Determination of isotope ratios for individual plutonium particles with ICP-MS

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(1) Clean laboratory in JAEA (CLEAR facility)

(2) Our analytical techniques for nuclear safeguards

(3) An analytical technique for individual plutonium particles

(4) Conclusions

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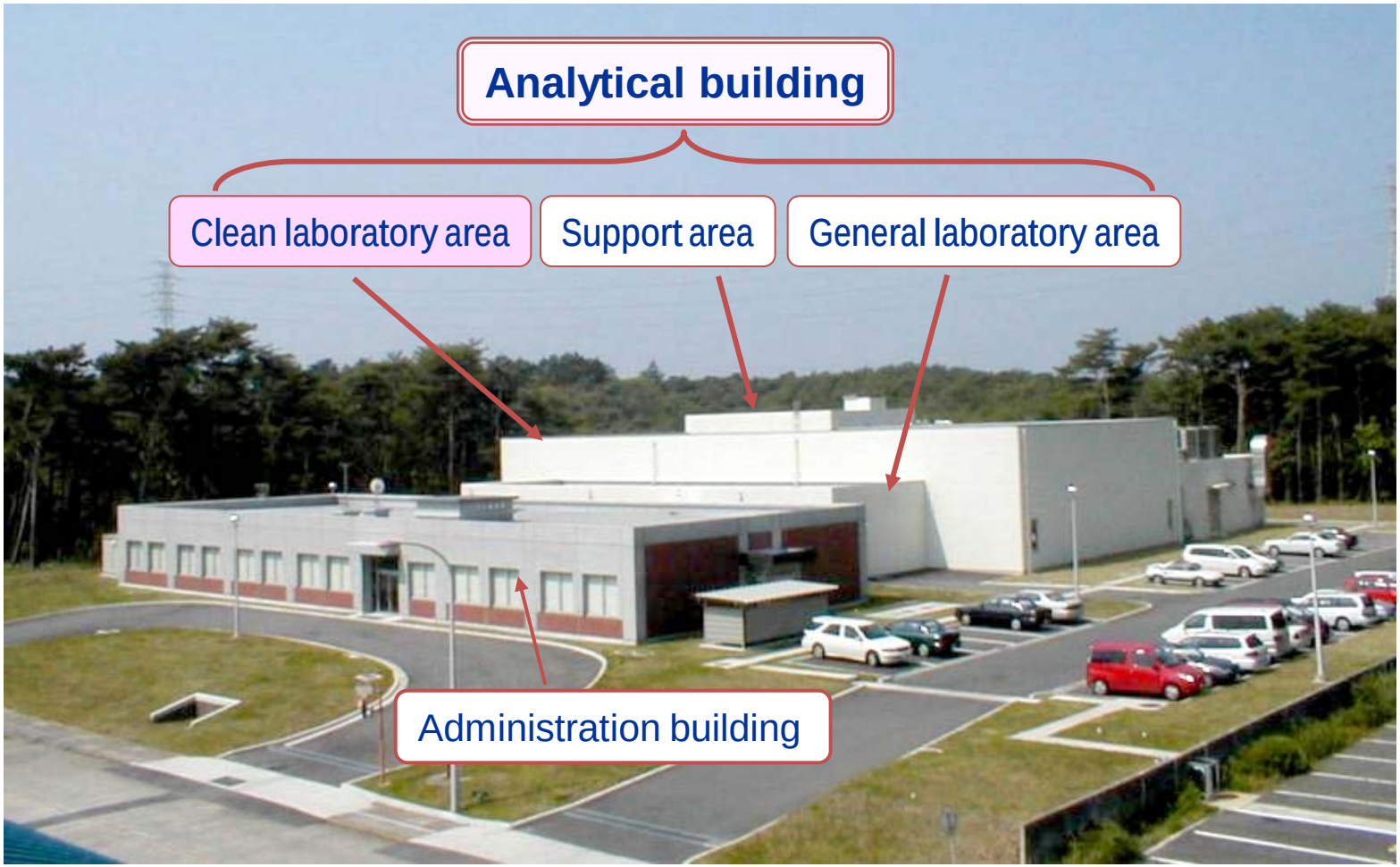
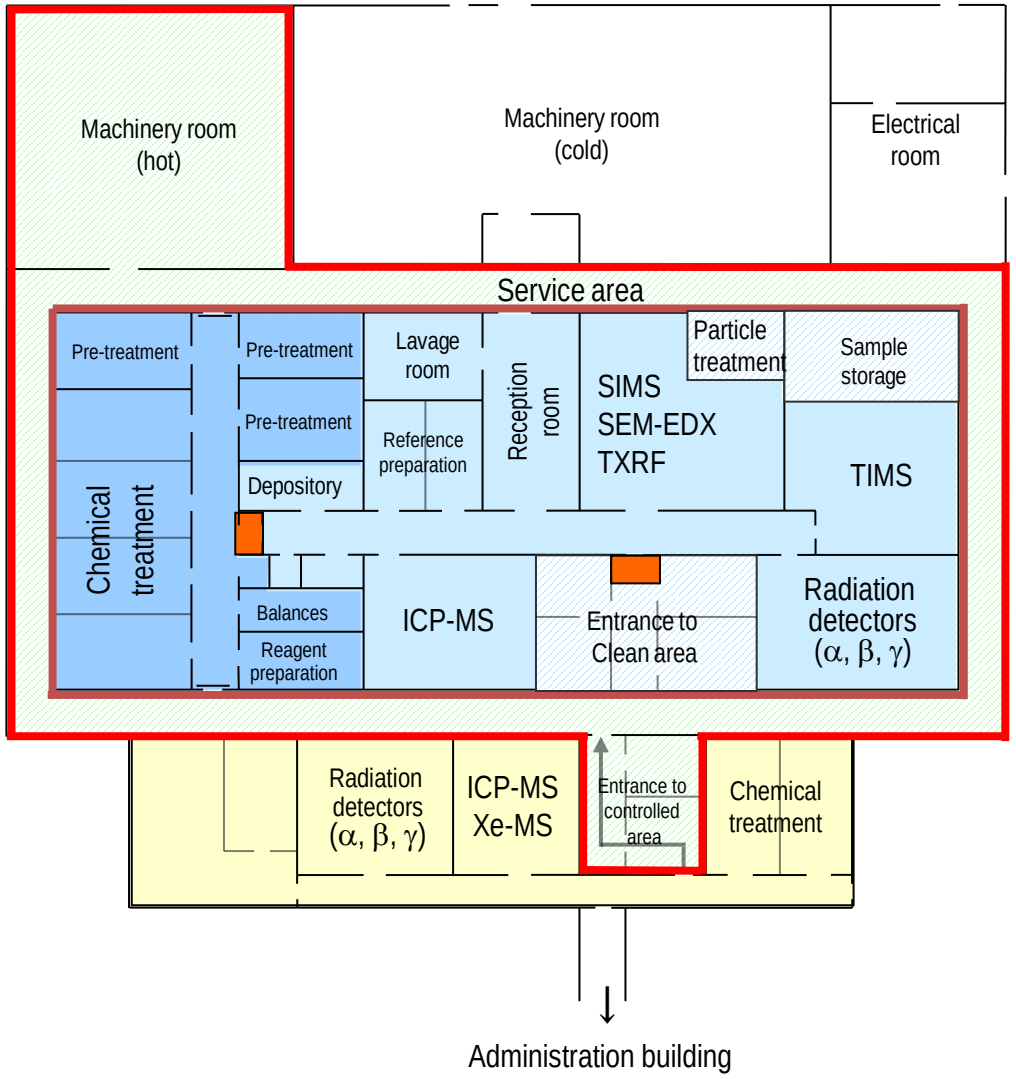
CLEAR facility in JAEA

