Identification of Origin of Actinides in Environmental Samples with Radioanalytical Technologies

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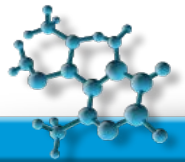


Outlines

1. Introduction, definitions: Nuclear forensics related with environmental radioanalytical chemistry
2. Analytical methods: Radiometric method, Mass Spec. method
3. Test cases (Fallout site, Nuclear fuel facilities, Weapon missile site) : Determination of Pu and U isotopes ratios in environmental samples
4. Summary

Nuclear terrorism ; illicit trafficking of nuclear materials

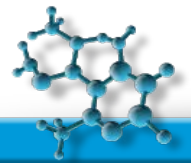
Alexander Litvinenko was a former officer of the Russian Federal Security Service, FSB and KGB, who escaped prosecution in Russia and received political asylum in the United Kingdom. He authored two books, "Blowing up Russia: Terror from within" and "Lubyanka Criminal Group", where he accused the Russian secret services of staging Russian apartment bombings and other terrorism acts to bring Vladimir Putin to power.

On 1 November 2006, Litvinenko suddenly fell ill and was hospitalized. He died three weeks later, becoming the first confirmed victim of lethal polonium-210-induced acute radiation syndrome. According to doctors, "Litvinenko's murder represents an ominous landmark: the beginning of an era of nuclear terrorism".

Litvinenko's allegations about the misdeeds of the Federal Security Service of Russia (FSB) and his public deathbed accusations that Russian president Vladimir Putin was behind his unusual malady resulted in worldwide media coverage (From TELEGRAPH, UK)

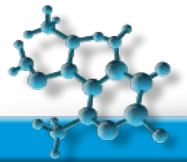
What is Nuclear Forensics?

- **Technical means by which unknown nuclear materials are characterized and interpreted**
- **Characterization relies on radioanalytical and materials science techniques**
- **Interpretation requires an understanding of relevant nuclear and chemical processes**
- **Both chemical signatures and isotopic signatures provide useful clues**
- **Nuclear forensics is similar to environmental radiochemistry**
  - ✓***Natural geochemical cycles***
  - ✓***Contaminant fate & transport***

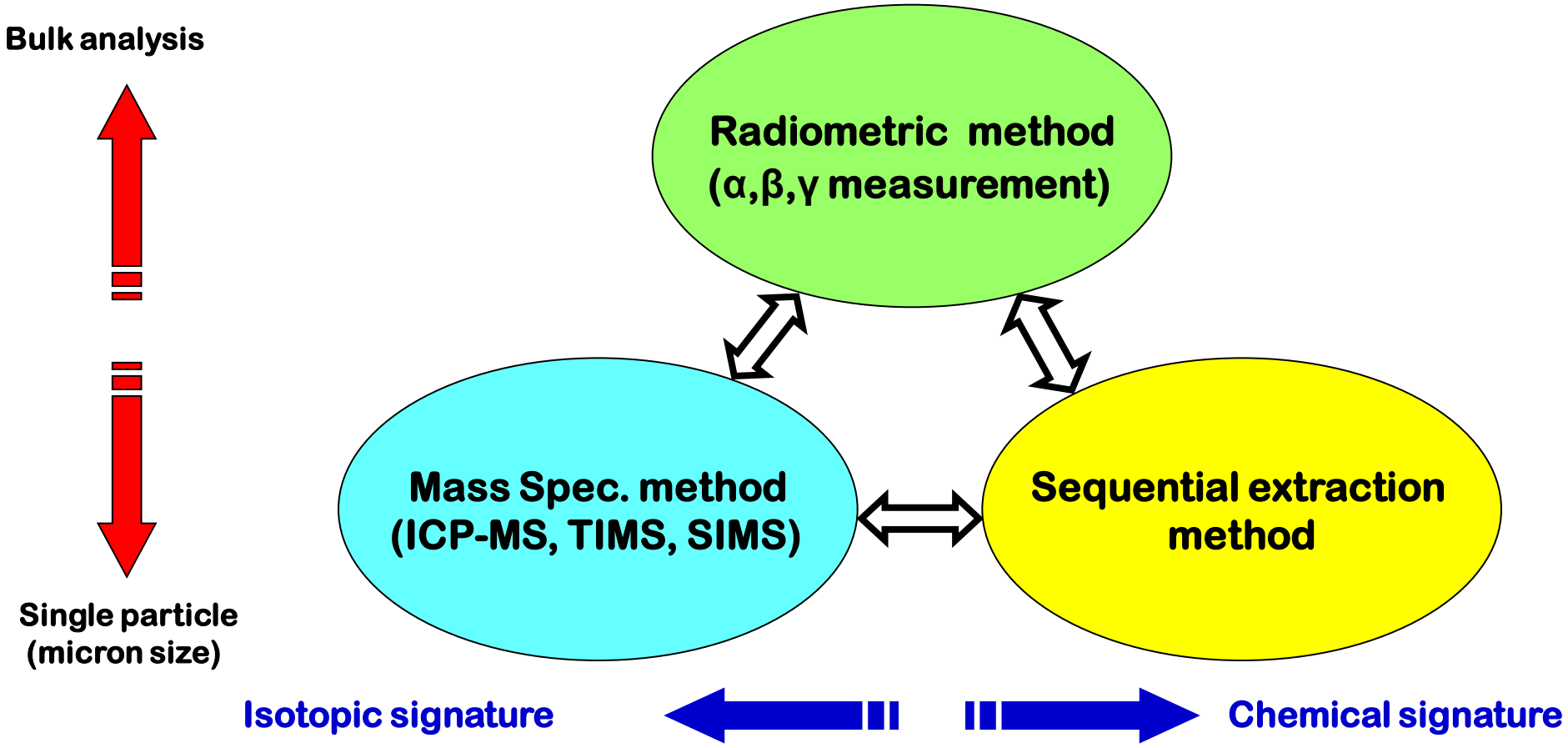


Environmental Radiochemistry vs. Nuclear Forensics: Similar approaches, different questions

