Savannah River
Nuclear Solutions, LLC
A Fluor Daniel Partnership

# Comparison of Routine Bioassay & Emergency Methods

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# The Age of Limited Resources & High Expectations

- Fewer Personnel to do the work
- Reduced work week (?)
- Flat or decreasing funding
- Need for quicker turn around
- Need for High Data Quality
- Need to be competitive with outside organizations
- Faster, better, cheaper…..can you do all three?

# Limitations & Needs

- Staffing
  - Reduced from 10 to 5 Lab Technicians
  - Day shift operations only M-Th (F); 4x10's
- Sample Load
  - 2500 to 3000 Actinide samples annually
    - 10,000 Actinide determinations annually
  - (6000+ tritium determinations annually)
- Cost Reduction
  - Budget flat (or worse)
  - Cost Ratio, downward pressure
- Incident Samples
  - Need for rapid screening

# Routine Bioassay Method vs. Emergency Method

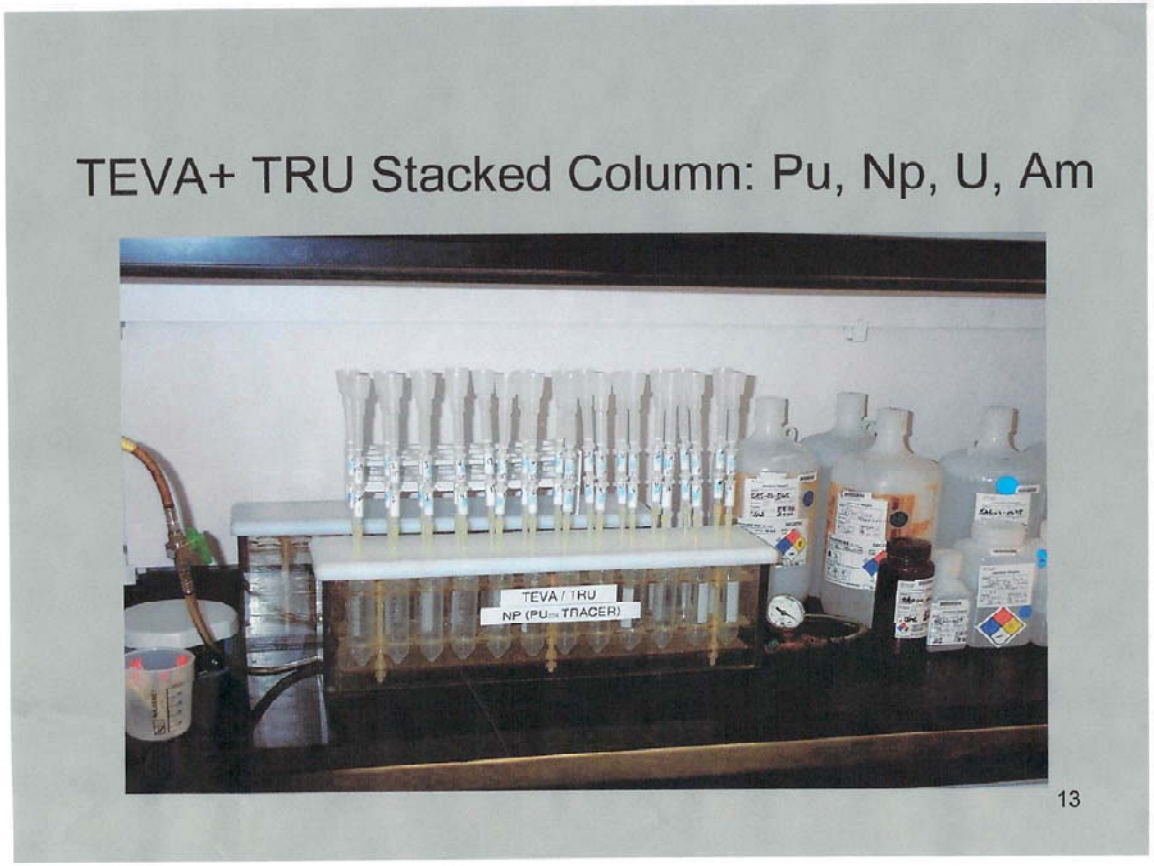
- Faster turnaround time
  - Routine samples: 14 days minimum (once batched)
  - Emergency samples: < 8 hours
- Quality – methods must
  - Have effective removal of interferences
  - Have consistent tracer/carrier recoveries
  - Be robust and reproducible
  - Meet Data Quality Objectives
- Reduce Cost
  - Lower labor cost