Clean Laboratory for Environmental Analysis and Research



Layout of analytical building



Radiation controlled area

Clean area (700m^2)

Instrumental analysis area (class 10,000)

Instrumental analysis area (class 1,000)

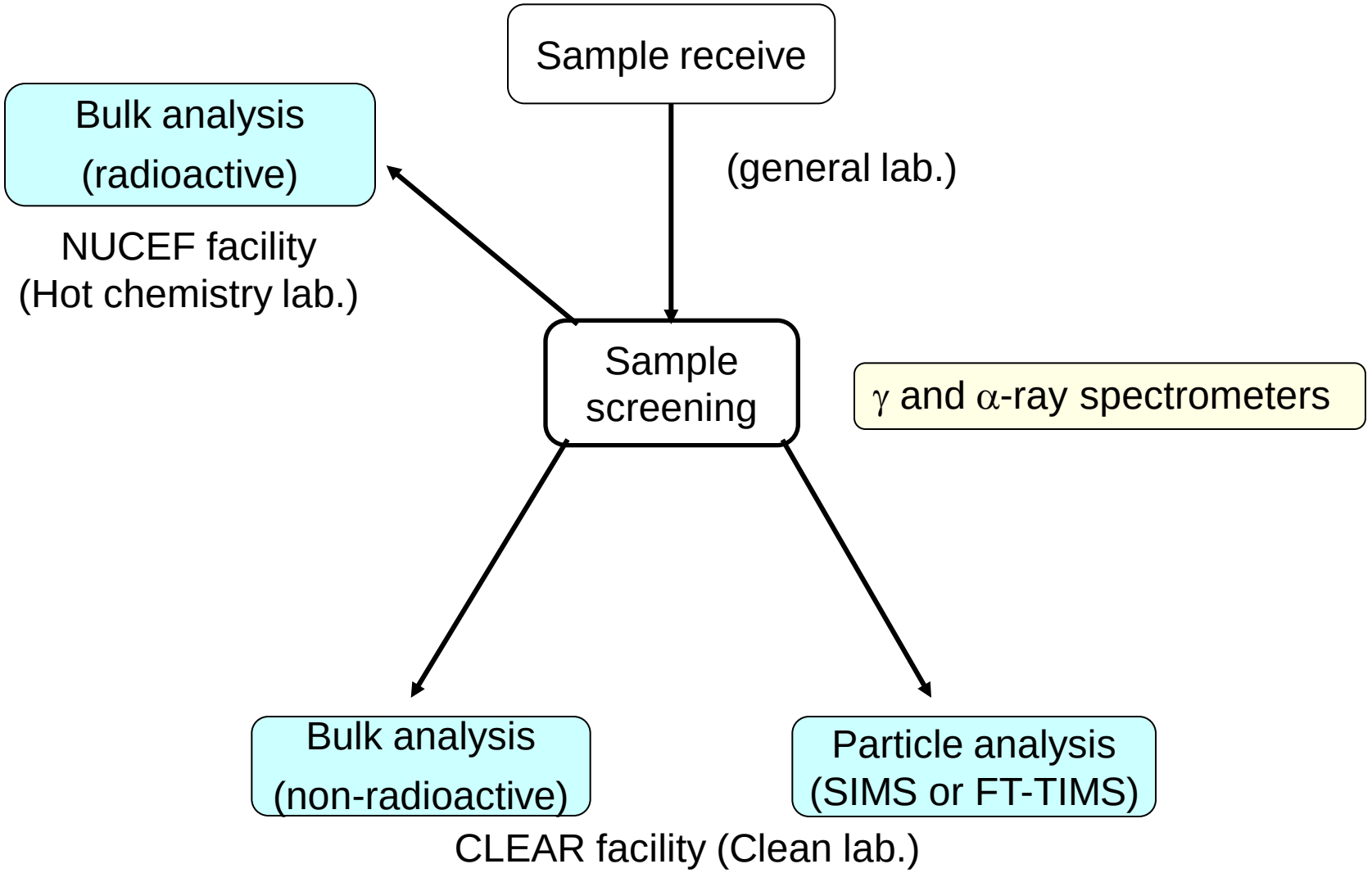
Chemical treatment area (class 100)