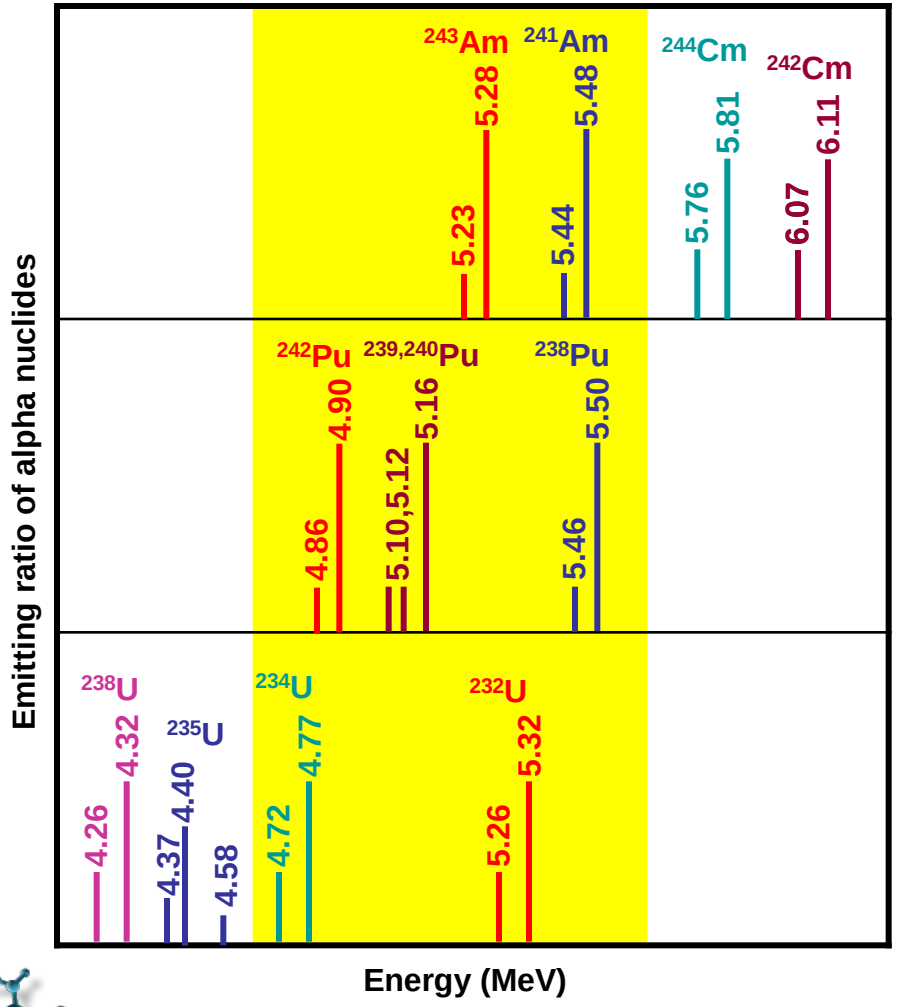
- *From environmental radiochemistry*
  - **Natural vs. anthropogenic radioactivity?**
  - **What is the source of the contamination?**
  - **What is the best approach for remediation?**
- *From nuclear forensics*
  - **What part of the nuclear fuel cycle does the signature represent?**
  - **How old is the unknown material?**
  - **What is the origin of the material?**



Analytical techniques for nuclear fingerprinting



Physical properties for alpha emitting nuclides



Nuclide	Type	Energy	Half-life	
^{239}Pu	α	5.15 MeV	24,390 y	Undiscriminating by alpha spectrometry
^{240}Pu	α	5.17 MeV	6,580 y	
^{238}Pu	α	5.49 MeV	86.4 y	Interference by ^{238}U
^{241}Pu	β	21 keV	14.4 y	Decay to ^{241}Am
^{241}Am	α	5.49 MeV	458 y	
^{244}Cm	α	5.81 MeV	18.9 y	
^{242}Cm	α	6.11 MeV	163 d	
^{235}U	α	4.40 MeV	7.1E+8 y	Nuclear fuel (1-90%)
^{238}U	α	4.32 MeV	4.5E+9 y	
^{234}U	α	4.77 MeV	2.5E+5 y	

Request on radioanalytical methods for nuclear forensic

Request on radiochemical analysis for identifying origin of unknown nuclear material

Reliable
(repeatability, accuracy)

- independent of variation in matrices
- concentration of nuclides

Fast
(Analytical time)

- numerous samples
- accidental

Cheap
(Analytical cost)

- numerous samples

Determination procedure for actinides in environmental samples

Sample pretreatment

- *Ashing sample (500 ºC, 8-10 h)*
- *Muffle furnace*

-Volume reduction
-Organics removal

Acid treatment

Radiochemical separation

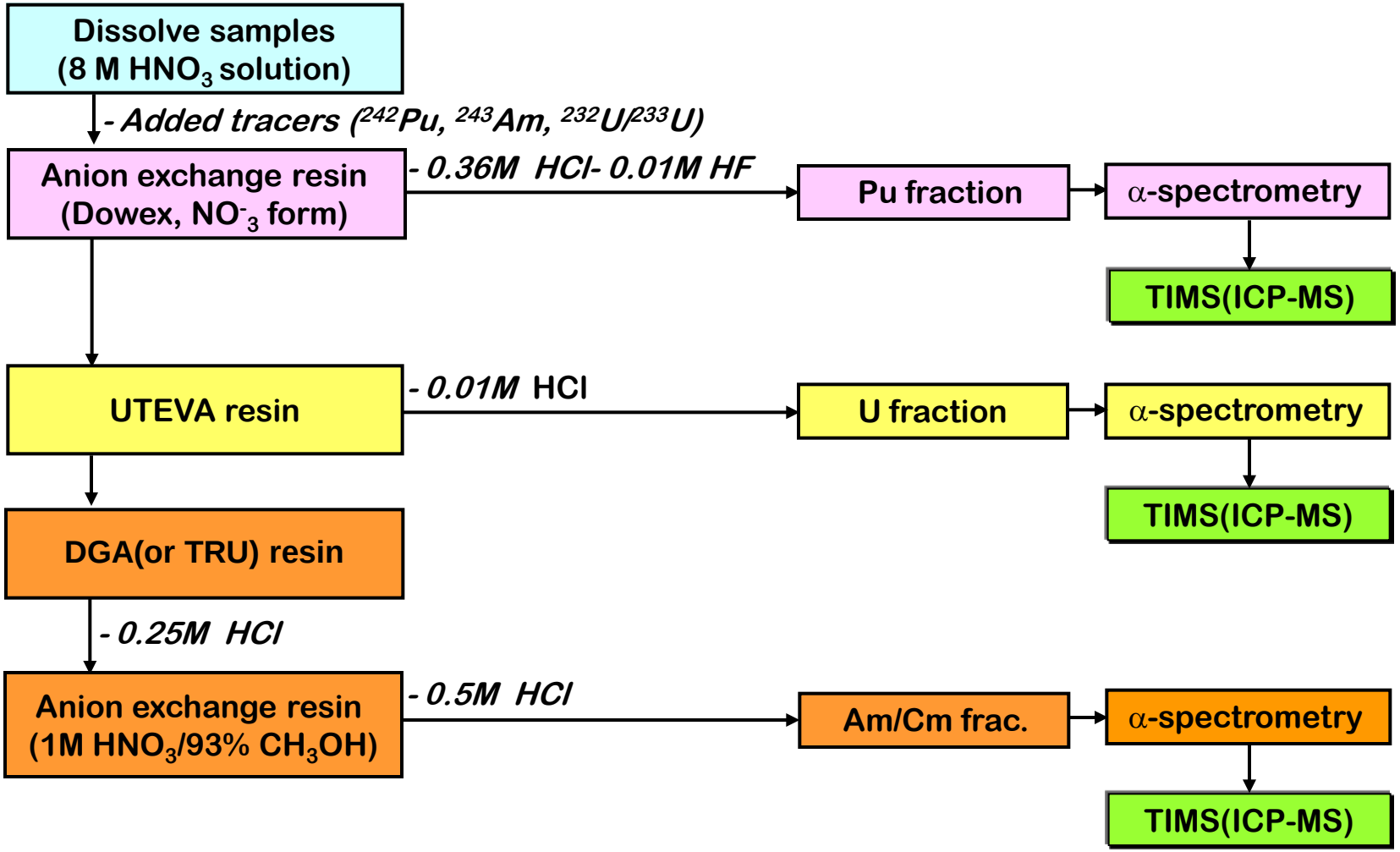
Purification of Pu, U
Extraction chromatography

