title:	Improved accuracy for Pu assay using hiRX
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Form 836 (7/06)

Improved Accuracy for Pu Assay using hiRX

George J. Havrilla

Los Alamos National Laboratory

High Resolution X-ray (hiRX) offers sensitive and selective detection of actinide elements found in spent nuclear fuel dissolver solutions. Monochromatic wavelength dispersive X-ray fluorescence (MWDXRF) technology is the basis for hiRX. The technical foundation of hiRX is the use of doubly curved crystal (DCC) optics for both excitation and detection of the targeted analyte. This work will highlight the capabilities of a prototype hiRX instrument designed for actinide characterization specifically plutonium. The excitation will be accomplished using the RhKa line at 20.214 keV. The Ka line is selected using a DCC that transmits only the RhKa line to the sample. The coupled DCC and low power (50W) x-ray tube provides a monochromatic excitation beam. The Rh offers efficient excitation of the target actinide La lines (Th-Cm). The monochromatic excitation lowers the background compared with bremsstrahlung excitation which is typically used. The emitted x-ray fluorescence for the prescribed analyte plutonium is selected using another DCC specifically passing the PuLa line at 14.279 keV. A silicon drift detector is used to measure the transmitted PuLa x-rays. The collection DCC further reduces the background and selectively passes only the analyte X-ray fluorescence with a band-pass of around 200 eV. The calculated detection limit for Pu is around 60 ng. This instrument has the potential to offer direct measurement of the Pu concentration in spent nuclear fuel dissolver solutions with improved accuracy over conventional gamma, neutron and hybrid K-edge measurements. The combination of low sample volume, high sensitivity and detection selectivity offers a range of potential applications for Pu and actinide measurements for safeguards operations.

Improved Accuracy for Pu Assay using hiRX

George J. Havrilla

SRNL H-Canyon Presentation
December 2011

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hiRX Research Team

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X-ray Optical Systems

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Objective

- The objective of this work is to improve the accuracy of plutonium assay for nuclear fuel reprocessing
- This is the 1st year of financial support from NA24

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 Pu Measurements

- Implement new X-ray optic technology for sensitive detection of Pu for safeguard applications
- Attain a sensitivity of at least 10 ppm for Pu detection
- Develop new sampling methodology to reduce sample size, improve safety and accuracy of Pu measurements

hiRX Technology

- Doubly curved crystal optics for excitation and collection
- Small spot excitation – several hundred micrometers
- Small sample requirements – 100 microliters or less
- Collection optic to reject background and collect only analyte signal

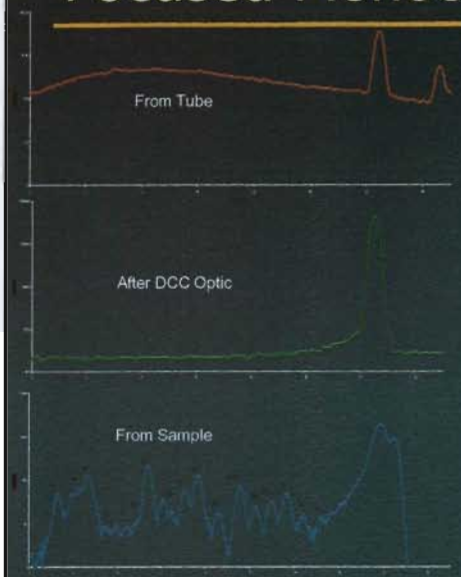
hiRX

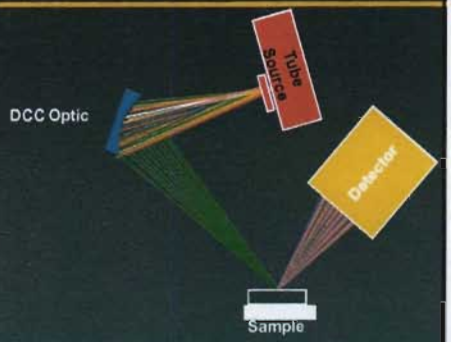
- DCC optics – focus and monochromatize X-rays Based on Bragg diffraction
  - Select both excitation and detection energies
- MWDXRF – monochromatic wavelength dispersive XRF
  - Monochromatic excitation using Rh Ka line 20.2 keV
  - Monochromatic detection – selected analyte target Pu at 14.28 keV
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

Conventional EDXRF

- Good for multi-element analysis
- Broad experience
- Limitations
  - Background due to scatter from excitation beam across whole spectrum
  - Peak overlap challenges
  - Not suitable for complex geometries and non-homogeneous areas

Focused Monochromatic EDXRF





- High intensity and spatially resolved
- Detect and quantify trace concentrations (excellent signal-to-noise ratio)
- Good results for small features
- Limitations
  - None above excitation energy
  - Drops-off below excitation energy

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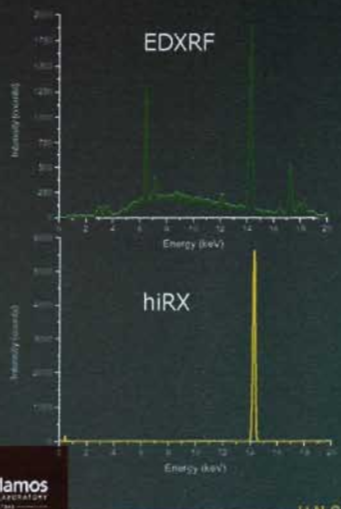
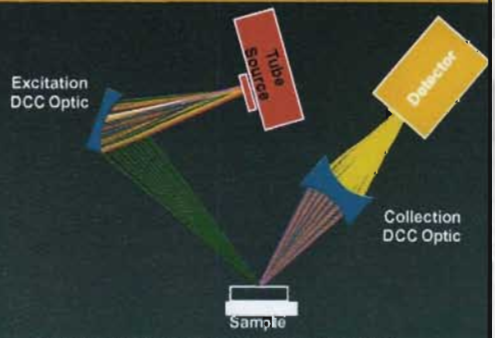
hiRX