# Routine Bioassay Method

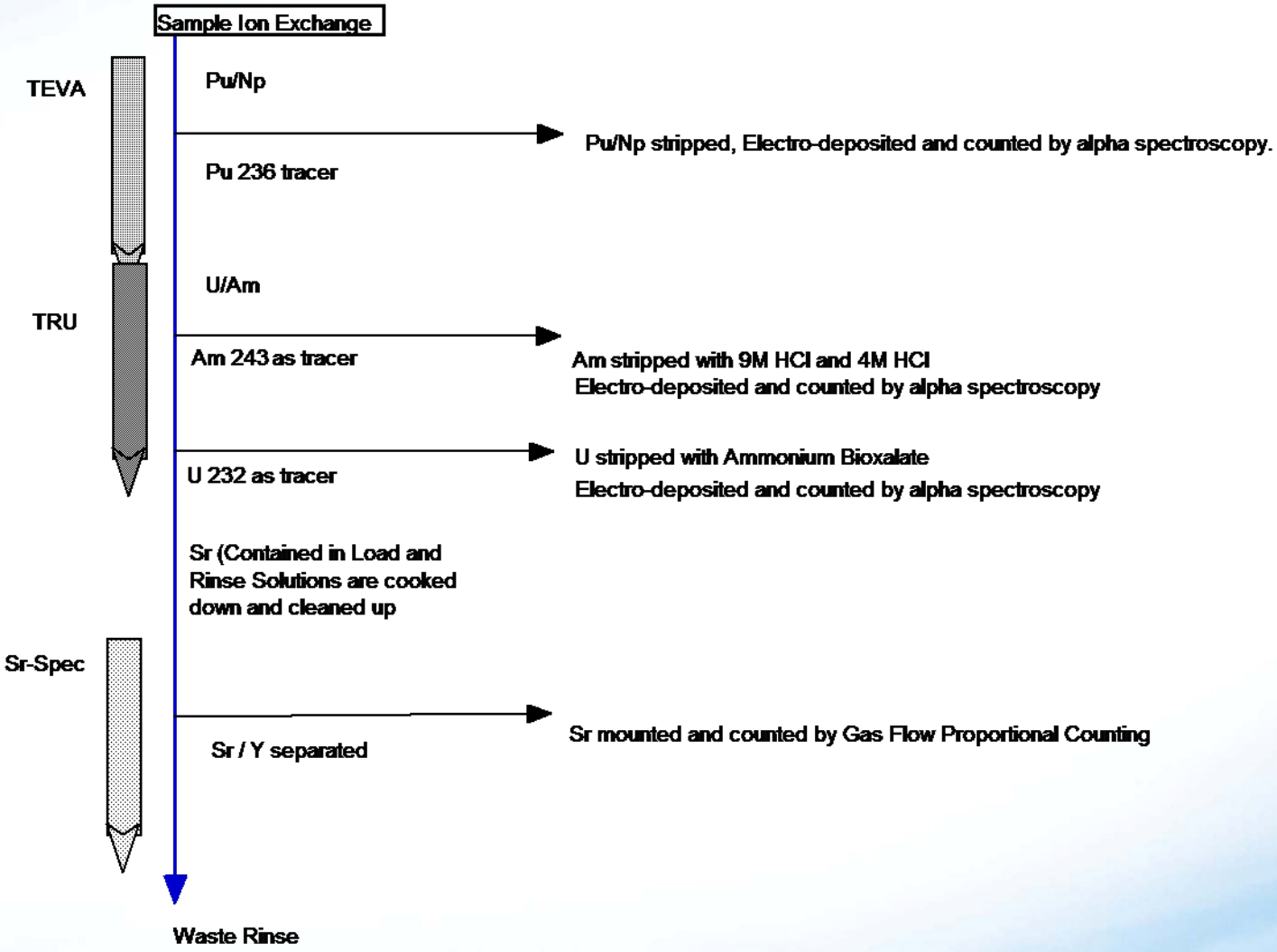
- Acidification (10% v/v con HNO3) – 2 hrs
- Precipitation (Calcium Phosphate) – 8 to 16 hrs
- Clean-Up (w/ HNO3 and H2O2) – 8 hrs
- Column Extraction (TEVA TRU Stacked Column) – 8 to 10 hrs
- Clean-Up (w/ HNO3 and H2O2) – 8 to 12 hrs
- Electrodeposition – 6 hrs
- Alpha Spectroscopy – 22 to 44 hrs