Source preparation

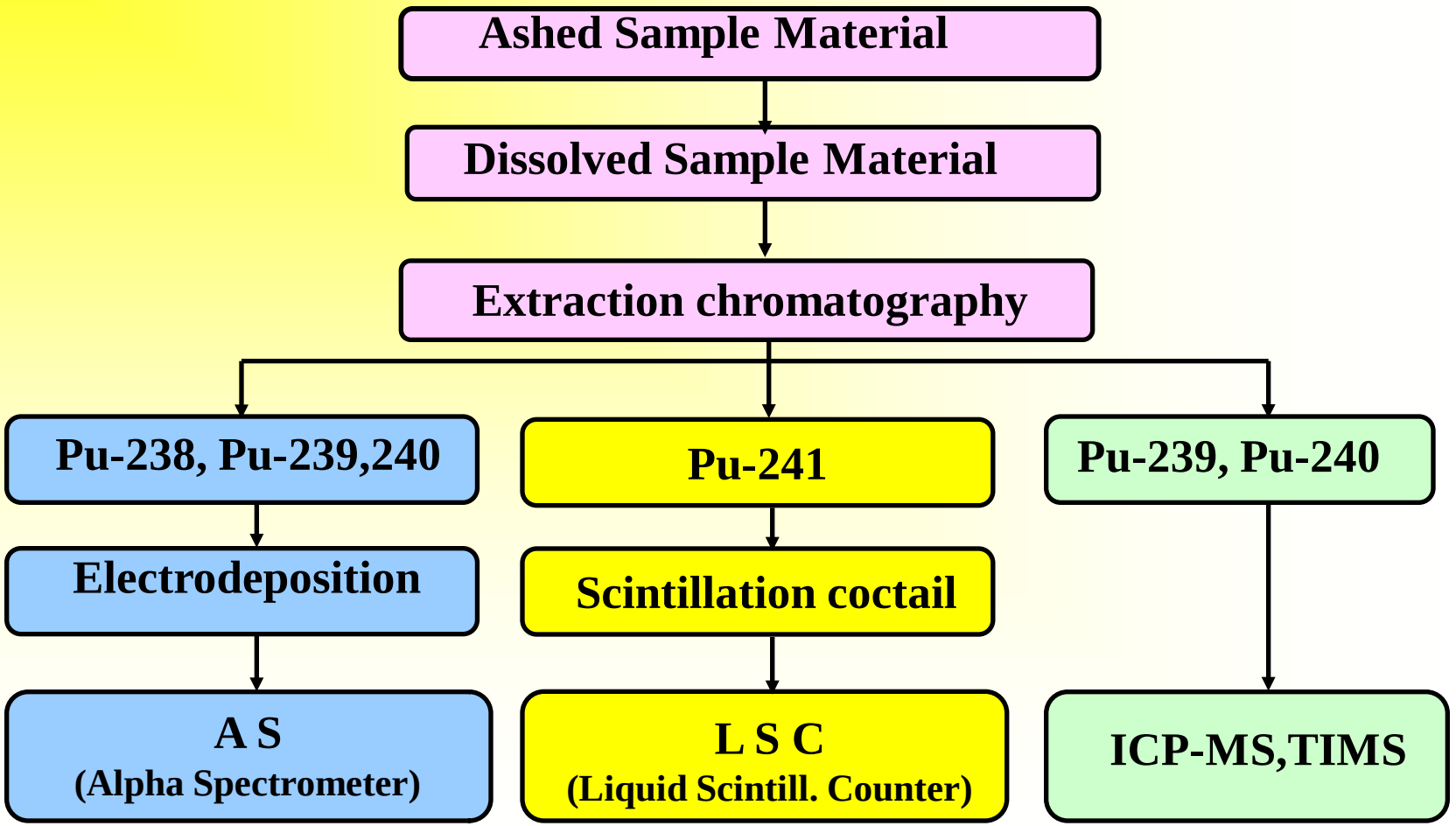
Alpha spectrometer

TIMS or MC-ICP-MS

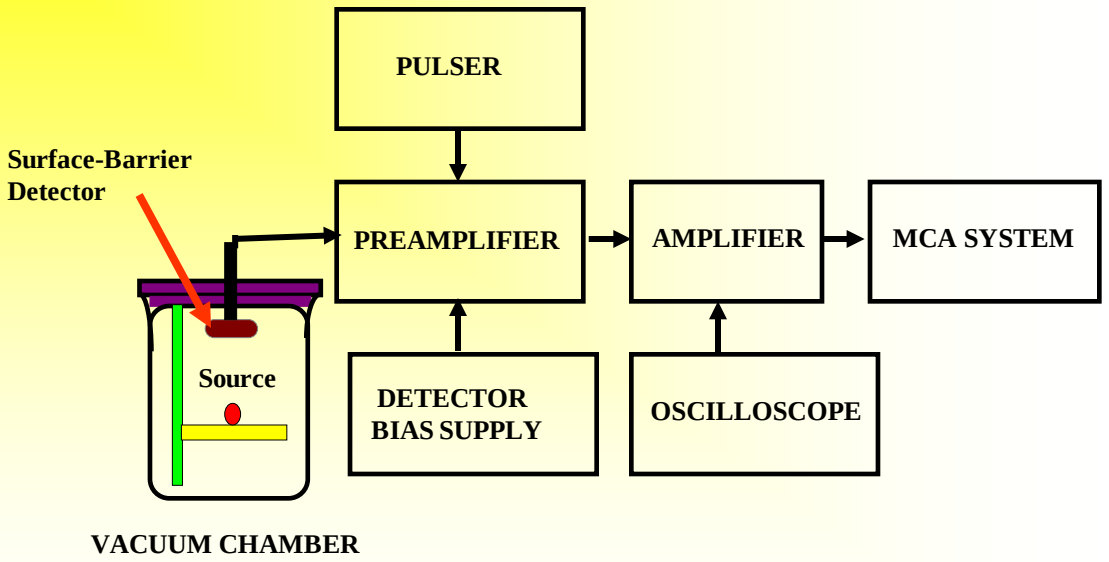
Determination of Pu, U and Am/Cm isotopes