- Single element detection with high intensity and spatially resolved
- Excellent signal-to-noise ratio, very low background
- Limitations
  - No elements above excitation energy
  - Limited to single element per channel

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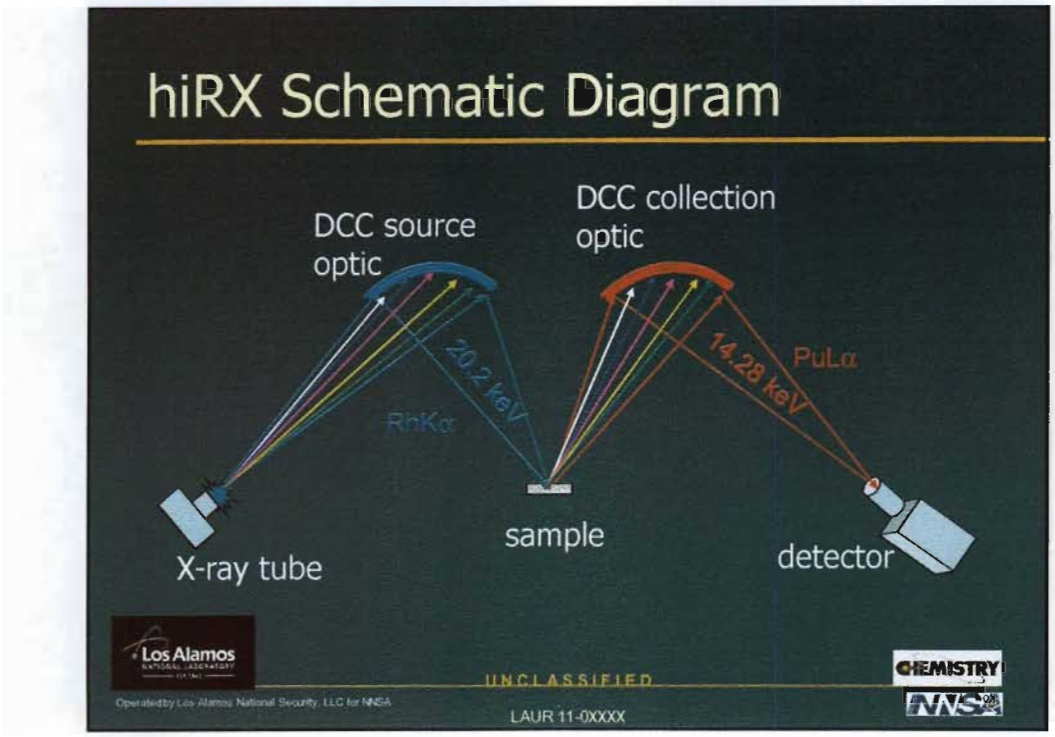
hiRX Schematic Diagram
DCC source optic
DCC collection optic
20.2 keV
RhKα
14.28 keV
PuLα
X-ray tube
sample
detector
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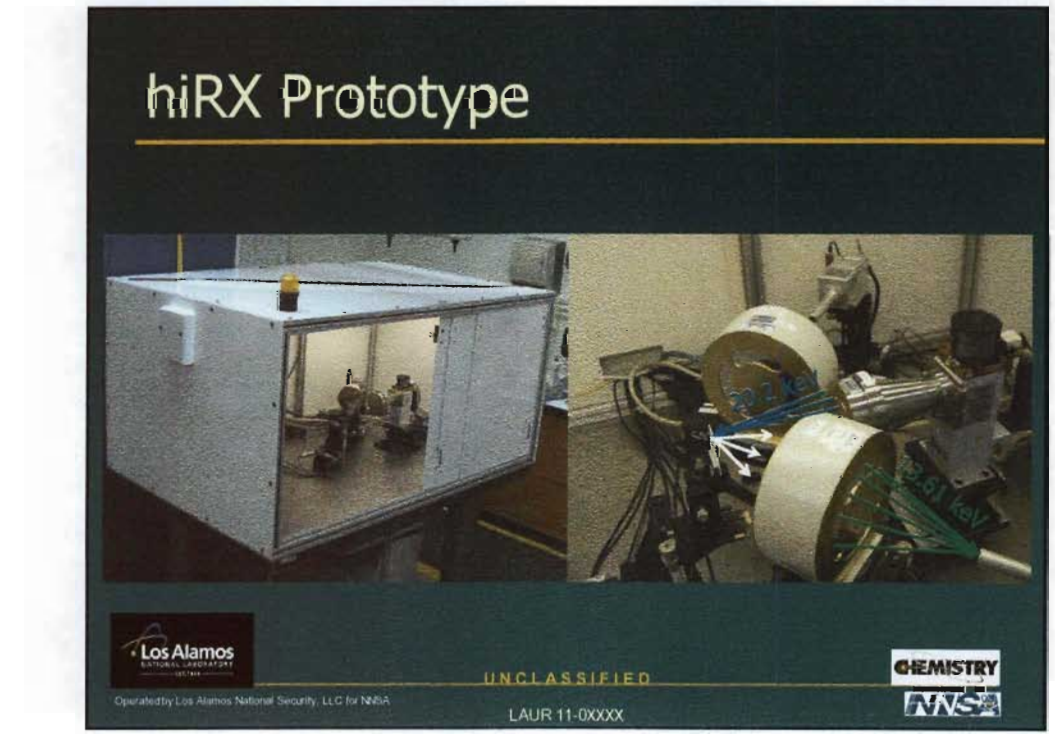
hiRX Prototype
20.2 keV
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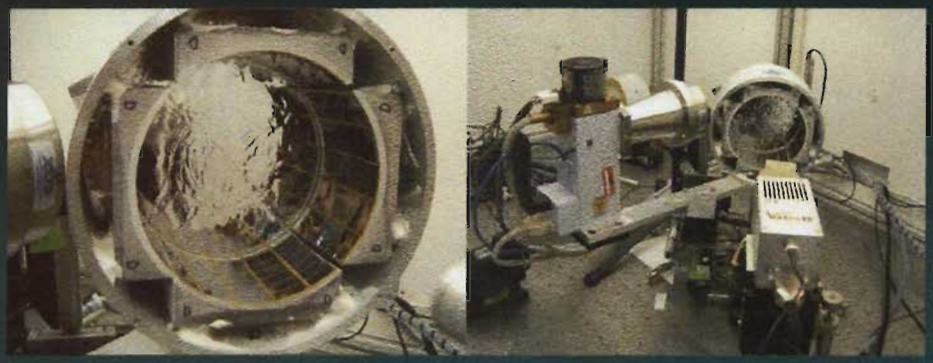
Pu hiRX Prototype