Air shower

General laboratory

Cleanliness class is defined as maximum number of particles (> 0.5μm) in 1 ft^3. No cleanness-controlled rooms, e.g. normal office rooms, sometimes contain the particle more than one million.

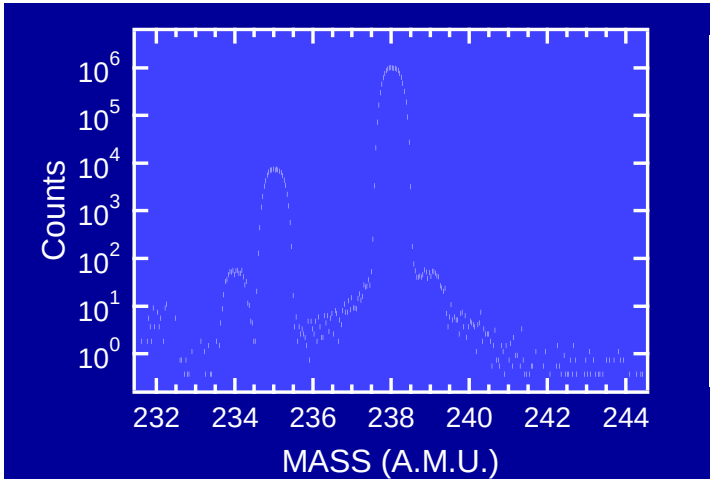
Analysis of environmental samples for SG



Procedure of bulk analysis

- Swipe samples
- Ashing
- Digestion
- Addition of spikes (^{233}U and ^{242}Pu)
- Chemical separation (U and Pu)
- Isotope ratio analysis (ICP-MS)
- Concentration (IDM, ICP-MS)