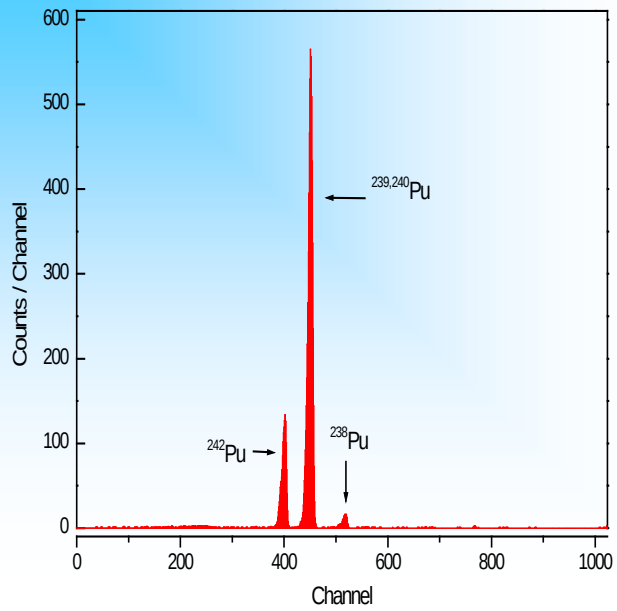


Determination of Pu isotopes

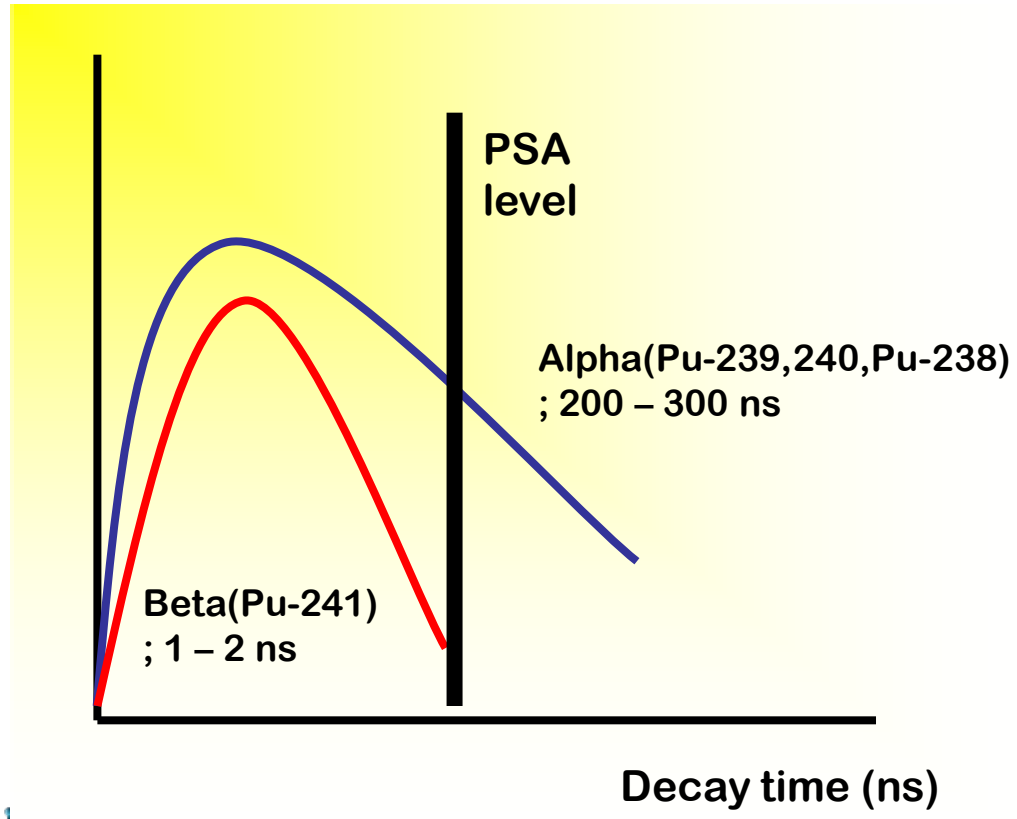


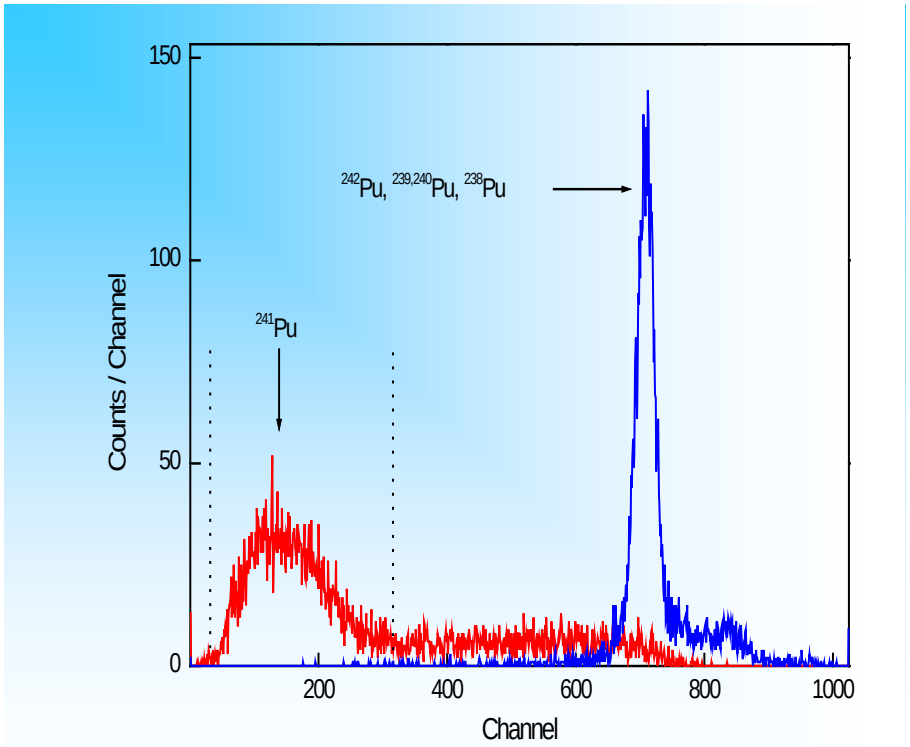
Measurement of Pu, Am and U isotopes by AP





