PUSHING THE LIMITS FOR DETECTION OF TRACE GALLIUM IMPURITIES IN MOX SPENT FUELS

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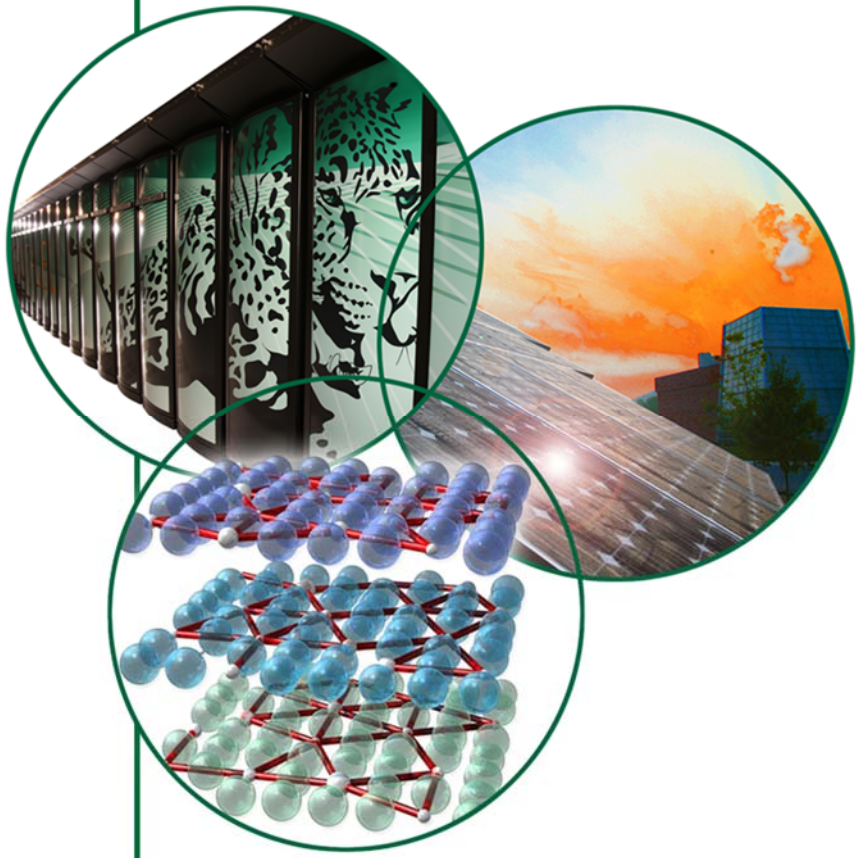

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
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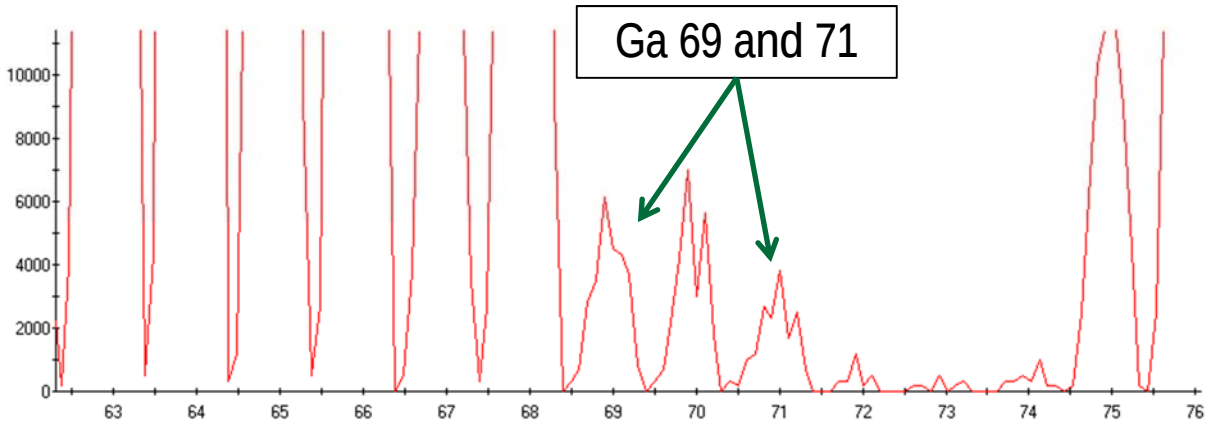
Presentation Overview

- Why Gallium?
- Small-scale MOX irradiations: Development and validation of a trace gallium analytical method
- Full-scale MOX run: Analytical overview and fuel digestions
- ICPMS isobaric interferences
- Separations for purified gallium aliquots
- Analysis summary (no data)
- Conclusions
- Acknowledgments