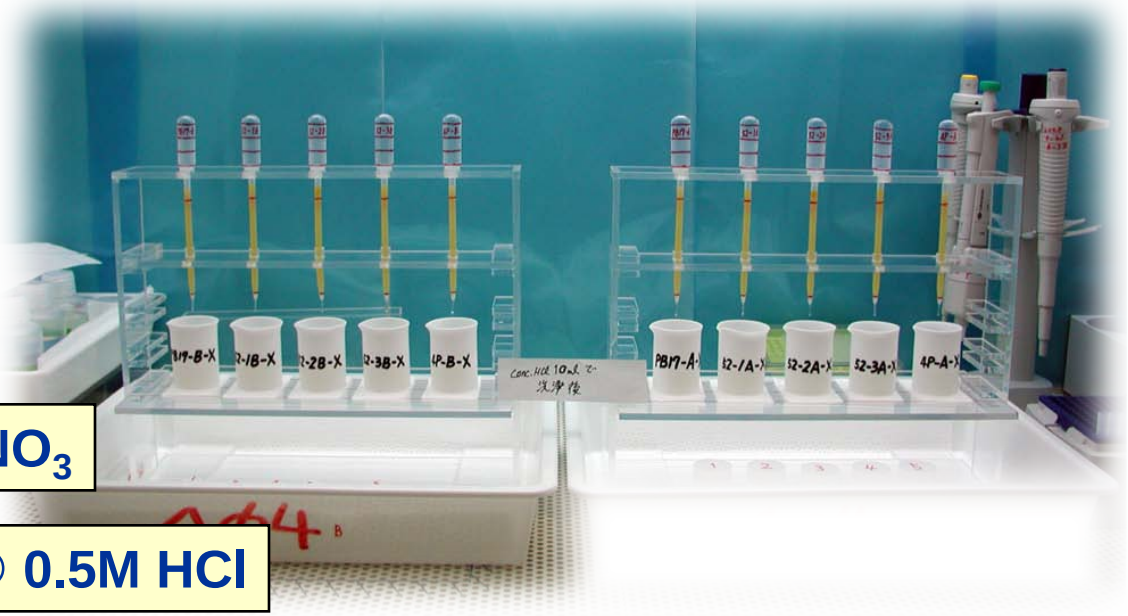
ICP-MS



Mass spectrum of uranium

Chemical separation

- 15M HNO_3 & Dry up
- 9.5M HCl & Dry up
- 1M HCl + 3M $NH_2OH \cdot HCl$
- Standing for 60 min.
- Dry up slowly
- 9MHCl + 0.2M HNO_3



① → **② 9.5M HCl + 0.1M HNO_3**

② 9.5M HCl

④ 0.5M HCl

③ 9M HCl+ 0.1M HI

Anion exchange
MCl GEL, CA08P(75～150μmϕ) 0.84ml

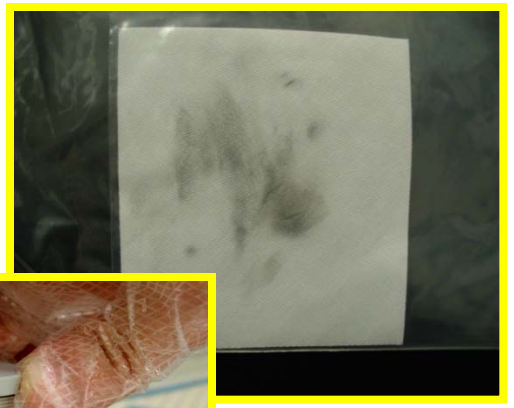
①② Alkaline metal etc

③ Pu

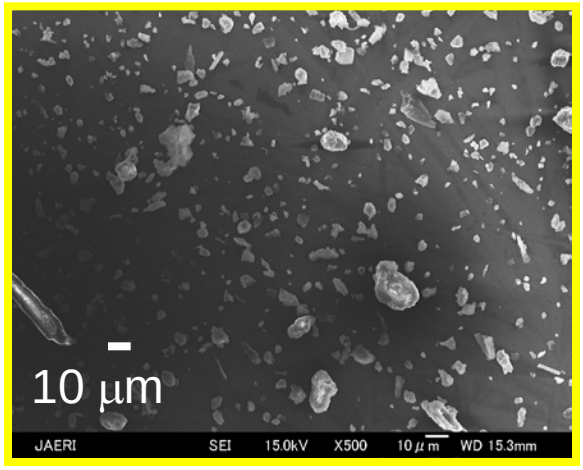
④ U

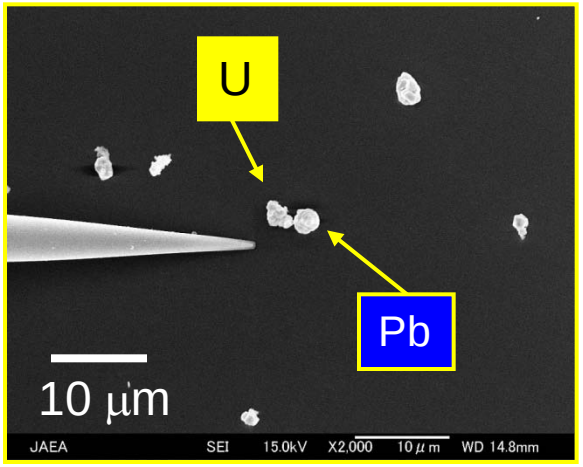
Procedure of particle analysis (SIMS)

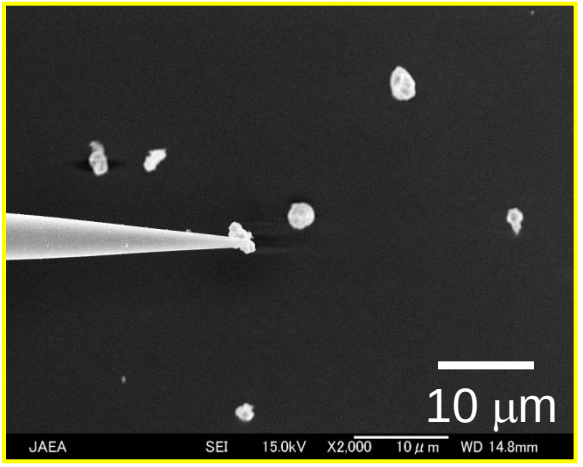
- Swipe samples
- Particle recovery (Impactor)
- Particle screening (TXRF)
- Particle search (SEM-EDX)
- Particle manipulation (SEM)
- Isotope ratio analysis (SIMS)

