

# Rapid Analytical Methods for Determination of Actinides

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# Challenges of Actinide Analysis

- Actinides are considered most hazardous radionuclides due to their high radiological and chemical toxicities, and long radioactive half-lives.
- Use of nuclear fission in energy generation and weapon testing have led to global spread of both natural and artificial actinides in the environment at ultra - trace levels.
- Rapid, accurate and sensitive determination of actinides in biological, environmental, and geological materials poses a significant challenge due to their extremely low concentrations in diverse sample matrices.

# Demands for Rapid Actinide Methods

- Actinides of interest:
  - Major actinides: U, Th, Pu
  - Minor actinides: Am, Cm, Np etc
- Sample types:
  - Biological samples: urine, feces, blood, tissue etc
  - Environmental samples: soil, sediment, water, swipe, air filter etc
- Emergency needs:
  - Fast turn-around analysis time: within 1 day
  - Rapid procedure: simple & effective, batch or automated processing
- Benefits from rapid methods:
  - Time/cost saving
  - High sample analysis throughput
  - More environment friendly: e.g., acid saving, less waste

# Selection of Actinide Methods

- Sample matrix and size
- Analytes of interest and their concentrations
- Time and cost of analysis
- Equipment availability
- Skill and training of the analyst

# Composition of Rapid Actinide Methods

- Appropriate radiotracer for chemical recovery monitoring
- Complete sample destruction: fusion, ashing, acid/microwave digestion
- Rapid and selective preconcentration and separation: co-precipitation, ion exchange, extraction chromatography, solvent extraction etc
- Sensitive and fast detection: ICP-MS, TIMS, alpha spectrometry, PERALS etc
- Automated separation and analysis: FI-ICP-MS

# Addition of Tracers

Element	Isotope	Detection Technique	Tracer	Comments
U	$^{238}\text{U}$ , $^{235}\text{U}$	ICP-MS, TIMS; $\alpha$ specs	$^{236}\text{U}$ ; $^{232}\text{U}$	$^{228}\text{Th}$ separation
	$^{234}\text{U}$ , $^{233}\text{U}$	$\alpha$ specs; TIMS, ICP-MS	$^{232}\text{U}$ ; $^{236}\text{U}$	$^{228}\text{Th}$ separation
Th	$^{232}\text{Th}$	ICP-MS	$^{230}\text{Th}$	
	$^{228}\text{Th}$	$\alpha$ specs	$^{230}\text{Th}$	
Pu	$^{239/240}\text{Pu}$	TIMS, ICP-MS; $\alpha$ specs	$^{242}\text{Pu}$ , $^{244}\text{Pu}$ ; $^{242}\text{Pu}$ , $^{236}\text{Pu}$	
	$^{238}\text{Pu}$	$\alpha$ specs	$^{242}\text{Pu}$ , $^{236}\text{Pu}$	
Am/Cm	$^{241}\text{Am}$ , $^{244}\text{Cm}$ , $^{242}\text{Cm}$	$\alpha$ specs	$^{243}\text{Am}$	$^{239}\text{Pu}$ daughter
Np	$^{237}\text{Np}$	ICP-MS; $\alpha$ specs	$^{236}\text{Np}$ ?; $^{239}\text{Np}$ ?	Availability? Short-lived $\gamma$ emitter

# Sample Decomposition: Fusion

- **Primarily used for decomposition of solid samples: rock, soil, sediment, fecal ash etc**
- **Different sample matrices require a careful selection of flux reagent**
  - Metaborates/tetraborates
  - NaOH/Na<sub>2</sub>O<sub>2</sub>
  - Pyrosulfates/hydrosulfates/bisulfates
  - Others: fluorides etc
- **Advantages:**
  - Complete sample dissolution
  - Ensure homogeneity between tracer and analytes
  - Rapid and vigorous
- **Disadvantages:**
  - High total dissolved salts
  - Contamination of Th and U due to impurities in the flux

# Sample Decomposition:

## Acid digestion

- **Selection of acids depend on chemical properties of the sample matrix and the element to be determined**
  - Typical acids for actinides:  $\text{HNO}_3$  and  $\text{HCl}$
  - Addition of  $\text{HF}$  for silicates: removal of  $\text{HF}$  after sample dissolution to avoid formation of insoluble actinide fluorides
  - Addition of  $\text{H}_2\text{O}_2$ : to oxidize organic materials
  - Microwave digestion: rapid, programmability for untended operation
- **Advantages**
  - Low total dissolved salts
  - Availability of ultra-pure acids
- **Disadvantages**
  - Incomplete dissolution of sample
  - Time consuming for conventional acid digestion