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Doubly Curved Crystal Optics

XOS

- Monochromatic optics
- Si, Ge, quartz, graphite or mica crystal material
- 10-20% reflectivity
- Useful for X-rays of energy 1.5 keV-35 keV

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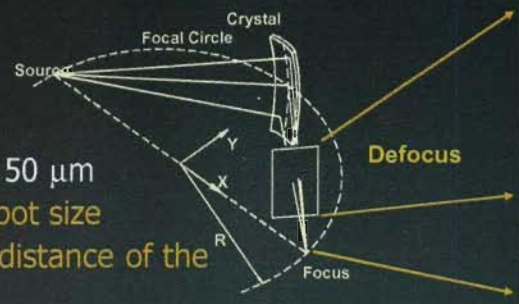
Johann Point Focusing DCC



- Spot size, ≥ 50 µm
  - Source spot size
  - Working distance of the optic
- Gain, Up to > 1,000x
  - Large collection solid angle, ≥ 0.1 sr

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Optic Comparison

	Polycapillary	Monocapillary	DCC	Aperture
Smallest Spatial Resolution		✓		
Highest Flux (cps)			✓	
Highest Flux Density (cps/area)	✓			
Fastest Data Acquisition	✓			
Lowest Detection Limits			✓	

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Sulfur Analyzers based on DCC Optics

XOS Proprietary

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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

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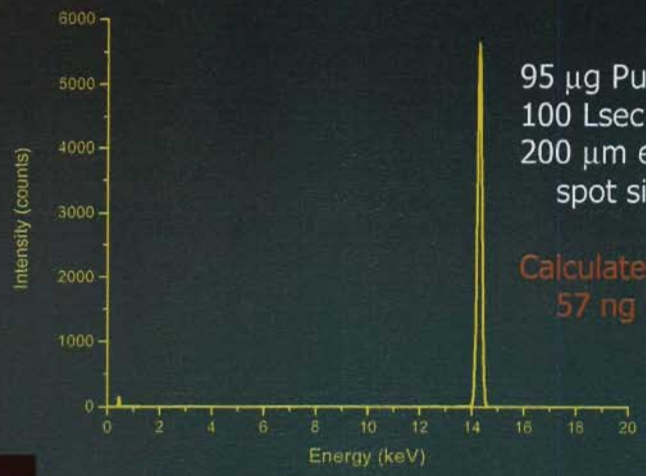
hiRX Prototype DCC Optics