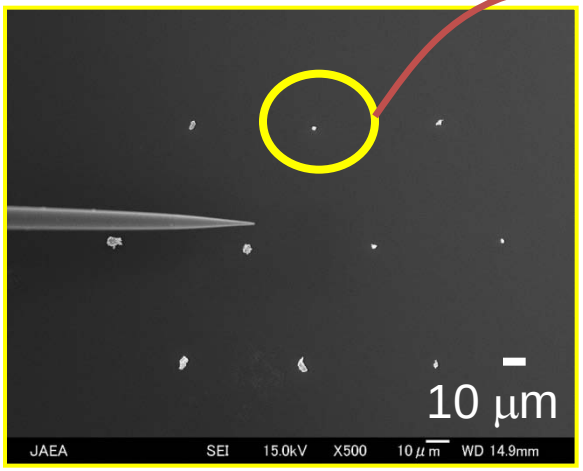


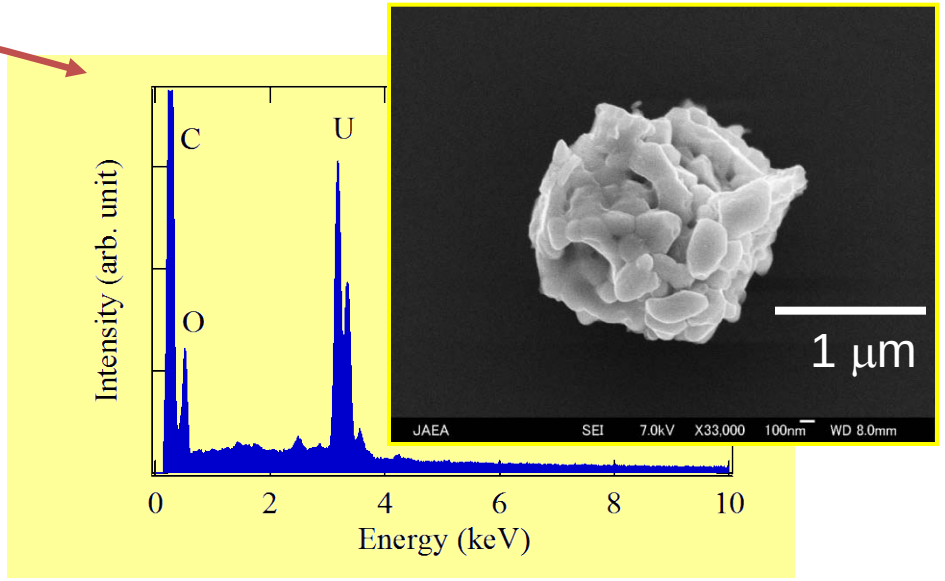
Particle manipulation



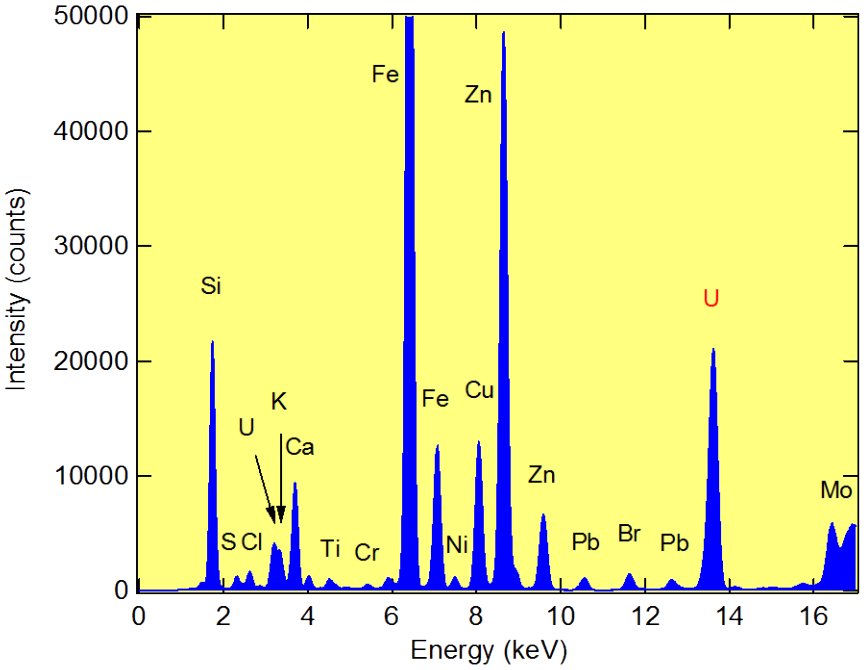




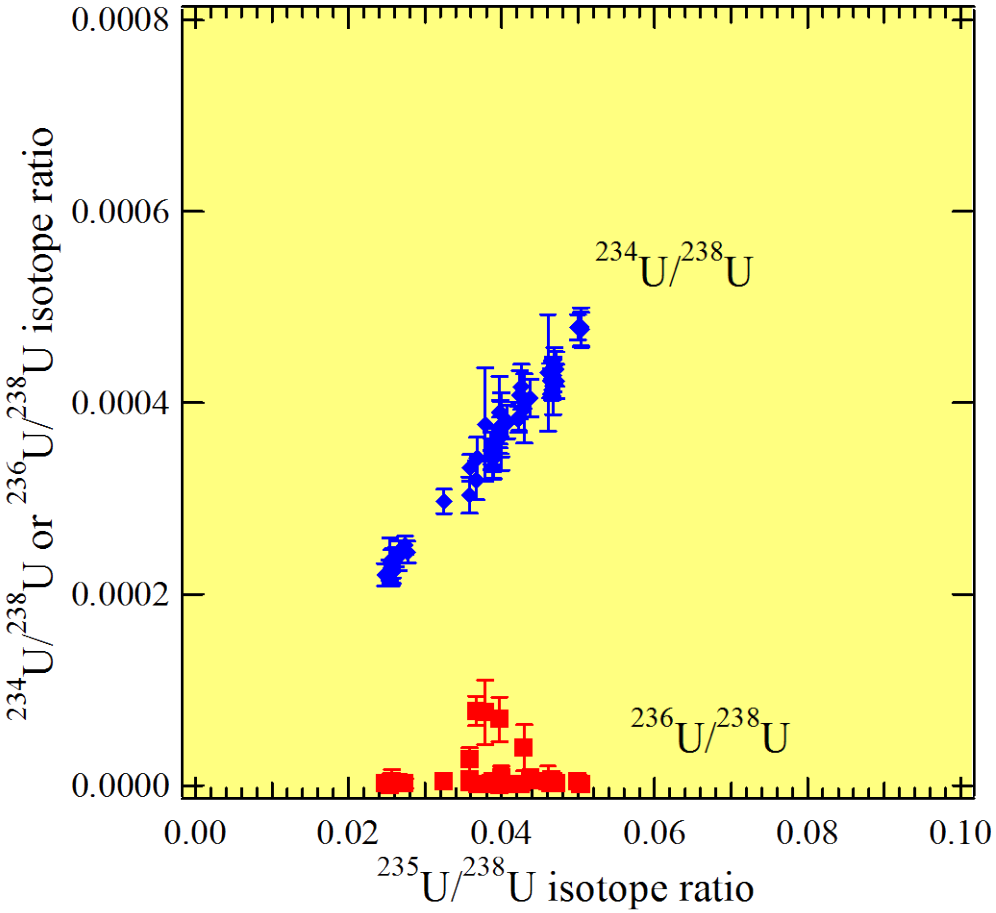




Result of particle analysis (SIMS)