# Rapid Preconcentration and Separation: Co-precipitation and solvent extraction

- **Co-precipitation:**

- Rapid preconcentration of actinides from a large solution volume: water or urine
- Often used for separation of actinides from sample matrix after fusion/acid decomposition
- Anions used for actinide co-precipitation:
  - Phosphates: calcium or bismuth phosphates
  - Fluorides: rare earth or calcium fluorides
  - Hydroxides:  $\text{Fe}(\text{OH})_3$ ,  $\text{MnO}_2$ , Hydrous Titanium Oxide (HTiO)

- **Solvent extraction:**

- A wide range of organic extractants have been used for actinides separation: ketones, ethers, esters, and phosphoric acid derivatives
- It is being replaced due to waste disposal and safety issues on use of toxic/flammable organic solvents

# Rapid Preconcentration and Separation: Ion exchange and extraction chromatography

- **Anion exchange:**
  - Bio-Rad or Dowex anion resins
  - TEVA
- **Extraction Chromatography:**
  - UTEVA
  - TRU
  - DGA
  - Actinide resin
- Many rapid actinide separation methods have been developed by combining anion exchange with extraction chromatography.
- Development of sequential column separation and use of vacuum box for column extraction can significantly increase sample analysis throughput.

# Sensitive Actinide Detection Techniques:

## Alpha spectrometry

- Detection of alpha particles with specific energies allows isotopic discrimination for most actinides, if sensitivity and precision is not critical.
- Prior to alpha spectrometric analysis, chemical separation and preparation of a thin-layer source are usually required.
- **Advantages**
  - High sensitivity for short-lived ( $<10^4$  years of half-life) actinides:  $^{241}\text{Am}$ ,  $^{243/244}\text{Cm}$ ,  $^{238}\text{Pu}$ ,  $^{228}\text{Th}$ ,  $^{233/234}\text{U}$  etc
  - Reasonably simple and straightforward quantitative spectral analysis
  - Affordable: low instrument and maintenance cost
- **Disadvantages**
  - Preparation of a thin-layer source required
  - Very long counting time may be required to achieve the highest sensitivity

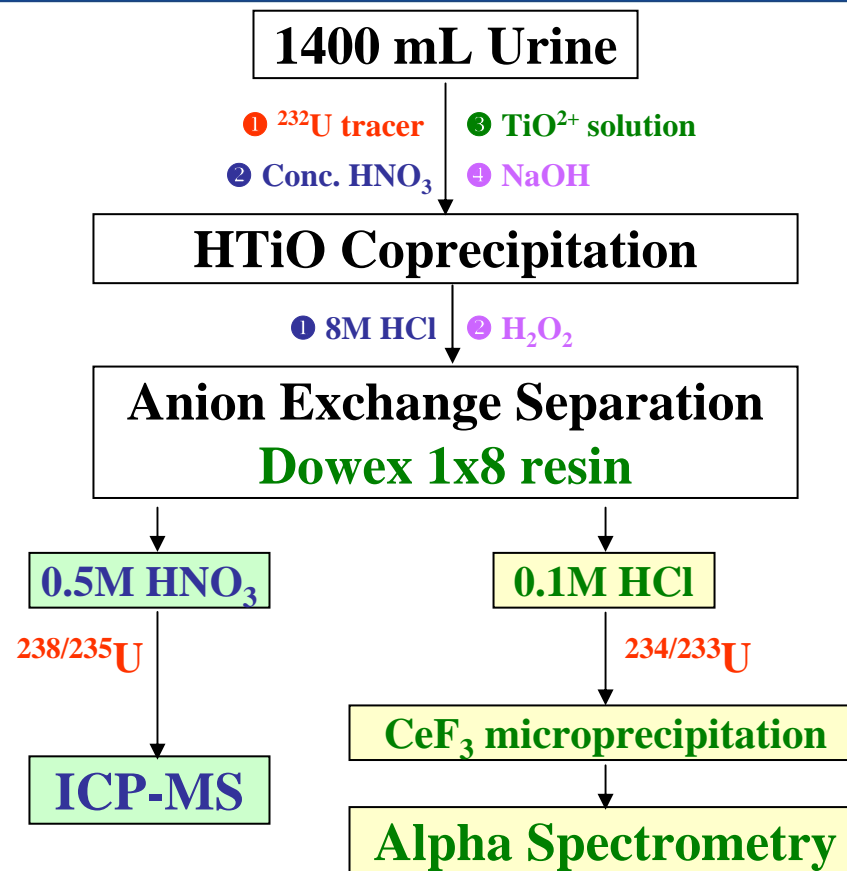
# Sensitive Actinide Detection Techniques: TIMS