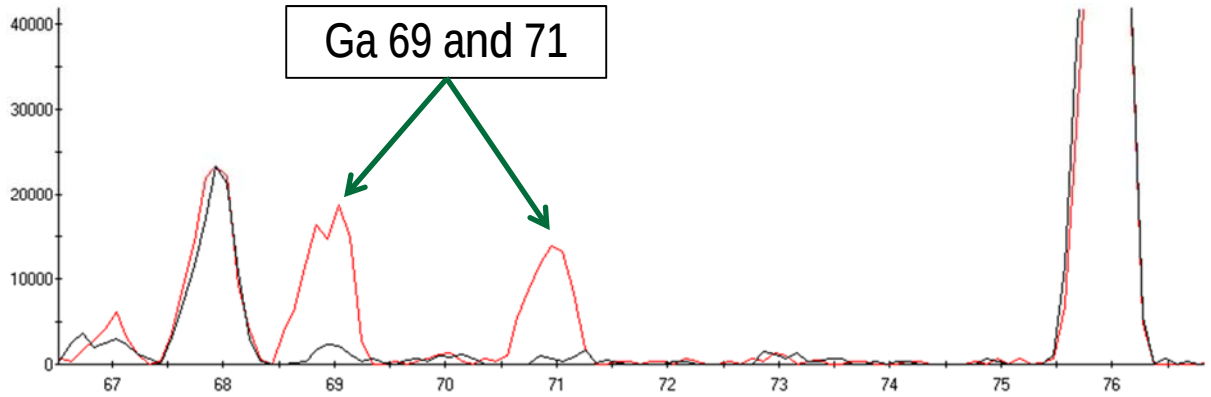
Why Gallium?

- Zircaloy, a zirconium alloy, is a preferred cladding material in nuclear reactors.
  - Among other physical properties it has excellent heat transfer capabilities conducting heat with very little loss from the fuel into the pressurized primary water system.
- It has been demonstrated in the lab that gallium will attack zirconium metal.
- United States (U.S.) produced plutonium, the major fissionable element in MOX, contains gallium.
- Will gallium migrate from the fuel into the clad material and cause degradation?
  - Empirical data required for U. S. Nuclear Regulatory Commission's qualification of MOX fuel.