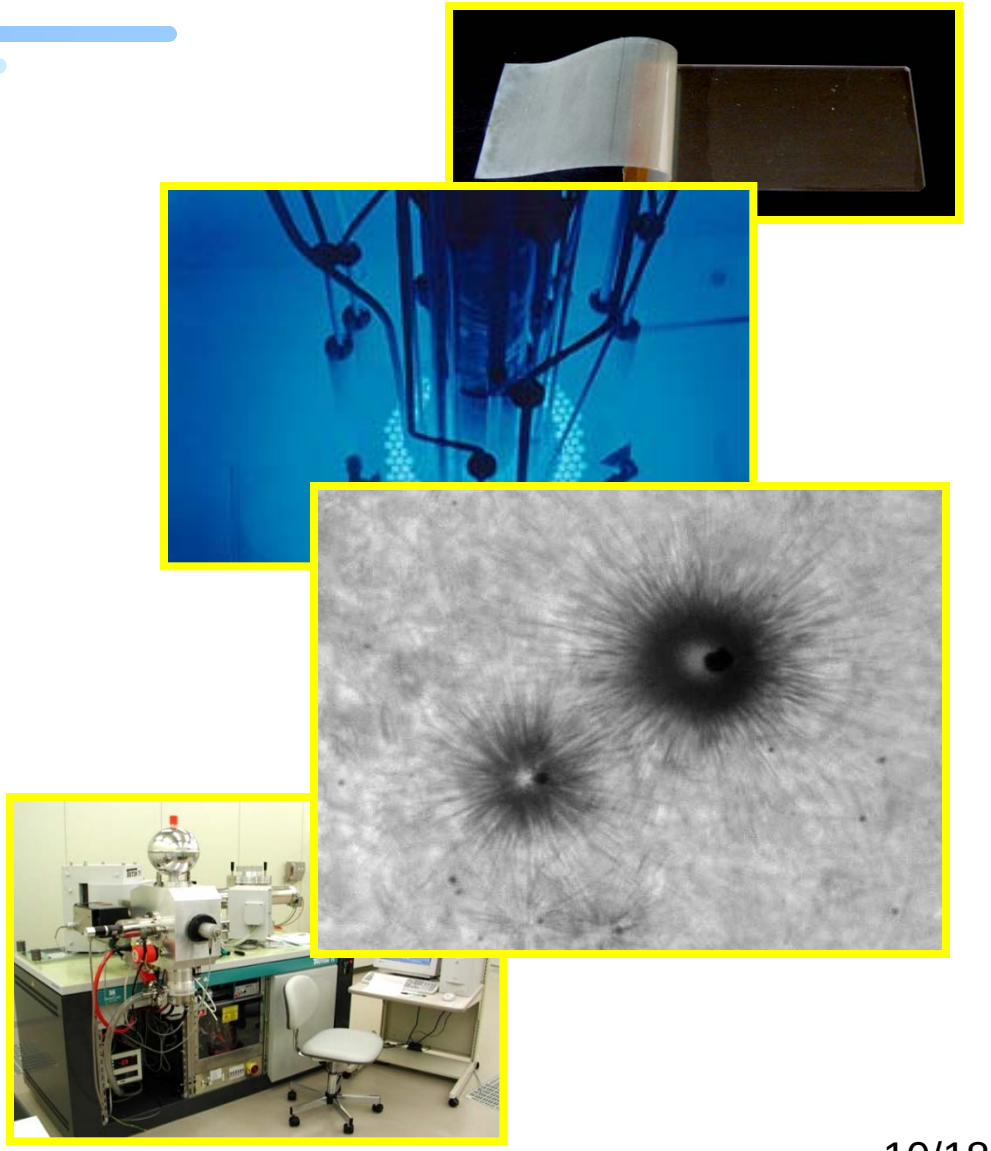
TXRF spectrum of a swipe sample



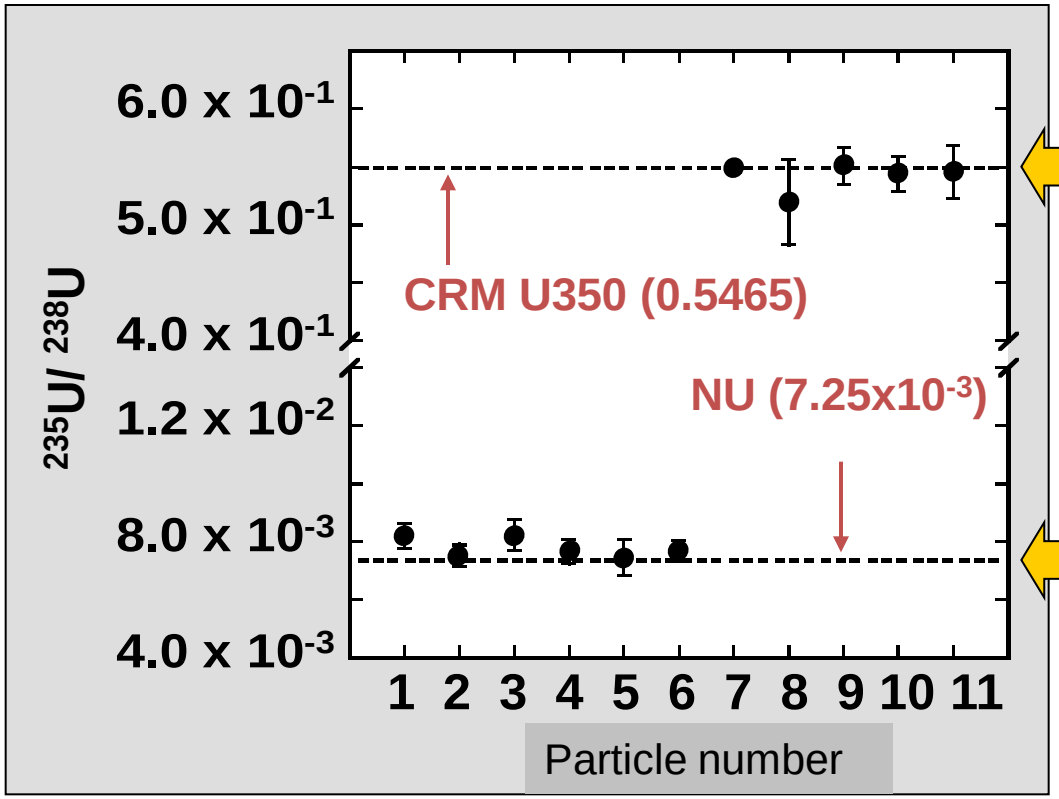
Uranium isotope ratios in individual particles measured with SIMS