- Thermal ionization sources produce an extremely stable, relatively intense supply of ions with a minimal energy spread, and minimal molecular and atomic interferences
  - **Advantages**
    - Extremely sensitive to long-lived actinides: Pu and U isotopes at femto-gram level
    - High precision isotopic ratio measurement at a very low concentration
  - **Disadvantages**
    - Extensive sample filament preparation
    - Complexity of the instrumentation
    - Expensive
- Prevents its adaptation as routine high-throughput analysis.

# Sensitive Actinide Detection Techniques: ICP-MS

- Direct analysis of actinides can be performed without any chemical separation.
- Sensitivity and precision of MC-ICP-MS and HR-ICP-MS could be comparable to TIMS.
- **Advantages**
  - Very high sensitivity for long-lived ( $>10^4$  years of half-life) actinides
  - High sample throughput
  - Multi-element analysis capability
  - Possible automation: FI-ICP-MS
- **Disadvantages**
  - Expensive instrumentation and maintenance cost

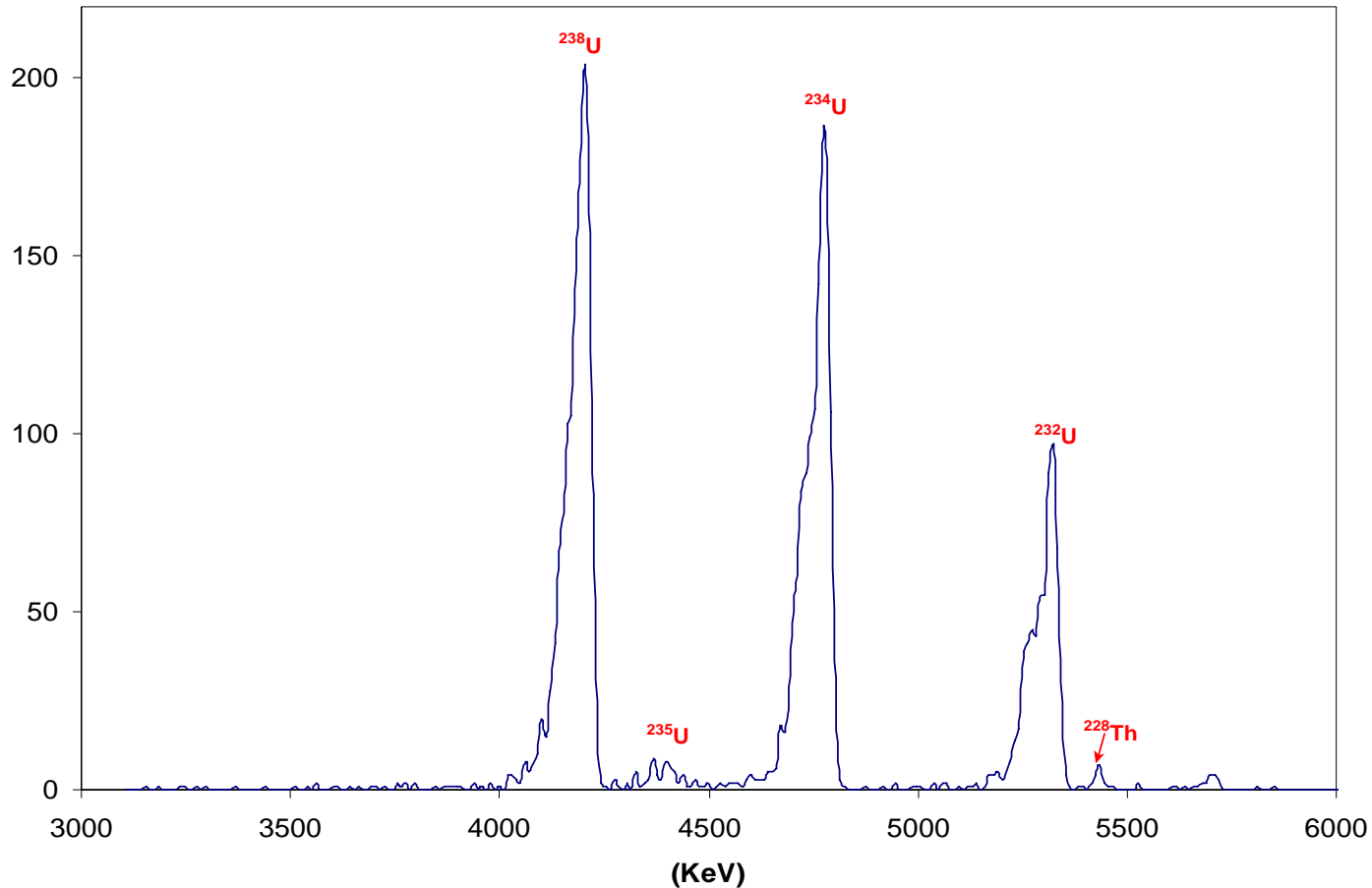
# Rapid Actinide Bioassay Methods at AECL: *Uranium urinalysis*