Gallium Scans of Unirradiated Specimens



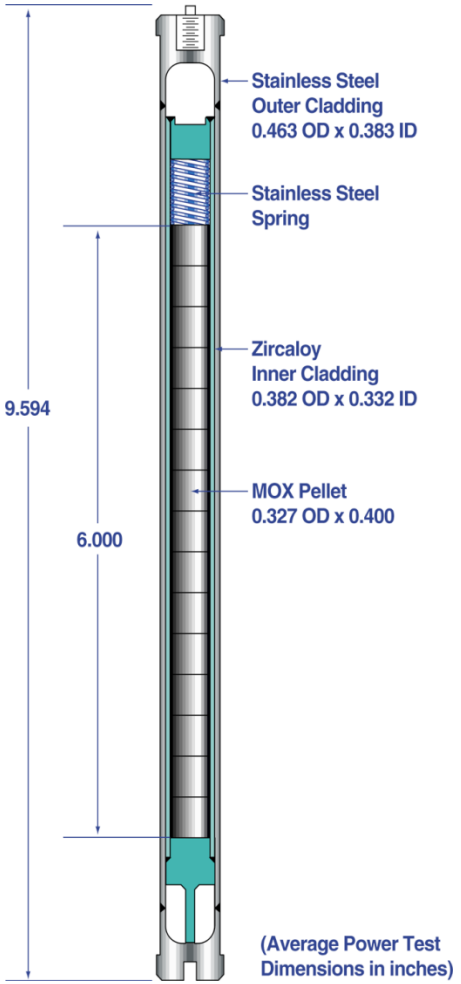
- Zircaloy clad



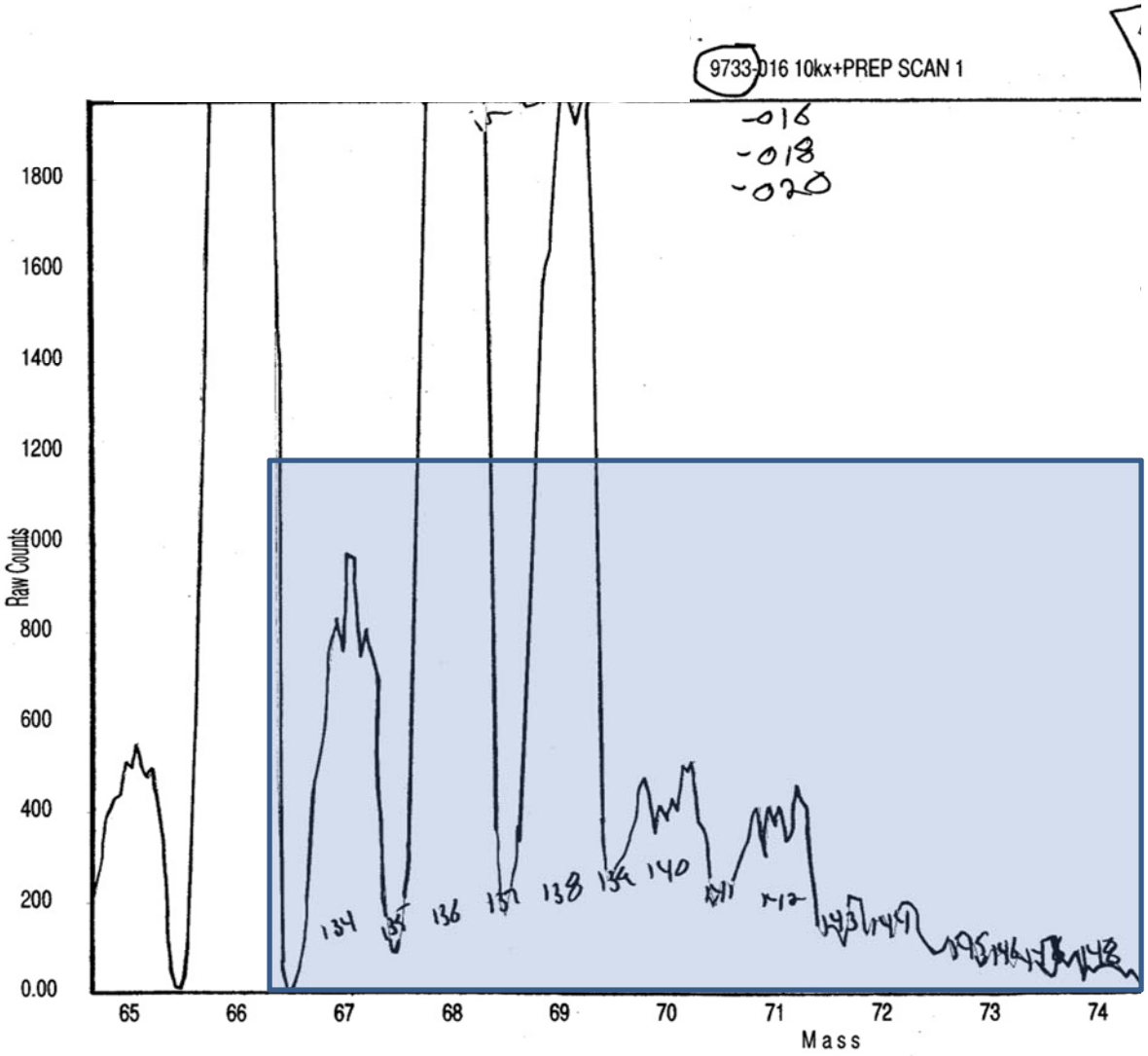
- Green MOX pellet

Development Work Started in the Late-1990s.

- Our work to develop, test, and establish an ORNL analytical method to measure trace gallium content in irradiate Mixed Oxide Fuels (MOX) and Zircaloy clads started in the late-1990s.
  - Test assemblies irradiated at INL's ATR reactor to burnups ranging from ~10 to ~50 GWd/MT (~1% to ~5.2% heavy element fissions).
- This development work was presented at the following Eichrom Users meetings:
  - *Eichrom Technologies Inc. Users Group Meeting May 2001*.
  - *Using Eichrom Resins to Simplify the Analyses for Gallium Content and Atom Percent Fission of Irradiated MOX Fuels*, Eichrom May 2005 Users Group Meeting.



Irradiated MOX Fuel Low Mass Scan



Doubly charged high mass fission products interfere with masses 67 through 74.

Signal 2-3% of isotope's mass response

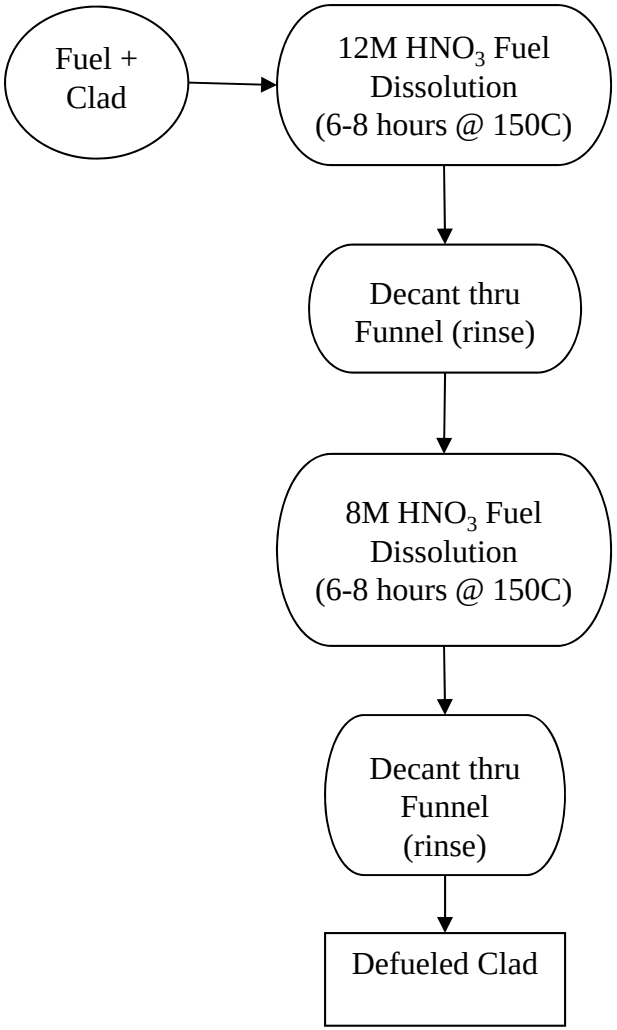
DOE-FMDP Full Scale MOX Fuel Qualification

- **Jan. 2009:** Five full length MOX fuel rods were delivered to ORNL's Irradiated Fuels Examination Laboratory (IFEL) after a full scale irradiation test at Duke Power's Catawba nuclear power plant.
  - ORNL conducted Post Irradiation Examinations (PIE) to verify fuel and clad performance
  - Predicted burnup range: 40-47 GWd/MT (2 year cooled and extremely radioactive)