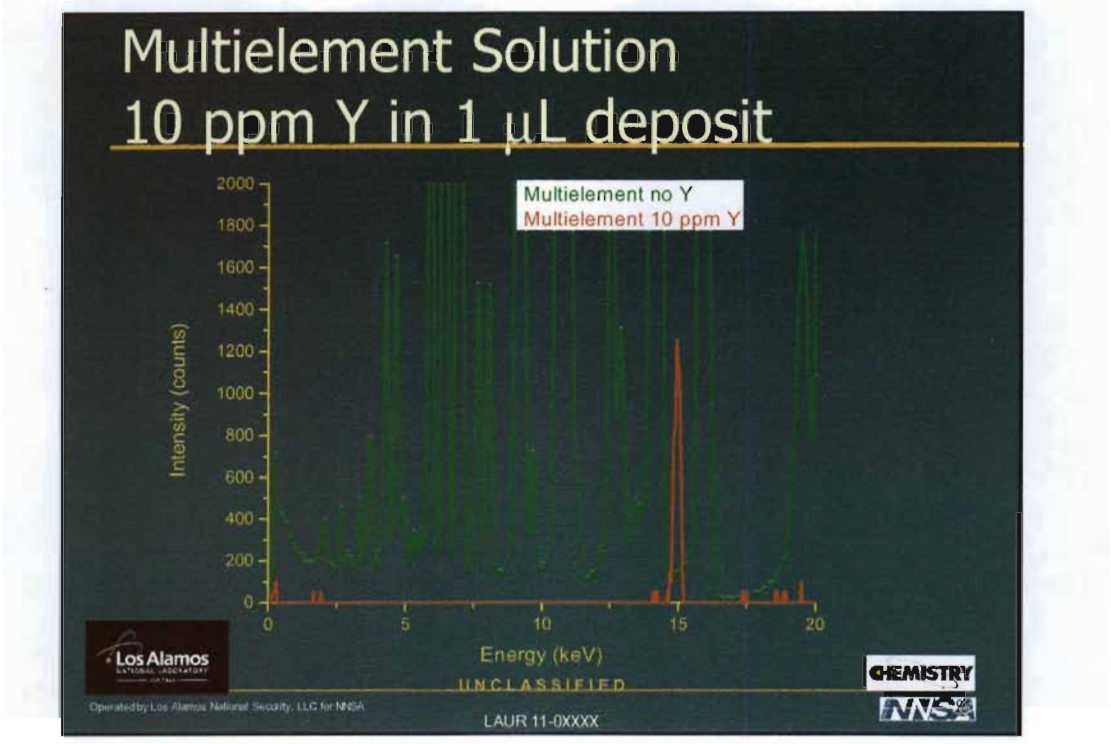
- X-ray source – XOS X-beam X-ray tube with DCC selecting Rh Ka at 20.21 keV, Si<220>, Johann geometry, solid angle of 1.2° x 51.2°, focal distance 200.3 mm, spot size 190 x 250 μm on sample
- Pu collection optic – DCC log spiral geometry, Si<400>, 14.28 keV, focal distance 144.4 mm, solid angle 0.22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