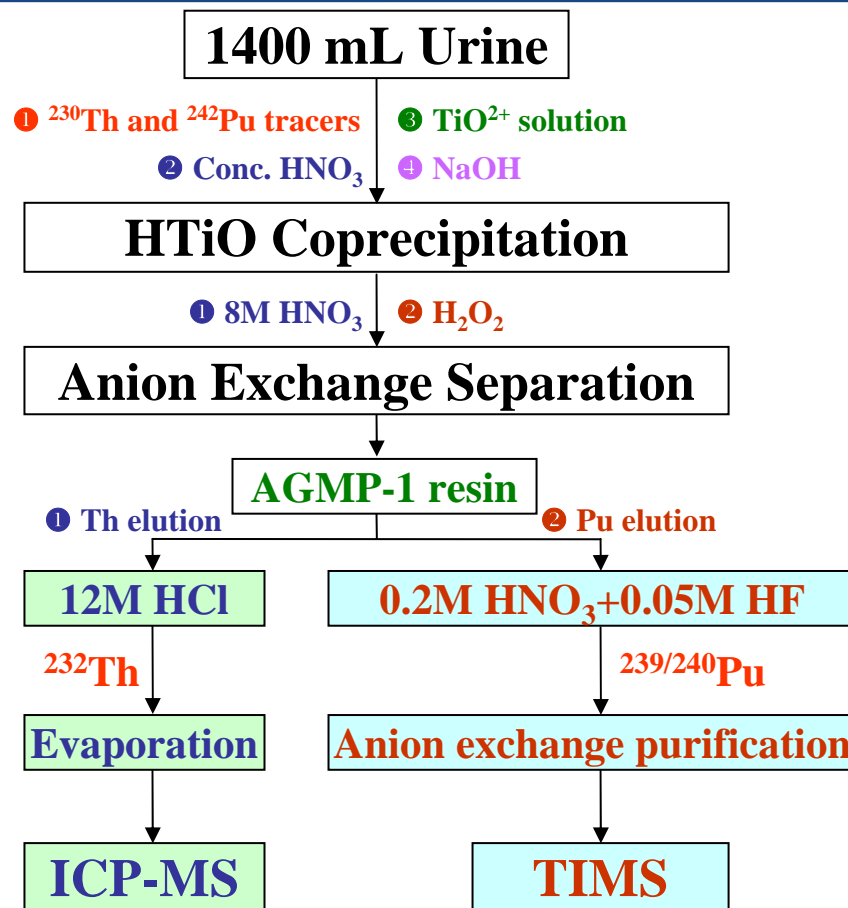
- Sample processing time: ~ 4 hours
- Alpha counting time: 48 hours
- MDA for  $^{234}\text{U}$  by alpha spec: ~0.3 mBq/L in urine
- Typical chemical recovery: ~75%