ORNL Destructive Analyses for Qualification of MOX Fuels

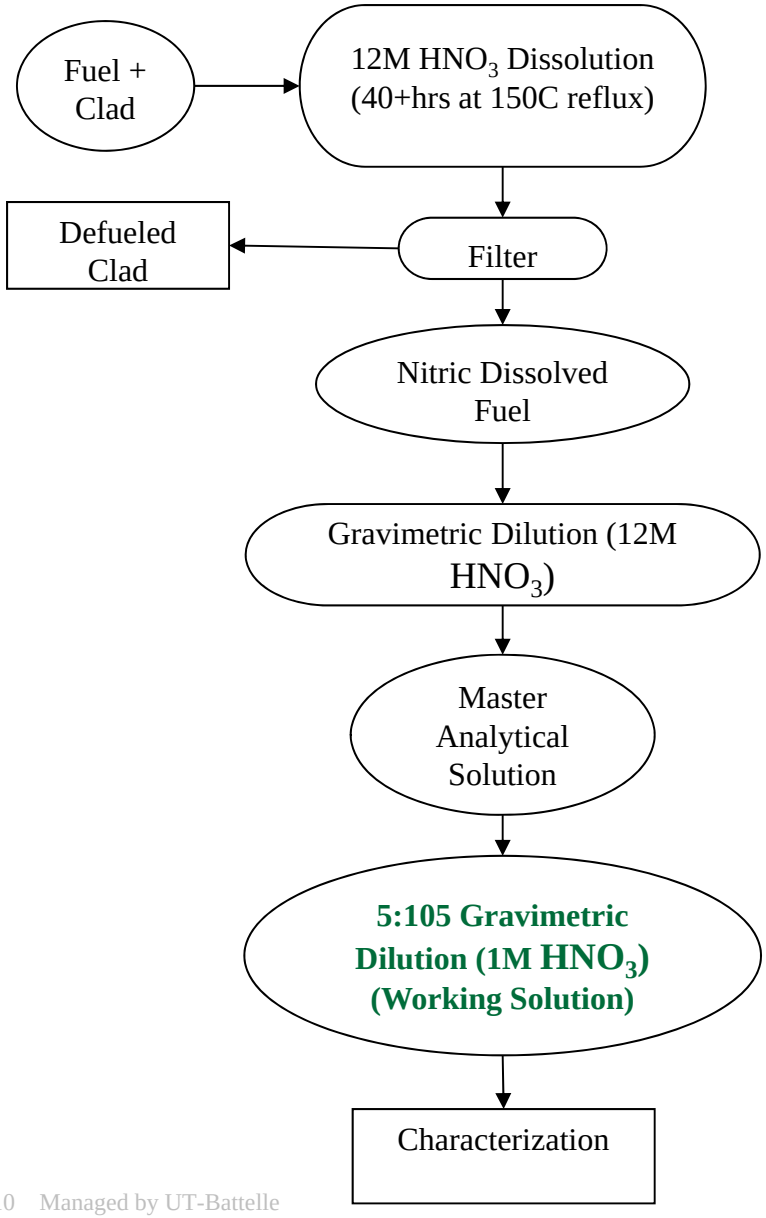
- 53 fuel specimens for destructive analyses (Feb 2010)
  - Defueling (31 specimens)
    - physical measurements on cladding
  - Clad hydrogen content (7 CHA specimens)
  - Clad/Pellet trace gallium (5 clads, 3 pellets)
  - Detailed isotopic analyses (13 specimens)
    - Radiochemical counting
    - High precision burn-up determinations (Nd-148 method)
    - Isotope Dilution Mass Spectrometry (IDMS) for key lanthanides and actinides

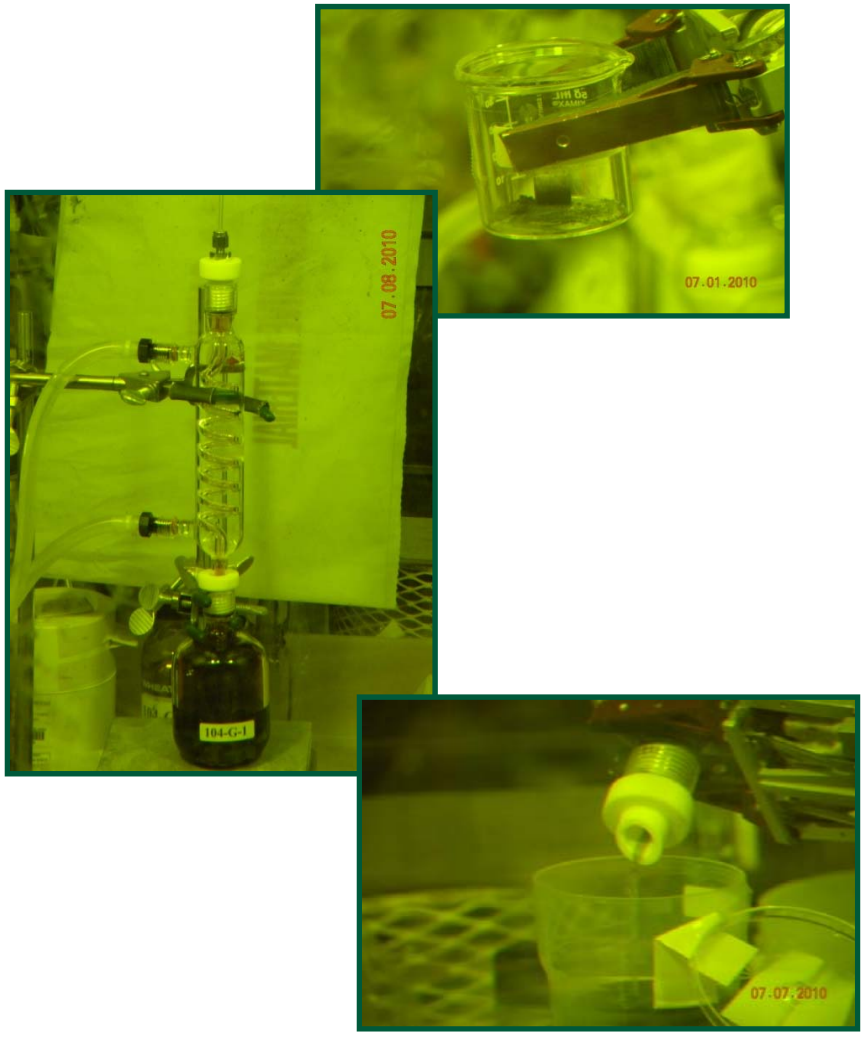
MOX Clad Defueling Scheme (43 segments)