hiRX Pu Spectrum



95 μg PuO_2
100 Lsec
200 μm excitation spot size

Calculated LOD 57 ng


Multielement Solution
10 ppm Y in 1 µL deposit
Multielement no Y
Multielement 10 ppm Y
Intensity (counts)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
5
10
15
20
Energy (keV)
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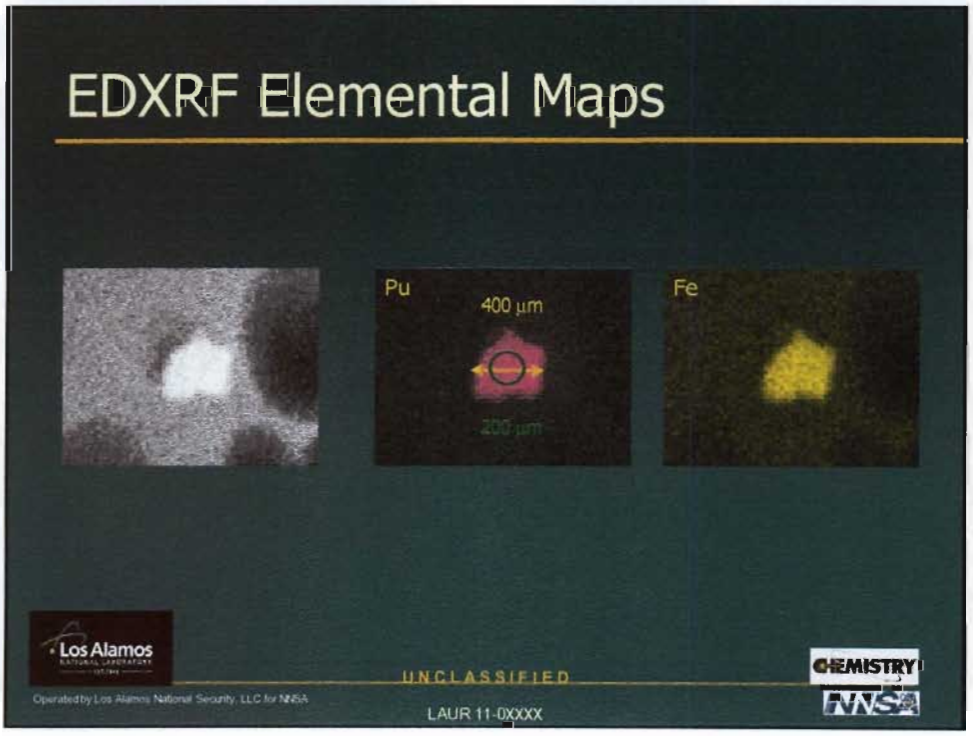
EDXRF Elemental Maps
Pu
400 µm
200 µm
Fe
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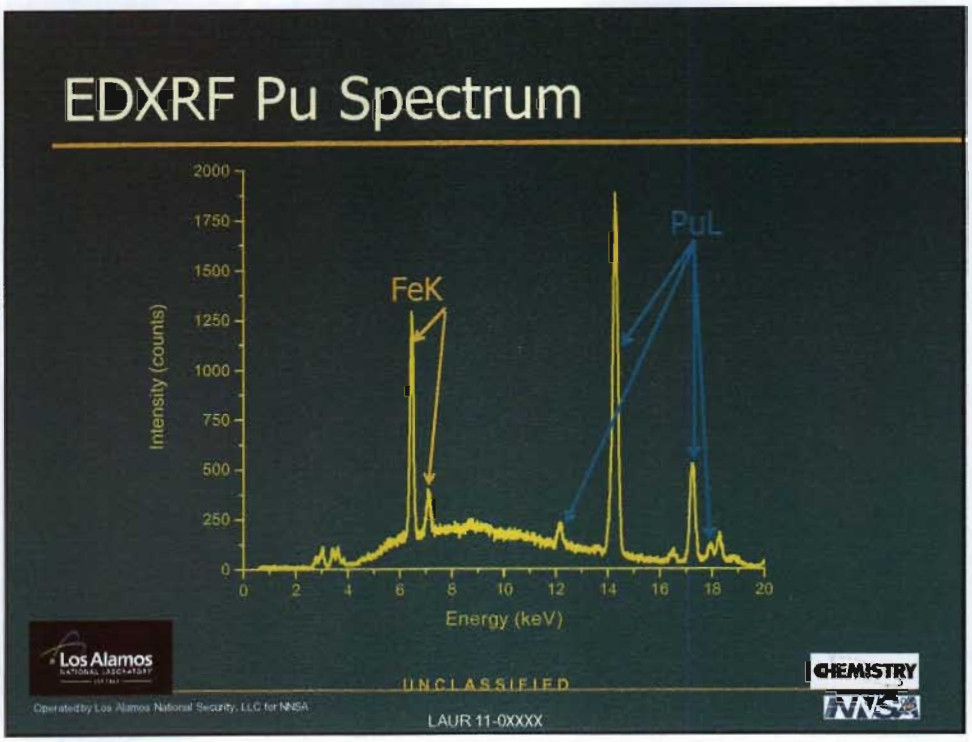
EDXRF Pu Spectrum
Intensity (counts)
Energy (keV)
FeK
PuL
2000
1750
1500
1250
1000
750
500
250
0
0 2 4 6 8 10 12 14 16 18 20
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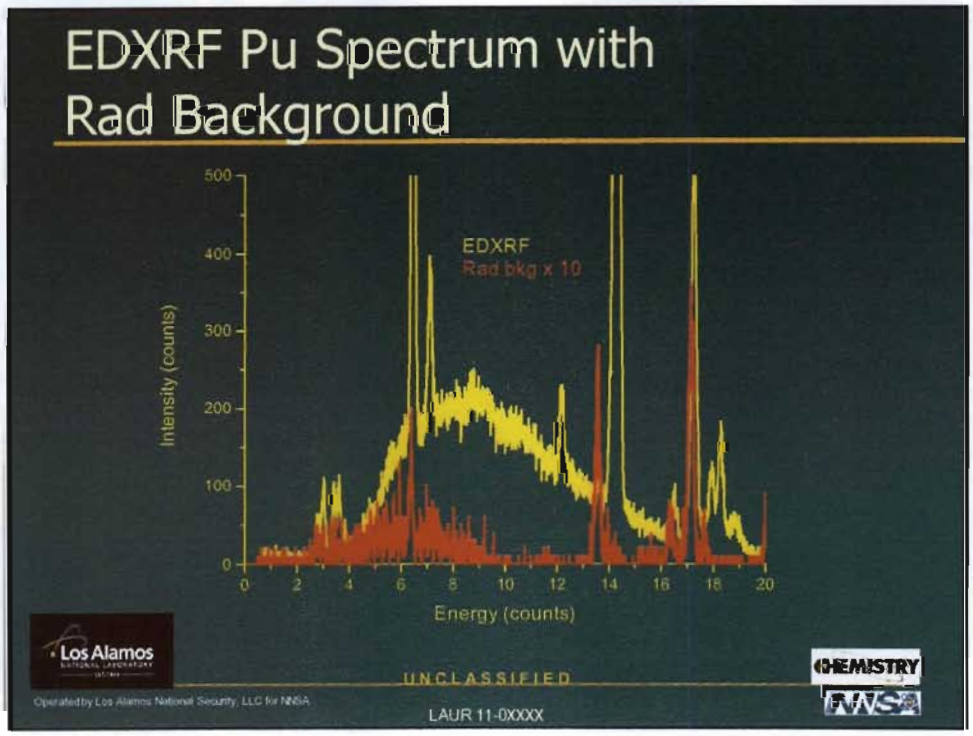
EDXRF Pu Spectrum with Rad Background
Intensity (counts)
Energy (counts)
EDXRF
Rad bkg x 10
500
400
300
200
100
0
0 2 4 6 8 10 12 14 16 18 20
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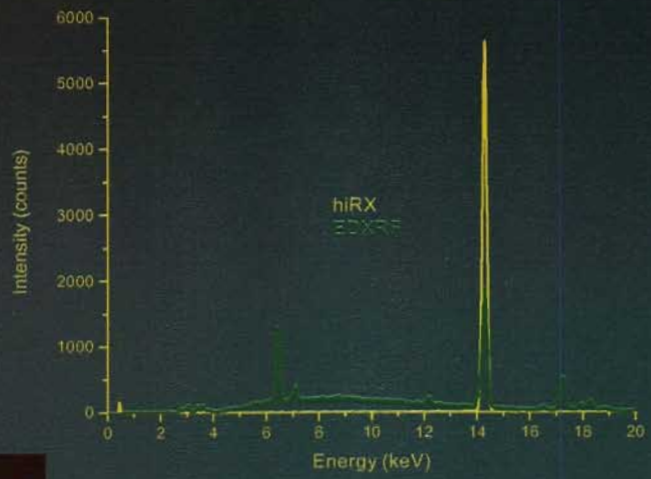
Comparison hiRX and EDXRF