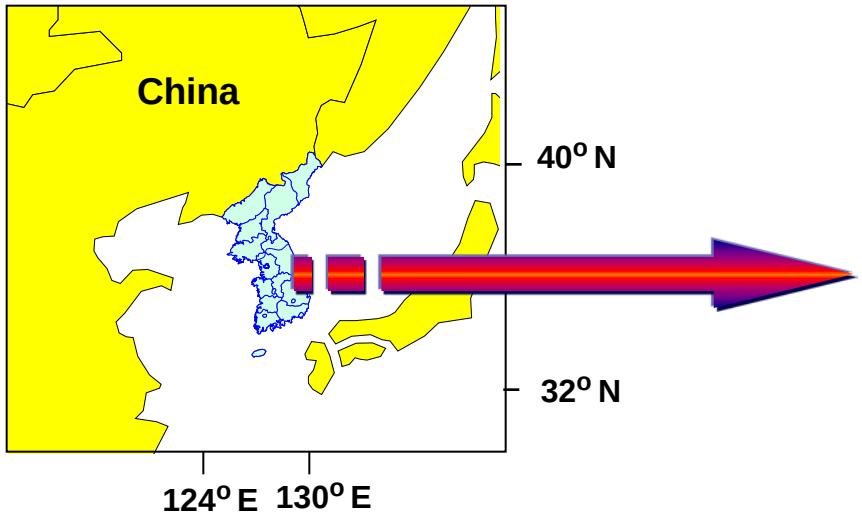
Measurement of Pu-241 by LSC

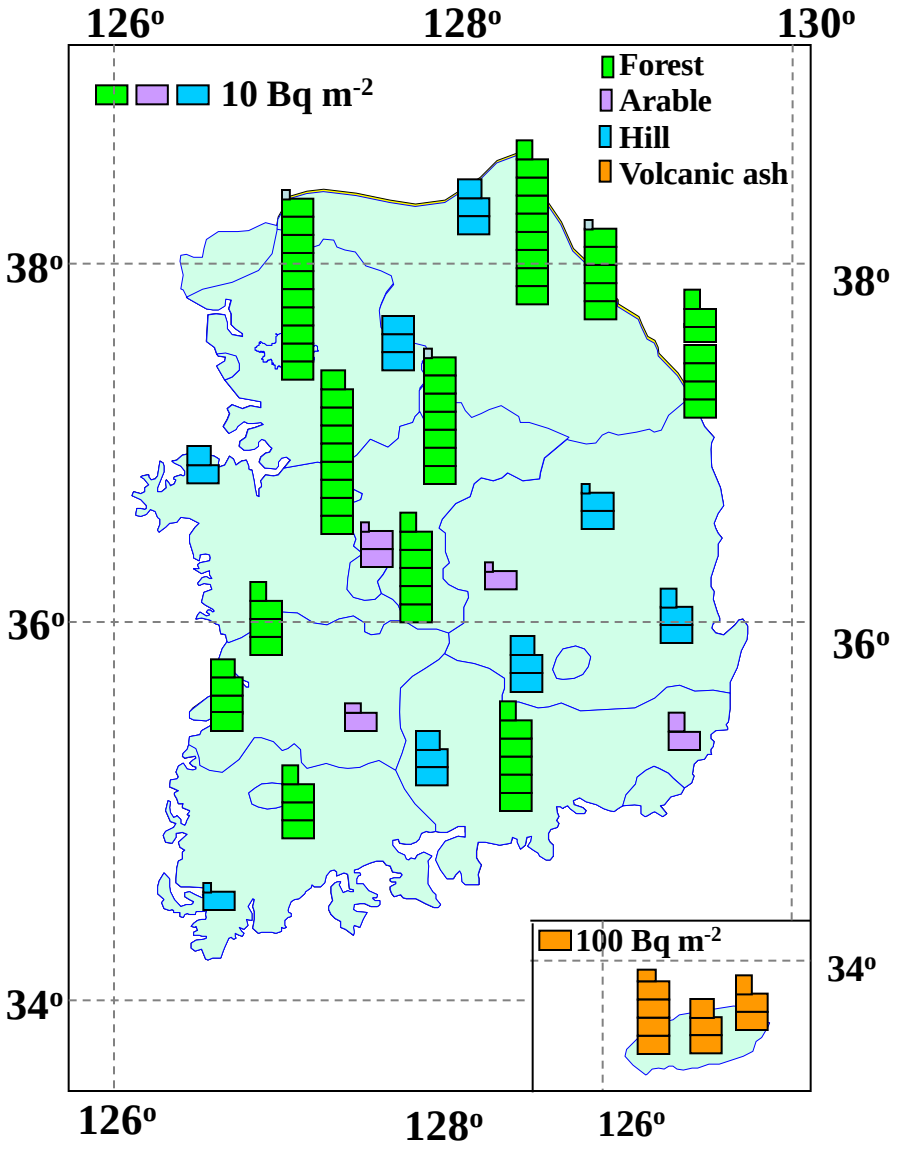




Test case # 1 : Cumulative deposition of Pu-239,240 in South Korea

(M. H. Lee et al., J. Environ. Radioact. 41, 99, 1998)





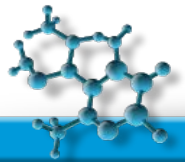
Parameters affecting deposition of fallout Pu isotopes

1. **Geographical location**
   - **Forest > Grassland > Arable**

2. **Organic matter content**
   - **Association of radionuclides with organic substances due to its large cation exchange capacity**

3. **Rainfall**
   - **Precipitation scavenging effect**

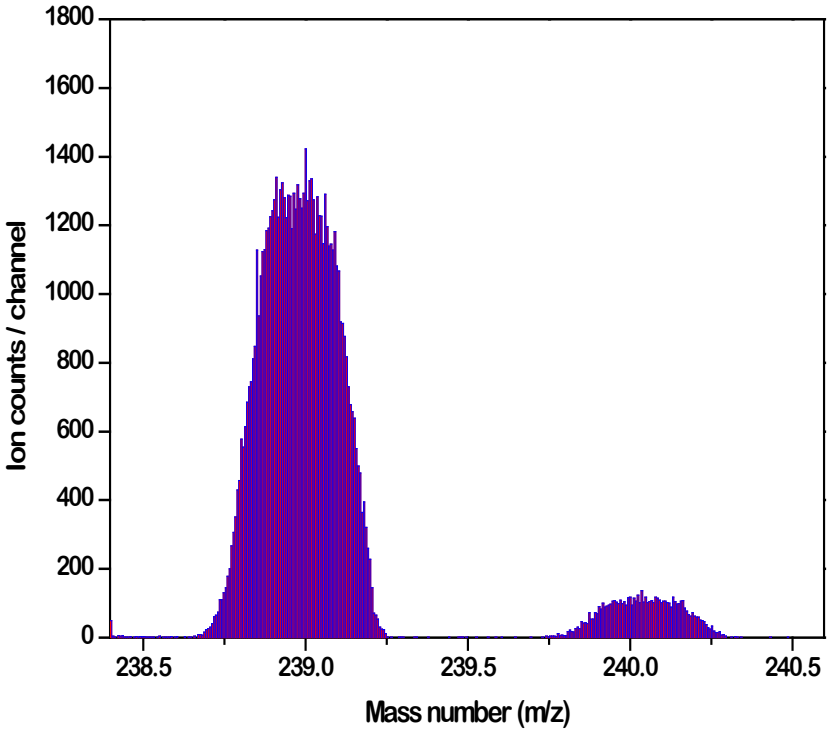
4. **Clay content**
   - **Increased surface area and the greater adsorption capacity**

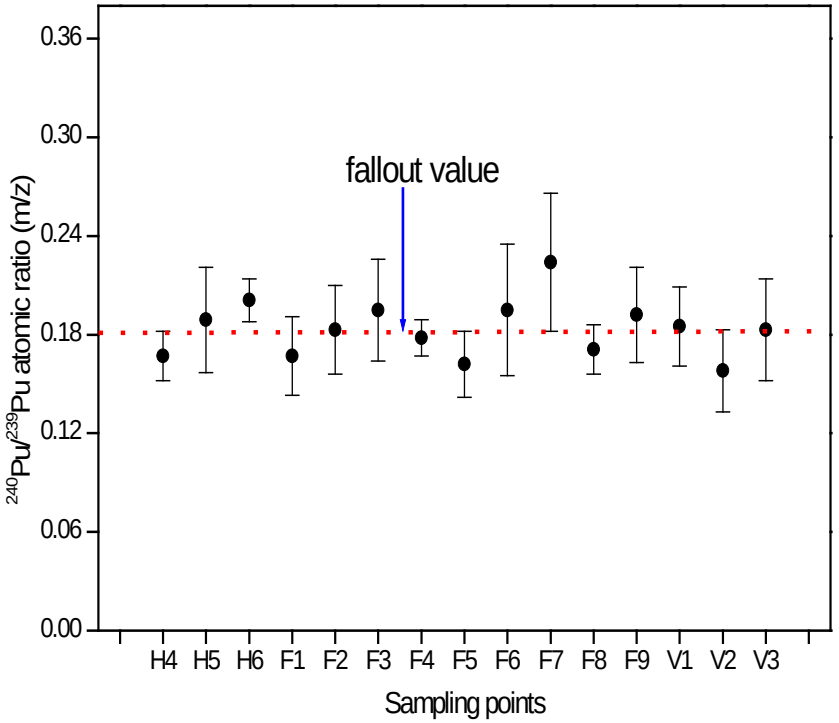


Activity ratios of Pu isotopes

	Pu-238/ Pu-239,240	Pu-241/ Pu-239,240
In this study	0.040	3.76
Worldwide fallout	0.037	3 ~ 8
Chernobyl fallout	0.47	85