- Short lived fission products on inner clad surfaces complicated the hotcell transfers and shipping
  - Short lived FPs Ru-106 and Ce-144 dominate activity
  - Detail planning required for high dose evolutions

MOX IAF Fuel Dissolution Scheme (13 segments)





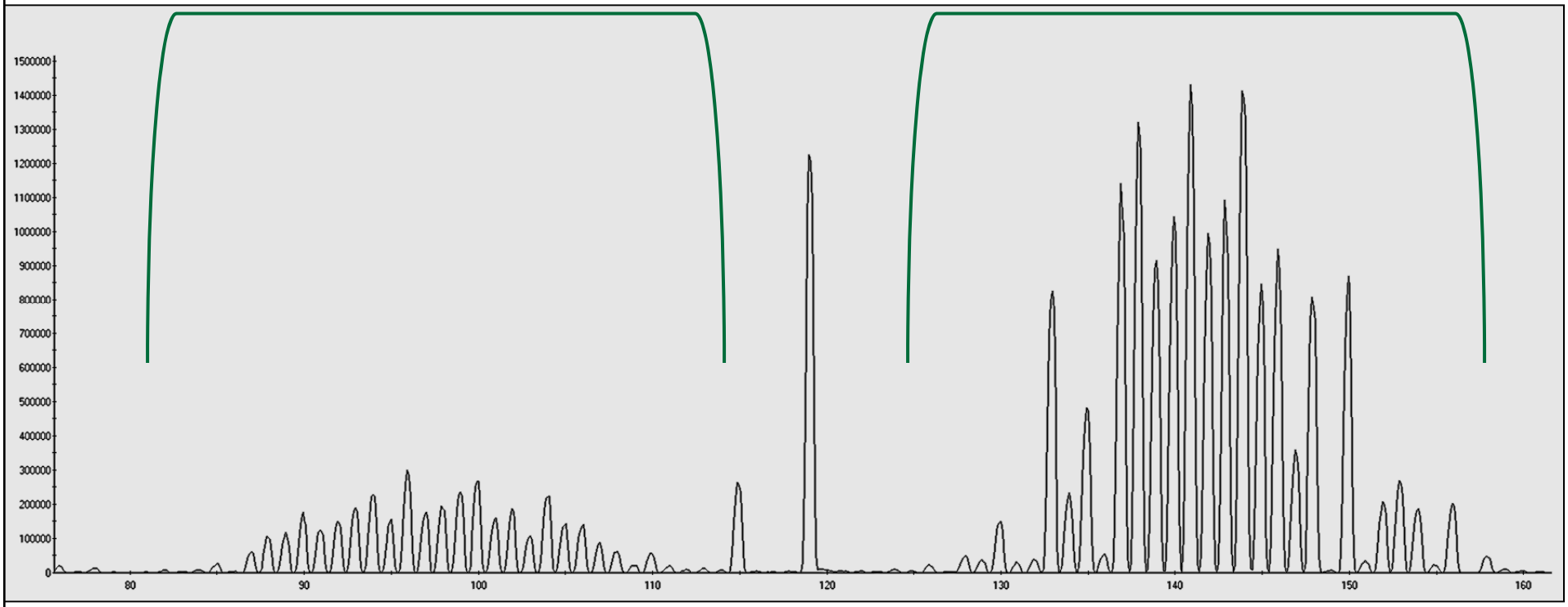
MOX Zircaloy Clad Dissolutions

- Clads were dissolved in Teflon beakers with 25ml of a concentrated HNO_3/HF (50%/50%) acid mixture
- Digests were covered with Teflon watchglasses and heated to 150C with moderate stirring
  - Brown vapors were immediately released and clads actually broke into pieces within 5 minutes
  - After 45 minutes clads appeared to be in solution
  - After heating for 1 hour clads were allowed to cool then transferred using DI H_2O into tared 125ml plastic storage bottles, rinsing watch glass and beaker
- Digests were diluted gravimetrically with DI H_2O (volumes were ~70-80ml)