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Summary

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

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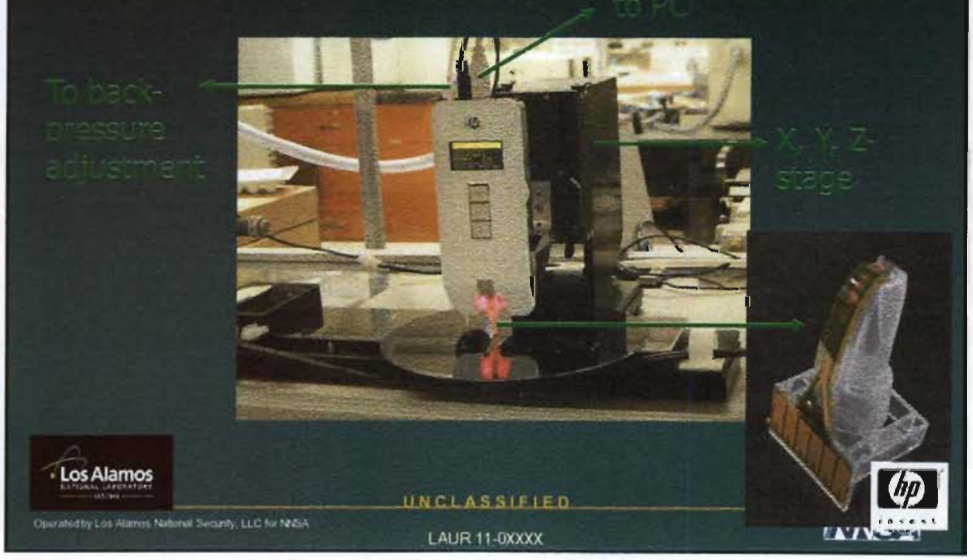
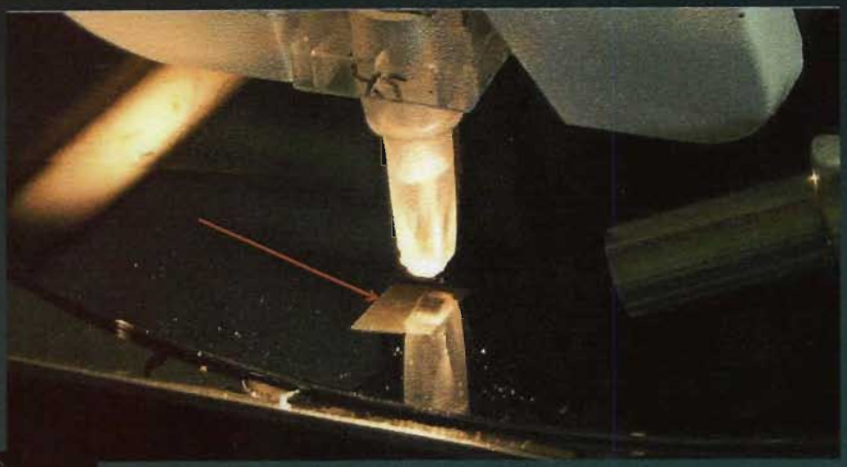
Small Volume Deposition - TIPS

- Small volume deposition matches excitation area of micro X-ray beam
- Low volume reduces exposure to radiation – ALARA – increased safety in sampling and analyses
- Aids in reducing matrix effects
- Controlled deposition increases accuracy and precision by generating well defined spots of size and composition

Instrumentation – HP-TIPS



88 x 87 Array of 10 pL Depositions Illuminated from the Side



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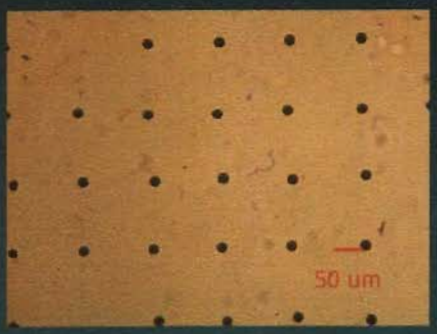
Magnified View of Array Deposit