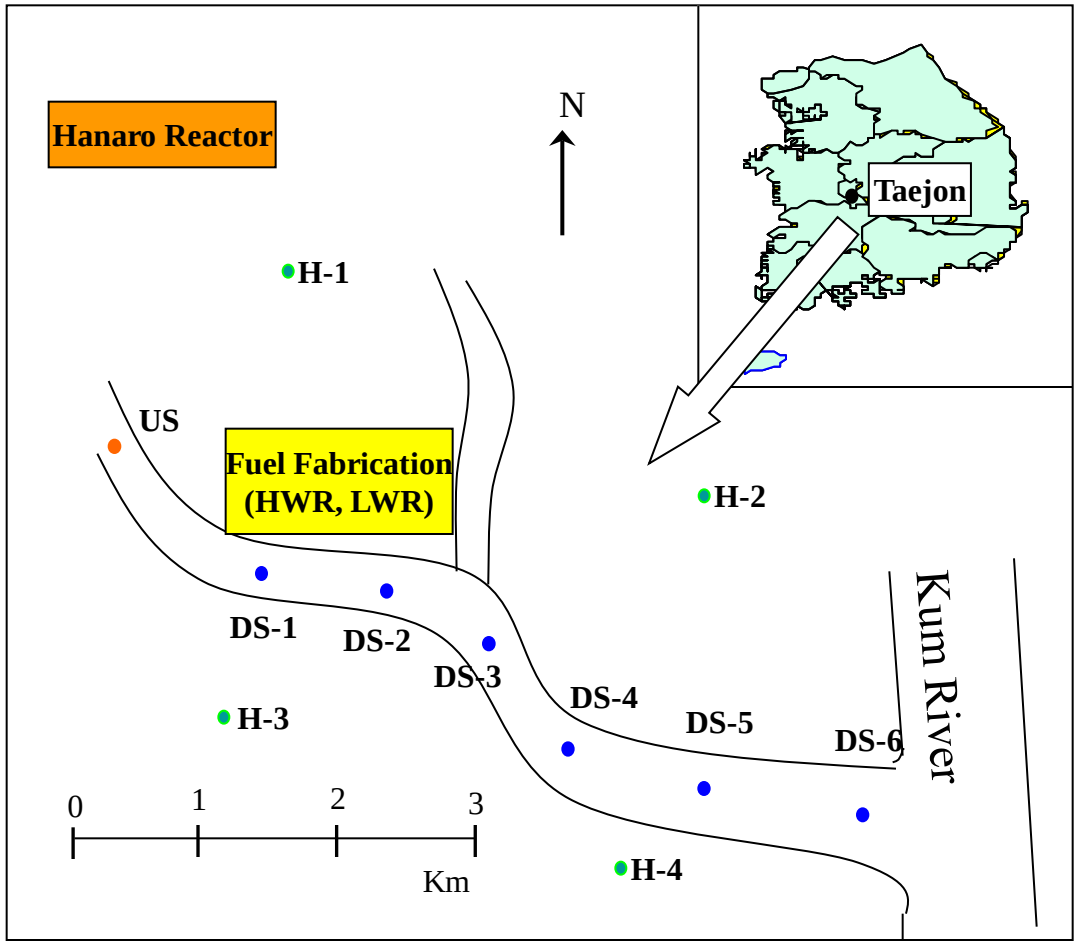
Measurement of Pu-239 and Pu-240 by ICP-MS

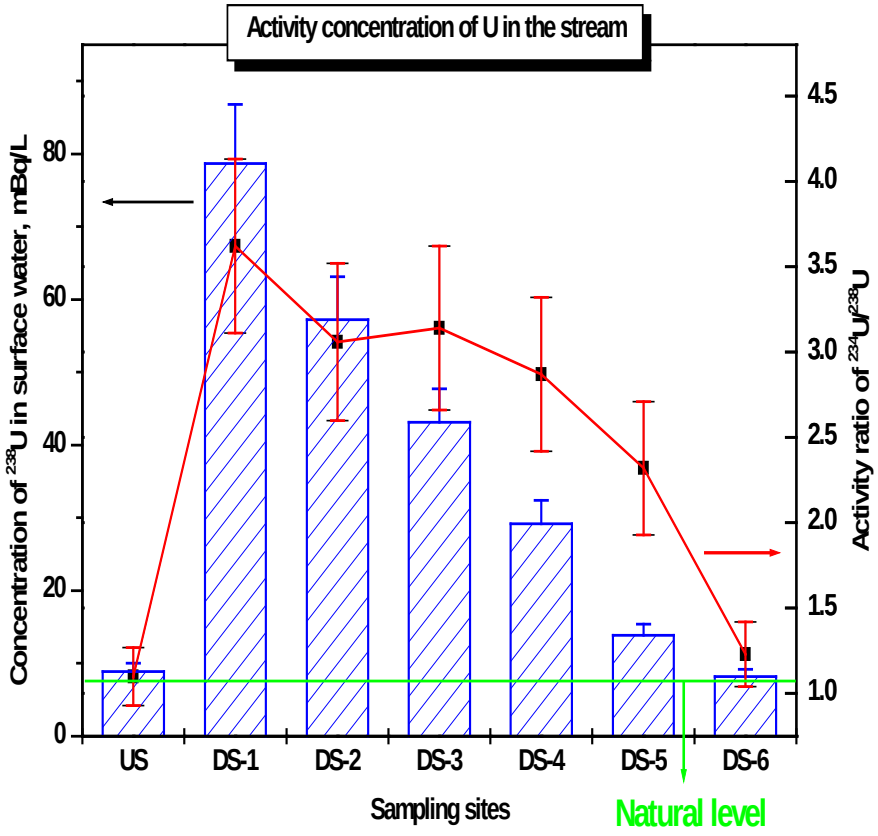




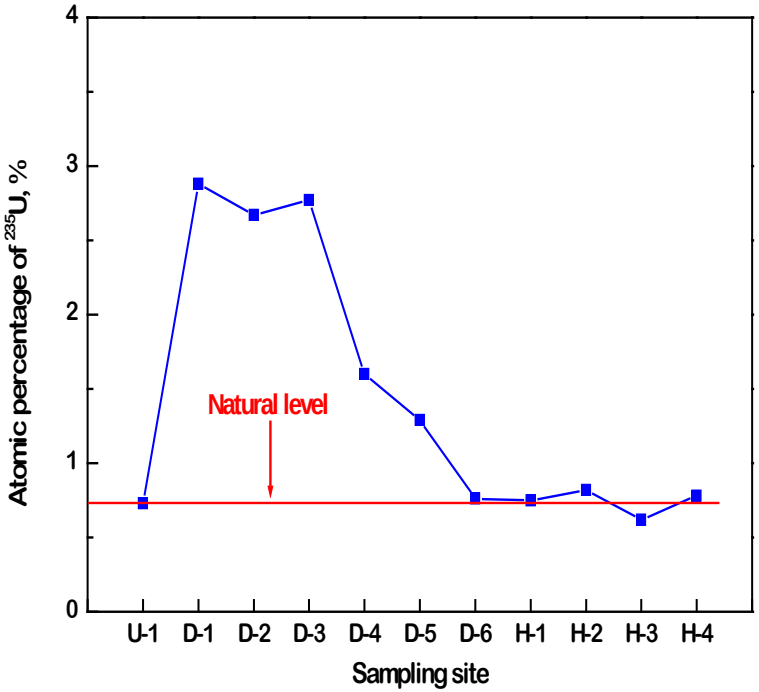
Atomic ratio of Pu-240/Pu-239 : 0.158 ~ 0.224 (average; 0.183)

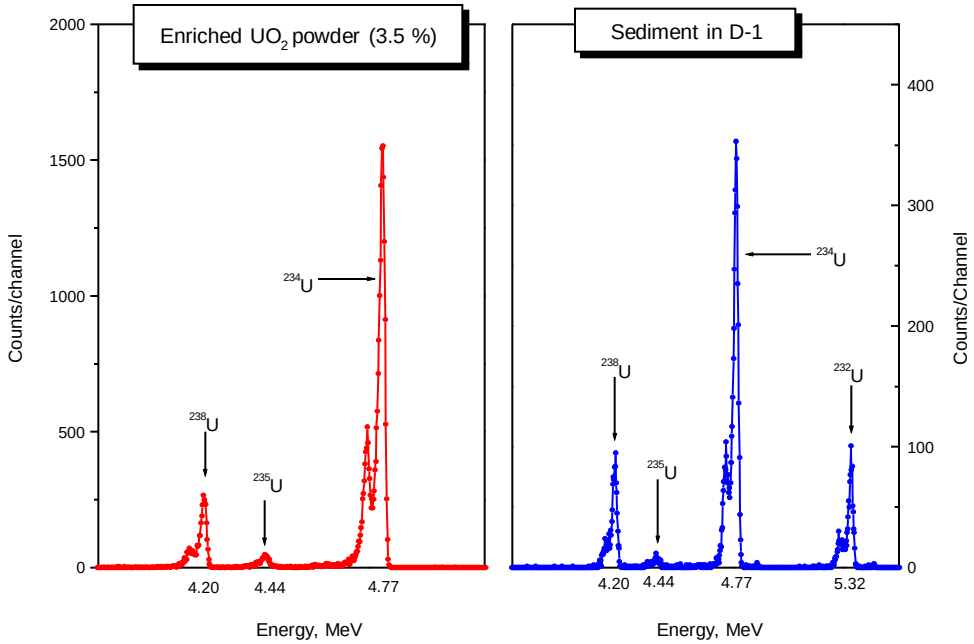
Test case # 2 : Activity concentrations of U isotopes around nuclear fuel facilities, Korea (M. H. Lee et al., J. Radioanal. Nucl. Chem, 249, 215, 2001)