# Rapid Actinide Bioassay Methods at AECL: *Uranium urinalysis*

Alpha spectrum of U isotopes in a urine spike test sample



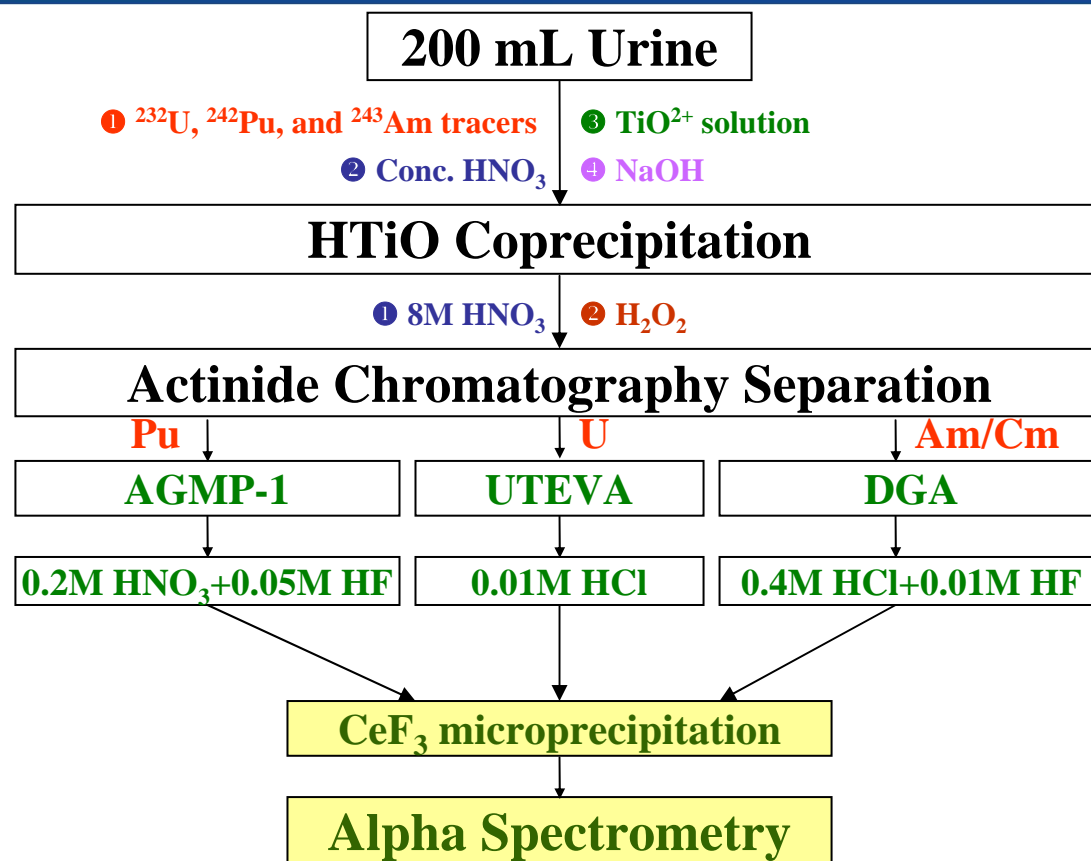
# Rapid Actinide Bioassay Methods at AECL: *Th and Pu urinalysis*



- Sample processing time: ~ 4 hours for Th and 10 hours for Pu
- Detection limit: < 0.5 ng/L for  $^{232}\text{Th}$  and < 5 fg/L for  $^{239/240}\text{Pu}$
- Typical chemical recovery: ~60% for Th and ~70% for Pu



# Rapid Actinide Bioassay Methods at AECL: Emergency *actinide urinalysis*



- Sample processing time: ~ 4 hours
- MDA: <5 mBq/L with 4 hours of counting
- Typical chemical recovery: ~75% for Pu, and ~80% for U and Am/Cm

# Summary

- **Development of rapid, sensitive and accurate analytical methods of actinides in biological and environmental samples represents a challenge to radioanalytical chemist.**
- **The state-of-the-art techniques for rapid actinide separation and determination are reviewed.**
- **New rapid and sensitive actinide urine bioassay methods have been recently developed at the Chalk River Laboratories, AECL.**

Thank You!

 AECL EACL