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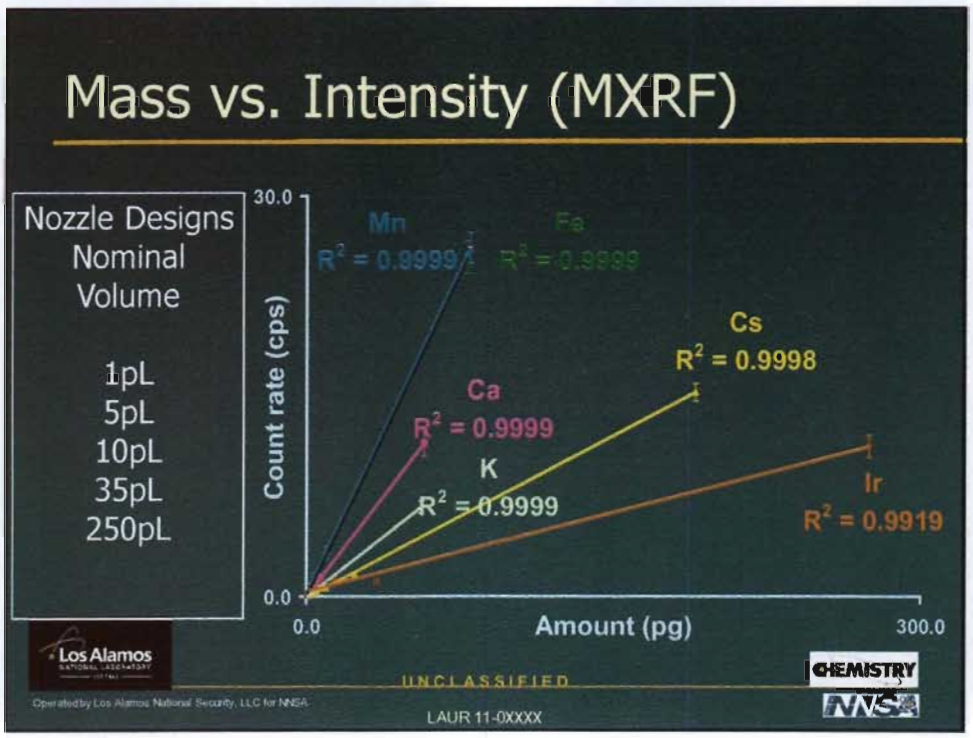
Mass vs. Intensity (MXRF)
Nozzle Designs
Nominal
Volume
1pL
5pL
10pL
35pL
250pL
30.0
0.0
Count rate (cps)
Mn
R² = 0.9999
Fe
R² = 0.9999
Cs
R² = 0.9998
Ca
R² = 0.9999
K
R² = 0.9999
Ir
R² = 0.9919
0.0
Amount (pg)
300.0
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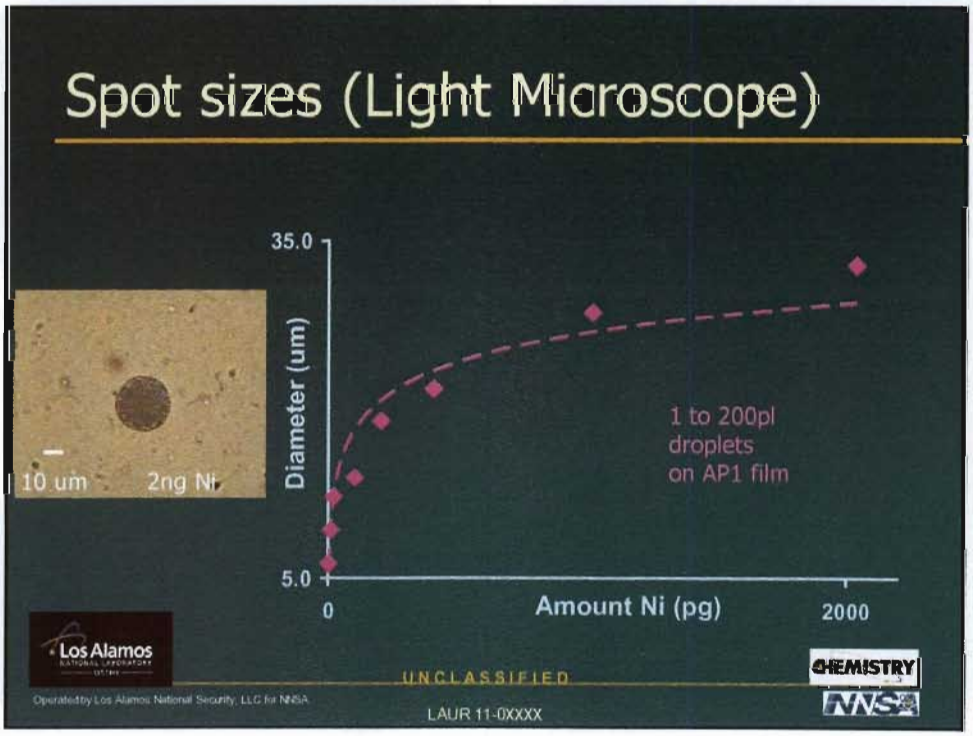
Spot sizes (Light Microscope)
10 um
2ng Ni
35.0
5.0
Diameter (um)
1 to 200pl
droplets
on AP1 film
0
Amount Ni (pg)
2000
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FY'12

- 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
- Develop microliter sampling strategy

Summary and Future

- hiRX works
- Need to demonstrate real spent fuel sample for Pu determination – known Pu concentration
- Design and develop prototype plant-lab-based instrument for demonstration

Responses to questions

1) How does your technology work?
   - X-ray excitation of the sample, detection of emitted X-rays
2) What does it measure?
   - Direct measurement of analyte of interest – Pu using X-ray Fluorescence
3) What kind of sample do you need?

Solid or liquid – prefer solid

Responses to questions

4) What sample size does it require?
   - Less than 100 microliters – actual deposition will be 1 microliter or less
5) How are the samples loaded into the instruments?
   - Samples are deposited onto thin polymer film, allowed to dry and then sealed with another film.

How are the measurements taken?