MOX Fission Products Scan

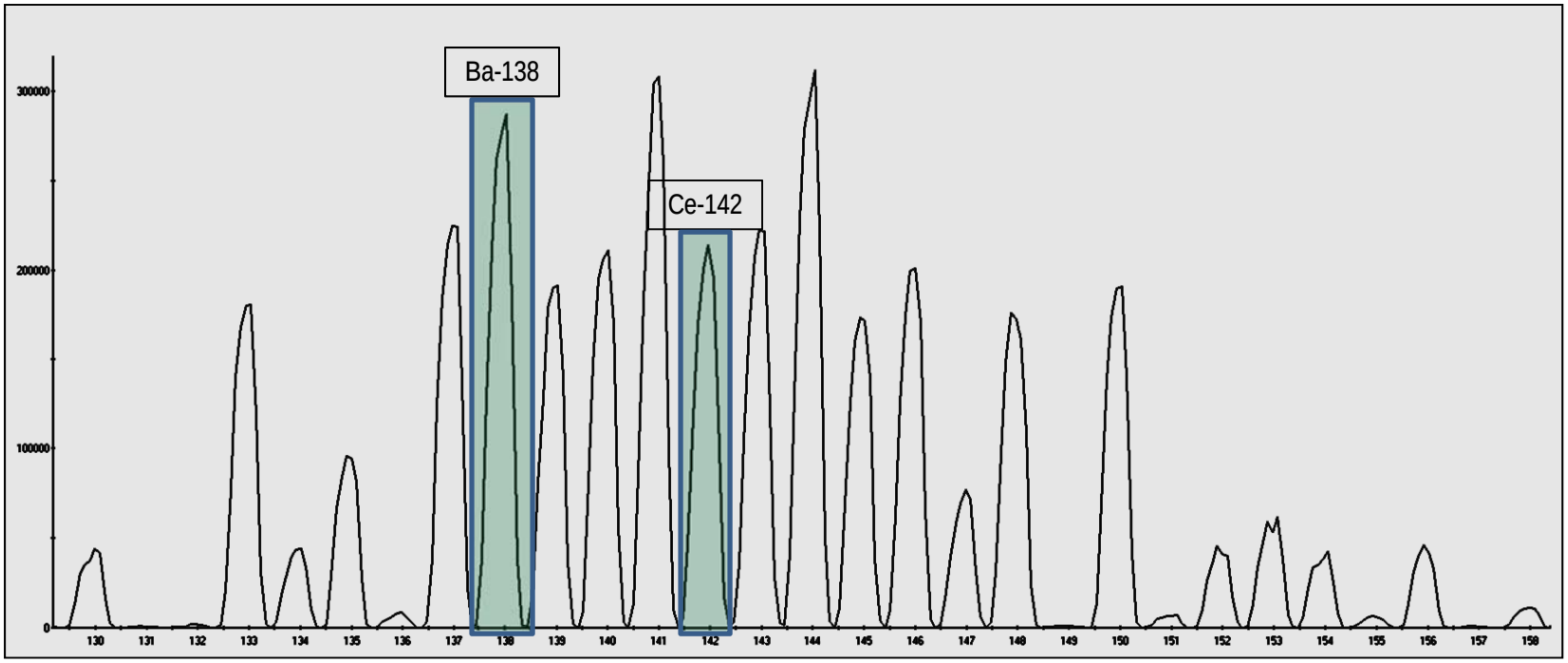
Low Mass

High Mass
(Ba, Cs, and Lanthanides)