- In other words – a LONG time = $$$$

# Routine Bioassay Method – Column Extraction



# Routine Bioassay Sample Process



# Emergency Method Actinides and Sr-89/90 in Urine

- TEVA/TRU/Sr Resin –triple stacked cartridges
  - One sample preparation
  - Pu, Np, U, Am, Sr, Th
  - Vacuum box flow rates increased
- Calcium phosphate ppt.
  - Sample aliquot directly in centrifuge tube- for smaller volumes
  - No heat


"Maxwell III, SL, "Rapid Column Separation for Actinides and Sr-89/90 in Water Samples", Journal of Radioanalytical and Nuclear Chemistry, Vol. 267, No. 3, p 537"

Maxwell, S.L, "Rapid Analysis of Emergency Urine and Water Samples", J. Radioanal. Nucl.Chem., 275 (3), (2008)

# Emergency Method Urine Samples

| | NRIP 2006 | NRIP 2007 | NRIP 2008 |
|---|---|---|---|
| • Am-241 | 7.4 hrs | 4.6 hrs | 3.1 hrs |
| • Pu-238, 239 | 7.4 hrs | 4.8 hrs | 3.3 hrs |
| • U-234, 235, 238 | 7.4 hrs | 5.2 hrs | 4.2 hrs |
| • Strontium-90 | 5.8 hrs | 3.9 hrs | 2.9 hrs |

# Differences: Urine methods

- Routine TEVA + TRU method (1998)
  - No water rinse of calcium phosphate/flat bottom centrifuge tubes/ long ashing times of residual urine
  - Sr collected, evaporated, redissolved- loaded onto Sr Resin
  - Pu stripped from TEVA with 0.1M HCL-0.05M HF-0.04M rongalite
  - Electrodeposition
- Emergency TEVA + TRU + Sr resin (2005)
  - Conical centrifuge tubes/ water rinse/ minimal ashing time (NRIP-08 no rinse/no ash)
  - Sr collected during load
  - Additional rinsing of TRU resin using 4M HCl-0.2M HF to remove any residual Th
  - Pu stripped from TEVA with 0.1M HCL-0.05M HF-0.03M titanium chloride
  - Cerium fluoride microprecipitation

# Differences: Fecal methods

- Routine Diphonix plus TEVA + TRU method (1999)
  - Diphonix used to collect actinides/Sr passes through
  - HEDPA used to strip actinides from Diphonix/destroy HEDPA
  - Sr collected, evaporated, redissolved- loaded onto Sr Resin
  - Pu stripped from TEVA with 0.1M HCL-0.05M HF-0.04M rongalite
  - Load plus rinse collected from TEVA, reduction/ loaded to TRU Resin
  - Electrodeposition
- Emergency TEVA + TRU + Sr resin (2007)
  - Adapted from soil method
  - Cerium fluoride matrix removal instead of Diphonix/Ca added to precipitate Sr (faster)
  - Stacked TEVA + TRU + DGA
  - Additional rinsing of TRU resin using 4M HCl-0.2M HF to remove any residual Th
  - Pu stripped from TEVA with 0.1M HCL-0.05M HF-0.03M titanium chloride
  - Cerium fluoride microprecipitation

# Comparison of Methods Using DOELAP

- Triennial Performance Demonstration
  - Synthetic Urine and Fecal Blinds
  - 45 Day reporting deadline
- On-Site Audit of Program
  - In-depth QA/QC assessment
- Deficiencies must be corrected to maintain certification
- Any program changes must be pre-approved
- Emergency Method used to cross-check Bioassay
  - Prove applicability to Bioassay samples