Specimen inserted into instrument, measurement started

Responses to questions

6) What is the timeline for the development of your technology, all the way through to deployment at H-Canyon?
   - FY12 initiate and develop collaboration
   - FY13 design, develop and build hiRX prototype with XOS and H-Canyon
   - FY14 test at LANL, then deliver to H-Canyon for testing, prepare report on performance and needed adjustments and improvements

Responses to questions

7) What kind of waste do you expect to result from your field test at H-Canyon?
   - Solids - dried residue on thin polymer films

8) How long would it take to conduct your deployment at H-Canyon (e.g., how many runs do you need to do to gain statistically significant data)?
   - Depends on processes being run through H-Canyon, XOS experience can provide some guidance

Responses to questions

9) What is the "total" foot print/size of the instrument, including the detector system, sample compartment, electronics, system enclosure, and supporting components?
   - Depends on plant prototype design, current prototype is ~2ft x 4 ft
10) What are the requirements for the enclosure (i.e. shielding from X rays, sealed enclosure for vacuums or inert gas environment)?
   - Instrument will be self-contained no external feeds

Responses to questions

11) Is regular maintenance or alignment of the instruments and/or components required?
   - Calibration check. No moving parts.
12) What are the power requirements? How is the system electrically connected?
   - 120V, for instrument and PC, wall outlet

Responses to questions

13) Are there any requirements in terms of electronic electrical/thermal sensitivity (this can be related to noise in signals due to thermal instability or noise in electronics due to vibration, high humidity or harsh environment)?

- We expect this instrument to be in a lab environment. We'll need to discuss with XOS during the design phase, they have plant deployment experience.

Responses to questions

14) How is the data collected and recorded? Is there a need for an external controller or PC? What would be the foot print of the controller and associated peripherals?

- This could all be in one box about 3 x 3 x 1.5 ft including processor

15) Are the components, sensing media and/or electronics sensitive to radiation or corrosive environments?

- Possibly, need to discuss with XOS and depends on placement in H-Canyon

Responses to questions

16) Are there any optical components or others that may be impacted by the presence of corrosive or high humidity or mechanical vibration or electronic noise?
   - X-ray optics, depends on environment

17) What is the physical weight of the equipment?
   - TBD – depends on design

18) Are there any additional requirements for the operation of the equipment?

Los Alamos NATIONAL LABORATORY no

Responses to questions

19) Is any of the equipment required to be kept at low/high pressure or low/high temperatures for optimum operation?
   - no

20) Are there any safety issues that may be of concern with operation of the instrument?
   - no

21) What kind of labor support would you need from H-Canyon?

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Responses to questions

22) Based on the H-Canyon feasibility study and the tours, where do you think your technology can be deployed at H-Canyon?
- TBD

23) Looking further into the future, how do you see your technology being deployed at safeguarded facilities (e.g., as part of the IAEA's toolbox, as part of a state accountancy system, used by the operator)?

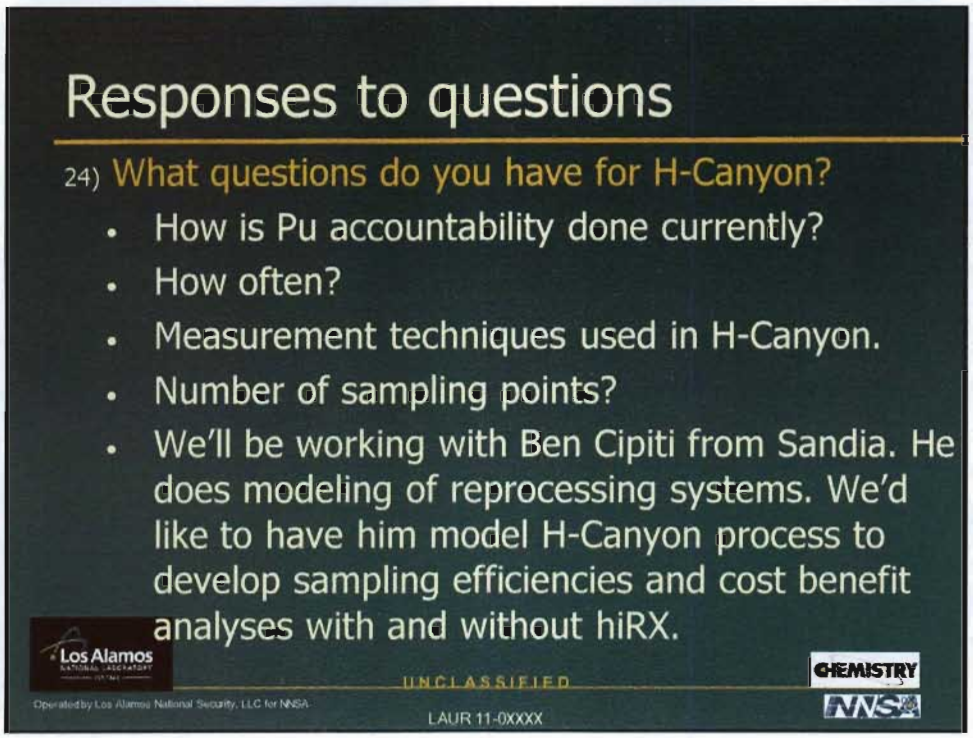
Yes – XOS would be the vendor

Responses to questions

24) What does H-Canyon need to provide in terms of consumables, durables, waste management, etc?
- Waste management

25) Are there any additional components required to manipulate samples or operate the equipment, such as sample holders/sample manipulators, gas / liquid flow cell? What would be the foot print of these components?

We'll supply sample cups etc.


Responses to questions
24) What questions do you have for H-Canyon?
• How is Pu accountability done currently?
• How often?
• Measurement techniques used in H-Canyon.
• Number of sampling points?
• We'll be working with Ben Cipiti from Sandia. He does modeling of reprocessing systems. We'd like to have him model H-Canyon process to develop sampling efficiencies and cost benefit analyses with and without hiRX.
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