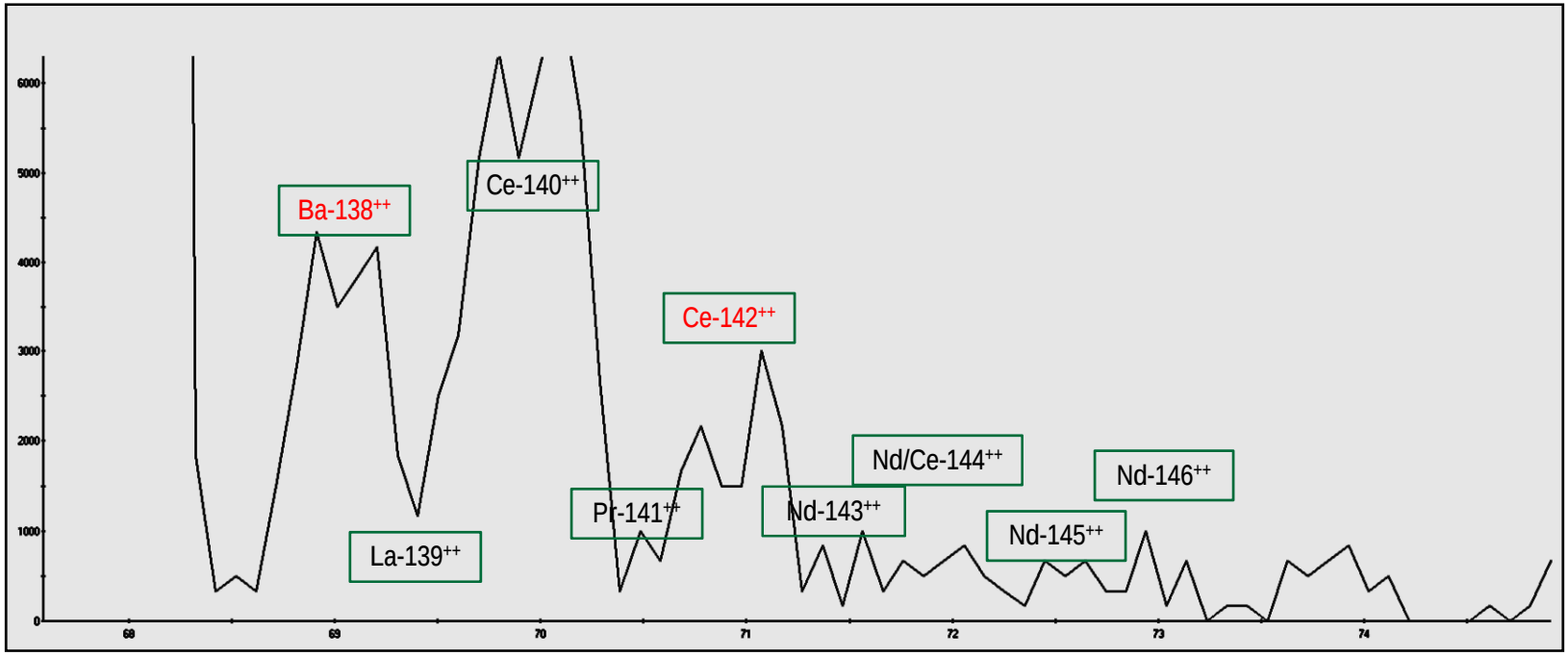
Mass 69 and 71 Interferences

- Ba-138^{++} and Ce-142^{++} species interfere at masses 69 and 71.
- Fission products impregnate into clad during irradiation and are not removed by a leach with nitric acid.

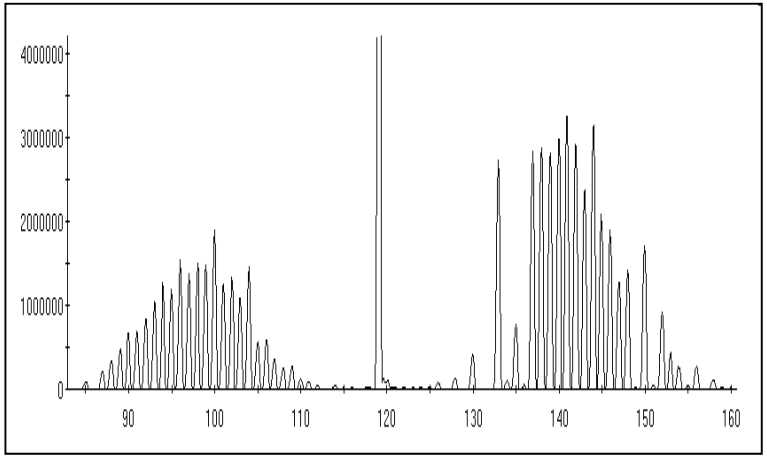


Mass 69 and 71 Interferences (MOX fuel scan)

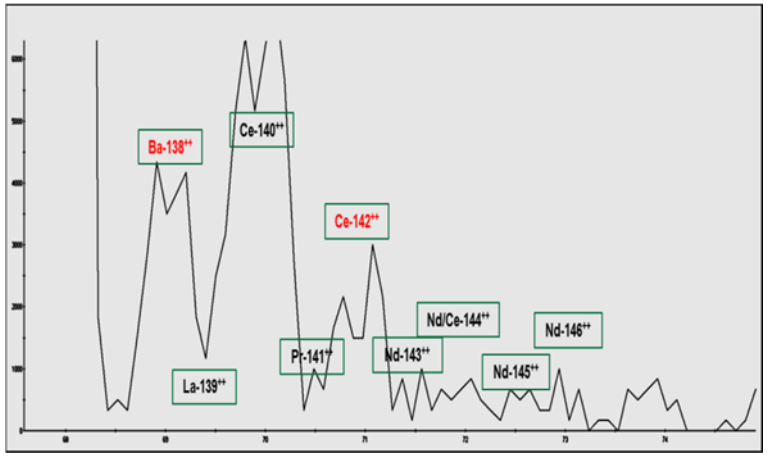
- Doubly charged isobaric interferences from high mass fission products
- Spent fuel and Zircaloy specimens