Atomic percentage of U-235 around nuclear fuel facilities





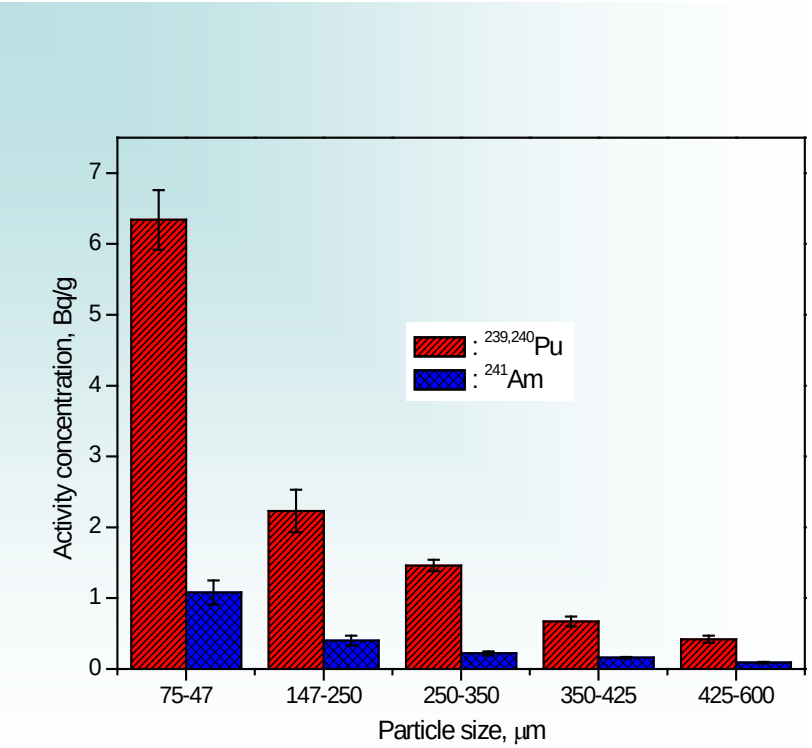
Test case # 3 : Activity concentrations of Pu isotopes around missile site, USA (M. H. Lee, Sue B. Clark, Environ. Sci. Technol. 39, 5512, 2005)

BOMARC (Boeing Michigan Aeronautical Research Center, NEW JERSEY, USA)

- BOMARC facility (occupies 218 acres) operated from `60 to `72
- An explosion and fire occurred BOMARC Missile Shelter 204 on June 7, 1960
- Plutonium fragments from the warhead were spread over an area surrounding the launcher
- Air forces deactivated in 1972s
- Air Force finally began a program to clean up the radioactive contamination of the BOMARC site between 1992 to 2002

Activity concentrations of actinides with particle size in missile site

Particle size (μm)	Pu-239,240 (Bq/g)	Pu-238 (Bq/g)	Pu-241 (Bq/g)	Am-241 (Bq/g)
75– 47	6.34±0.42	0.11±0.008	15.28±0.98	1.08±0.17
147–250	2.23±0.30	0.049±0.006	4.50±0.62	0.40±0.07
250–350	1.46±0.08	0.038±0.002	2.54±0.39	0.22±0.03
350–425	0.67±0.07	0.022±0.003	0.92±0.12	0.16±0.01
425–600	0.42±0.05	0.010±0.001	0.67±0.10	0.09±0.01



Age determination of Am-241 produced from Pu-241

$^{241}Pu \xrightarrow[T_f: 14.35\ y]{} {}^{241}Am \xrightarrow[T_f: 458\ y]{} {}^{237}Np$

Theoretical value of Activity of Am for 43 y

(2003 y-1960 y)

$A_{Pu\text{-}241}$ **at 43 years ago; 15.28 (Bq/g) x**

Exp (0.693x43/14.35) = 147.3 Bq/g

$A_{Am} = \lambda_{Am} N_{Am} = \lambda_{Am} / (\lambda_{Am} - \lambda_{Pu})\, A_{Pu}$

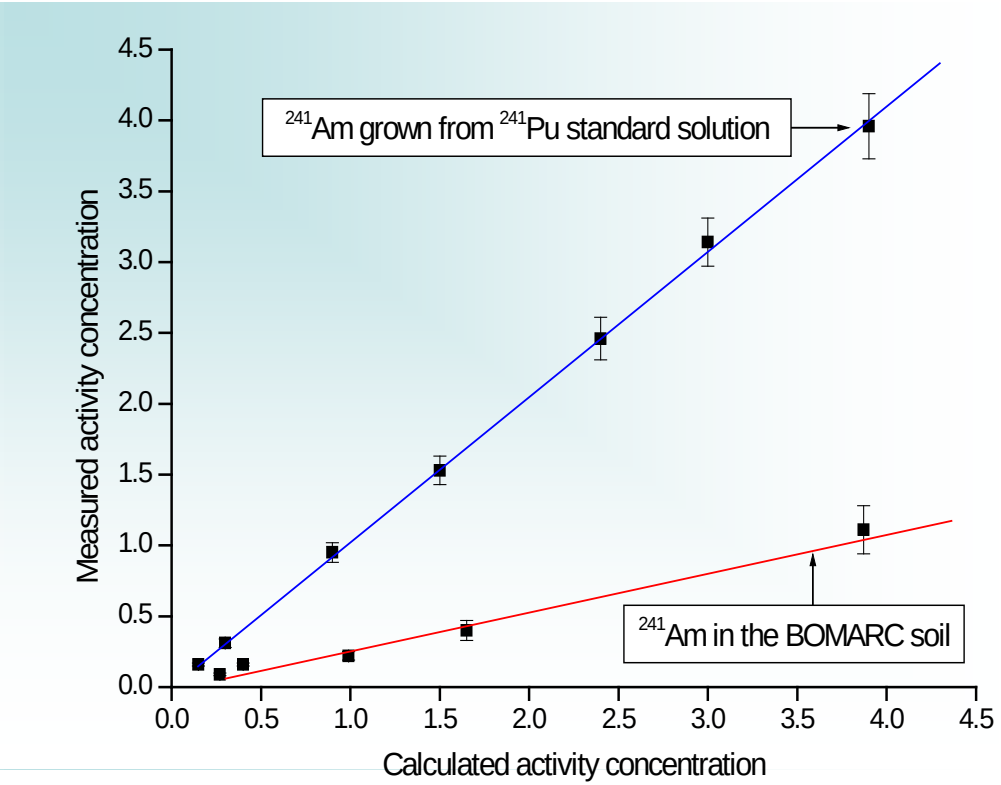
$(e^{-\lambda Put} - e^{-\lambda Amt})$, $N_{Am}^{0} = 0$