# DOELAP SESSION 11

- Performance Demonstration
  - Synthetic Urine and Fecal Blinds
  - 45 Day reporting deadline
- February – March 2008
- Synthetic Urine and Fecal Samples
- Target Isotopes:
- On-Site Audit of Program
  - In-depth QA/QC assessment
- Focus – Alpha Emitters & Sr-90 in Urine/Fecal, cross-check of Bioassay Analysis Results vs. Emergency Analysis

| | Isotope | Urine | Fecal |
|---|---|---|---|
| β/γ | H-3 | X | |
| | Sr-90 | X | X |
| | Cs-137 | X | |
| | Co-60 | X | |
| α | Am241 | X | X |
| | U238 | X | X |
| | U234/235 | X | X |
| | Pu238 | X | X |
| | Pu239/240 | X | X |
| | Th228/230 | X | |
| | Th-232 | X | |
| | Np-237 | X | X |

# Comparison of Results - Urine

**DOELAP SESSION 11**

**URINE**

| Analyte | BIO Avg | %RSD | NRIP AVG | NRIP %RSD | DOELAP | BIO %D | NRIP %D |
|---|---|---|---|---|---|---|---|
| Am-241 | 2.02 | 7.80 | 2.00 | 4.8 | 2.13 | -5.20 | -5.89 |
| Np-237 | 1.95 | 10.11 | 2.02 | 11.0 | 1.953 | -0.02 | 3.23 |
| Pu-238 | 3.99 | 6.21 | 4.34 | 6.1 | 3.9 | 2.26 | 11.27 |
| Pu-239 | 3.25 | 4.79 | 3.16 | 7.5 | 3.21 | 1.37 | -1.62 |
| U-234 | 5.00 | 4.84 | 5.31 | 0.4 | 5.66 | -11.66 | -6.12 |
| U-238 | 4.91 | 5.51 | 5.08 | 9.7 | 5.88 | -16.58 | -13.56 |
| Th-228 | 4.12 | 3.22 | 4.42 | 11.3 | 4.32 | -4.72 | 2.38 |
| Th-230 | 2.32 | 0.80 | 2.92 | 11.3 | 2.28 | 1.82 | 27.93 |
| Th-232 | 3.98 | 2.92 | 4.37 | 6.5 | 4.32 | -7.79 | 1.05 |
| Sr-90 | 287.2 | 5.6 | 287.1 | 6.2 | 293 | -1.97 | -2.01 |

Results in pCi/L

# Comparison of Results - Fecal

**DOELAP SESSION 11**

**FECAL**

| Analyte | BIO Avg | %RSD | NRIP AVG | NRIP %RSD | DOELAP | BIO %D | NRIP %D |
|---|---|---|---|---|---|---|---|
| Am-241 | 2.44 | 3.73 | 2.52 | | 2.59 | -5.62 | -2.78 |
| Np-237 | 3.55 | 5.97 | 3.83 | | 3.91 | -9.24 | -2.08 |
| Pu-238 | 4.94 | 7.62 | 4.75 | | 4.74 | 4.13 | 0.26 |
| Pu-239 | 3.89 | 5.96 | 3.90 | | 3.9 | -0.22 | 0.02 |
| U-234 | 6.11 | 1.83 | 5.38 | | 6.88 | -11.17 | -21.77 |
| U-238 | 5.98 | 3.72 | 5.63 | | 7.14 | -16.27 | -21.09 |
| Sr-90 | 339.8 | 6.2 | 318.3 | 9.26 | 355 | -4.28 | -10.34 |

Results in pCi/Sample

# ISSUES

- Negative Bias on Uranium Results
- Insufficient removal of Po-210 from TRU Resin
- Po-210 interference ($\alpha$ energy of Po-210 & U-232 tracer un-resolvable)
  - Po-210: 5304 kev (~100%)
  - U-232: 5320 kev (68%)
- Gives “high” U232 tracer recovery = negative bias on U-234/238 results
- Commonly seen in Soils analysis
  - High levels of Natural U and Th is soil samples
  - Not expected on low-level samples typical of routine Bioassay
  - Present in DOELAP samples due to high Natural U and Th
- Additional rinsing can eliminate excess Po-210
  - 8M HNO3 rinse on TRU resin
  - Low [Ti+2] rinse to reduce Po to [+2]

# Summary

- Improve Efficiency of Routine Bioassay Method
  - Adopting CeF3 for screening incident samples
  - Methods for emergency urine analysis can be applied to routine Bioassay methods
- Both speed and quality are achievable
  - Both meet DOELAP data acceptance criteria
- Adapting rapid techniques to improve turnaround time, lower cost, without significant impact to quality of data