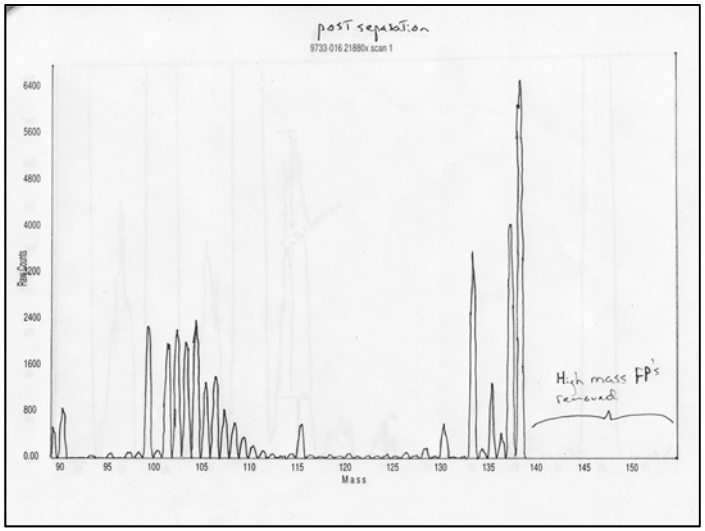
Separations Overview

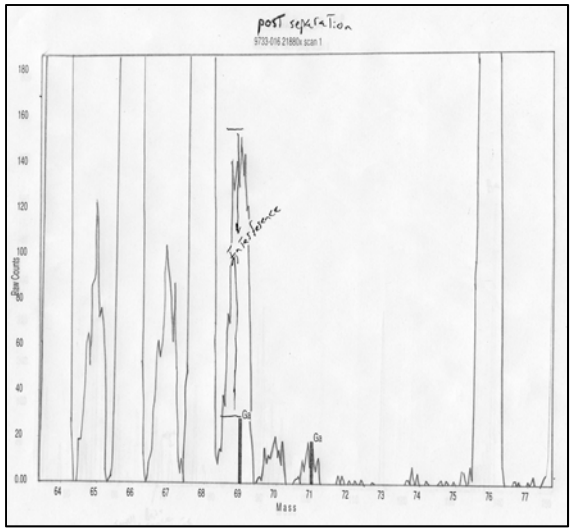


Neat sample

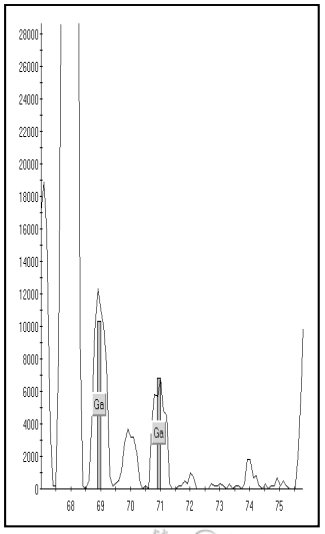


TRU Resin



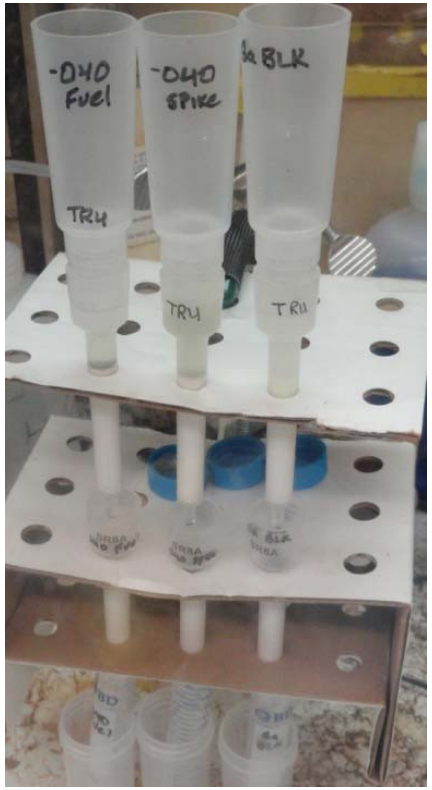


Sr Resin



MOX Gallium Separations (stacked columns)

- Gallium Separation Scheme*
  - Condition columns with 4M HNO_3
  - Matrix adjustment to 4M HNO_3 on a 2mL aliquot of the 5/105 working solution
  - Load matrix adjusted sample aliquot
  - Elute Ga^{+3} using 7mL 4M HNO_3
  - Dilute to a final volume of 10mL (5-fold dilution + hotcell prep)
- Additional 5-fold dilution performed at ICPMS for a total of 25-fold + hotcell prep dilutions



* High levels of Zr in clad digestions interfered with column chemistry resulting in inadequate removal of high mass fission products and Ba. Thenoyltrifluoroacetone (TTA) extraction performed on matrix adjusted aliquots prior to column loading dramatically reduced the Zr^{+4} concentrations allowing for successful purification of the samples.

MOX Gallium Analysis Summary

- Detailed chemical purification and optimization of the ICPMS instrument combined to achieve gallium detection limits as low as possible
  - Isotopes 69 and 71 detection levels on the ICPMS were typically within 10X of the instrument's detection limit of 0.0002 ng Ga / mL fuel/cladding digest
  - Low calibration standard of 12 ppt Ga-69
  - Calibration verification at 3 ppt recovered at ~85% for all of the ICPMS runs
- Removal of high concentrations of dissolved solids in the digested solutions allowed for minimal total dilution of the sample for low method detection limits

MOX Gallium Analysis Summary (cont'd.)

- Ba is not 100% removed using the Sr Resin, but it is decreased to a level in the fuel preps that is a manageable interferent.
  - A small manual correction was applied to the data for mass 69 using a Ba standard of similar concentration that were seen in the analyzed aliquots
- Recoveries of chemical separations consisting of a matrix spike and laboratory control samples were greater than 90%.
- Total relative 2-sigma uncertainty estimate of +/- 30% was assigned to the reported results.

Conclusions

- With Eichrom resins, purified concentrated aliquots of gallium in spent nuclear fuels and irradiated Zircaloy could be accurately analyzed by ICPMS.
  - High levels of fission products Ba-138 and Ce-142 create isobaric interferences at gallium isotope masses 69 and 71 and were successfully removed to achieve interference free detection of the trace gallium isotopes.
  - High zirconium matrix issues eliminated using TTA prior to column separation.
- Achieved project required detection levels of <10 ppb concentrations for gallium isotopes 69 and 71 in highly radioactive cladding and spent MOX fuel (MDL established at <5 ppb).
- ORNL successfully developed and validated a trace level gallium methodology for irradiated Zircaloy and spent nuclear fuels for the qualification of MOX fuel in the United States.
- *AREVA Summary Report on Postirradiation Examinations of MOX Fuels* submitted to the Nuclear Regulatory Commission in February 2012.

Acknowledgements

- DOE-Fissile Material Disposition Program Office (FMDP)
- AREVA Inc.