$= (0.693/458) / (0.693/458 - 0.693/14.4)$

$* 147.3\ (Bq/g) * (e^{-0.693/14.4*43} - e^{-0.693/458*43})$

= 3.87 Bq/g (calculated value)

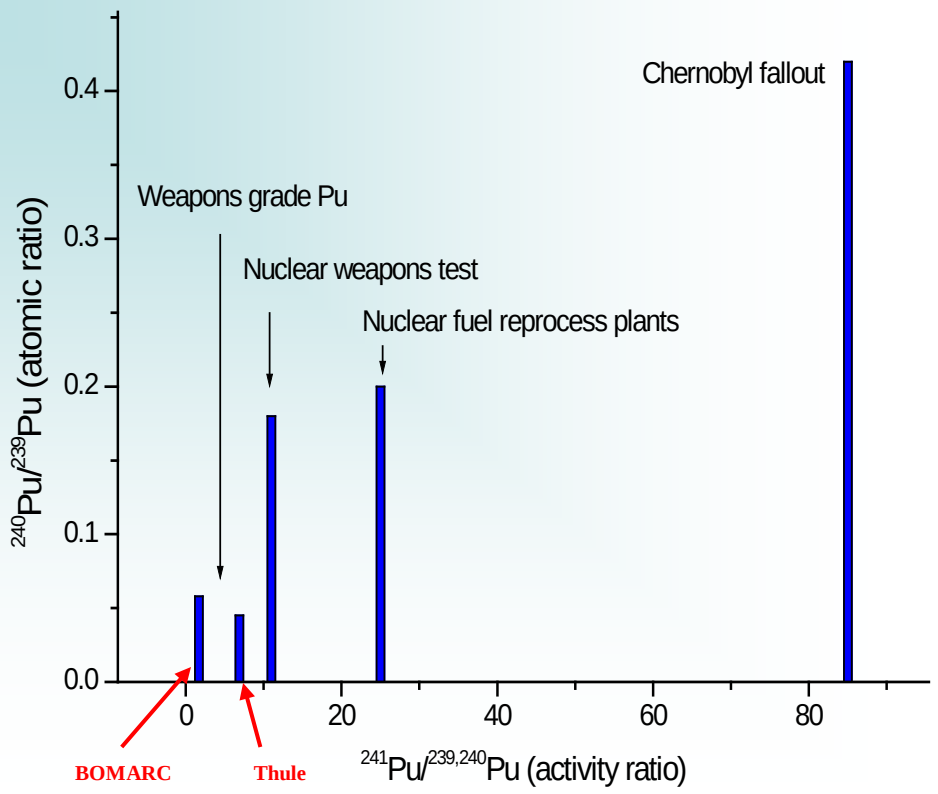
≠ 1.11 Bq/g (measured value)



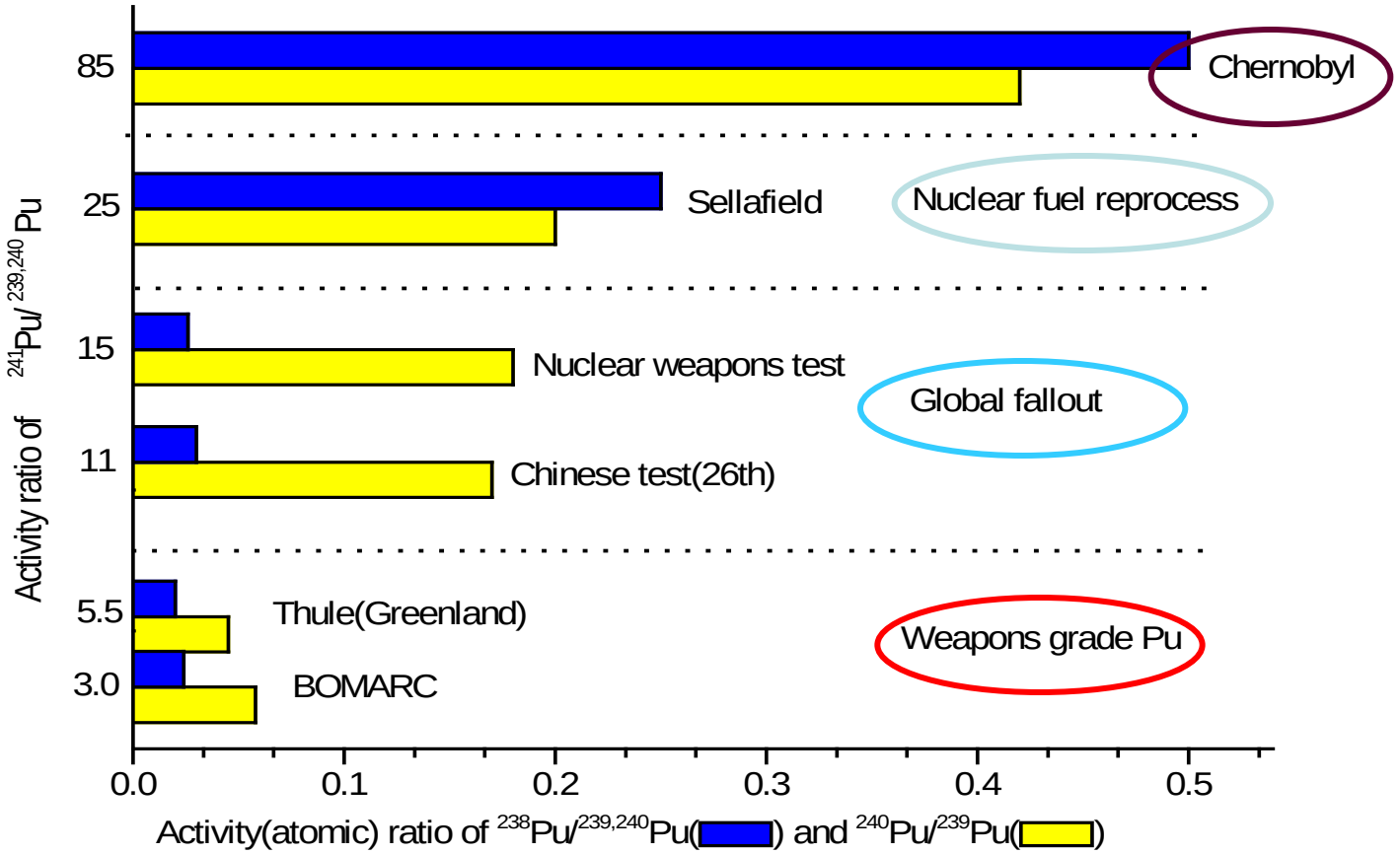
Am is more mobile than plutonium in the environment ?

Atomic ratio of Pu-240/Pu-239 in missile site

Particle size (μm)	Atomic ratio (Pu-240 / Pu-239)
75– 47	0.0567 ± 0.0009
147–250	0.0588 ± 0.0017
250–350	0.0571 ± 0.0014
350–425	0.0559 ± 0.0013
425–600	0.0594 ± 0.0010



Activity (atomic) ratios of Pu isotopes emitted from different sources



Summary

1. Application of radioanalytical techniques (radiometric, mass spectrometric method) to environmental samples
2. Update of reference databases for “nuclear fingerprinting”
   - activity and atomic ratios of Pu isotopes in soil samples (Korea Peninsular)
   - activity and atomic ratios of U isotopes in environmental samples (Nuclear fuel facilities)
   - activity and atomic ratios of Pu and Am isotopes (age determination) in soil samples (BOMARC Missile site)
3. Identification of origin of unknown nuclear material comparing reference data from set-up databases

Thank you for your attention !!!