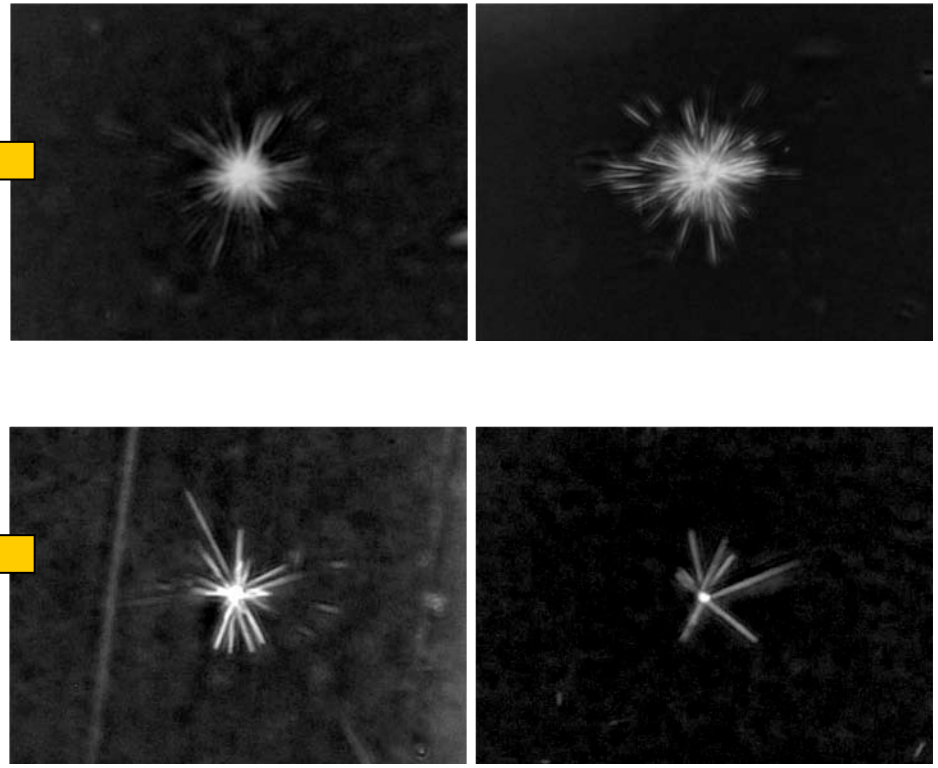
Procedure of particle analysis (FT-TIMS)

- Swipe samples
- Sample preparation
- Neutron irradiation
- Chemical etching
- Observation of fission tracks
- Particle transfer
- Isotope ratio analysis (TIMS)



Result of particle analysis (FT-TIMS)





10 μm

Uranium isotope ratios measured with TIMS

Fission tracks of uranium particles

Analysis of individual plutonium particles

Isotope ratio analysis for individual plutonium particles is difficult in SIMS and FT-TIMS analyses.

The problem is the isobaric interference of Am-241 to Pu-241 in a Pu particle.

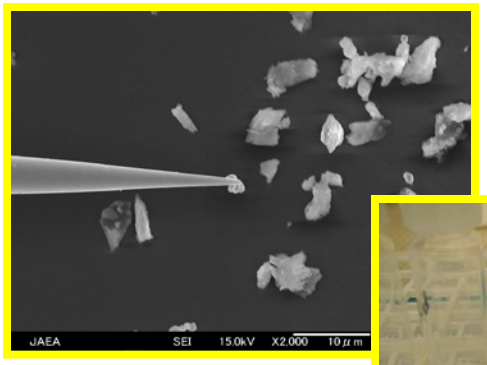
(Am-241 is the decay product of Pu-241)

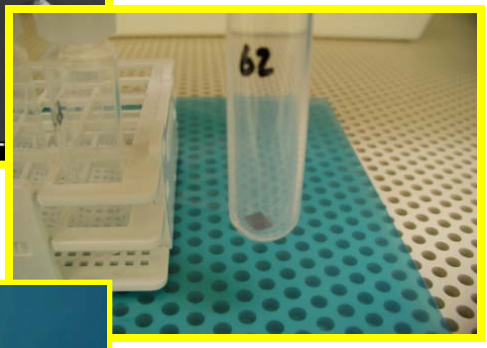
Another approach is necessary to perform the analysis of individual plutonium particles accurately

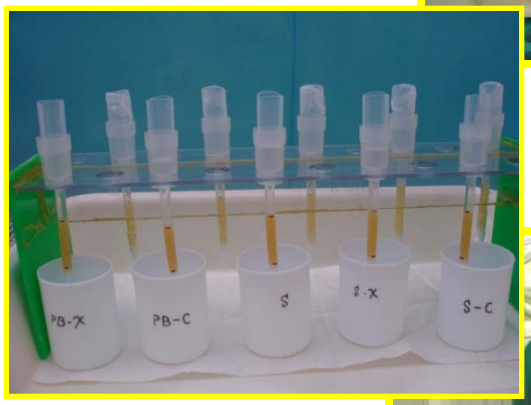
We propose a method by a combination of chemical separation and inductively-coupled plasma mass spectrometry (ICP-MS)

Procedure of particle analysis (Pu)

- Swipe samples
- Particle recovery (Impactor)
- Particle search (SEM-EDX)
- Particle transfer
- Dissolution of each particle
- Chemical separation
- Isotope ratio analysis (ICP-MS)







Analytical condition

ICP-MS parameter

Parameter	Setting
ELEMENT-1 (Thermo Electron Co.)	
RF power	1184 W
Cooling gas flow rate	16.0 L/min.
Auxiliary gas flow rate	0.85 L/min.
Sample gas flow rate	1.0 L/min.
Solution uptake rate	0.18 mL/min.
Sampling time per isotope	50 ms
Scan par replicate	400
Number of replicate	5
Sensitivity	1700 cps/ppt
Resolution (M/ΔM)	300

ICP-MS (Element-1)

Desolvation sample introduction system

Procedural blank values (Pu)

m/z	Counts / s	
	Without desolvation	desolvation
239	0.3 ± 0.2	0.7 ± 0.2
240	0.1 ± 0.1	0.3 ± 0.1
241	0.1 ± 0.1	0.1 ± 0.1
242	0.1 ± 0.1	0.3 ± 0.2

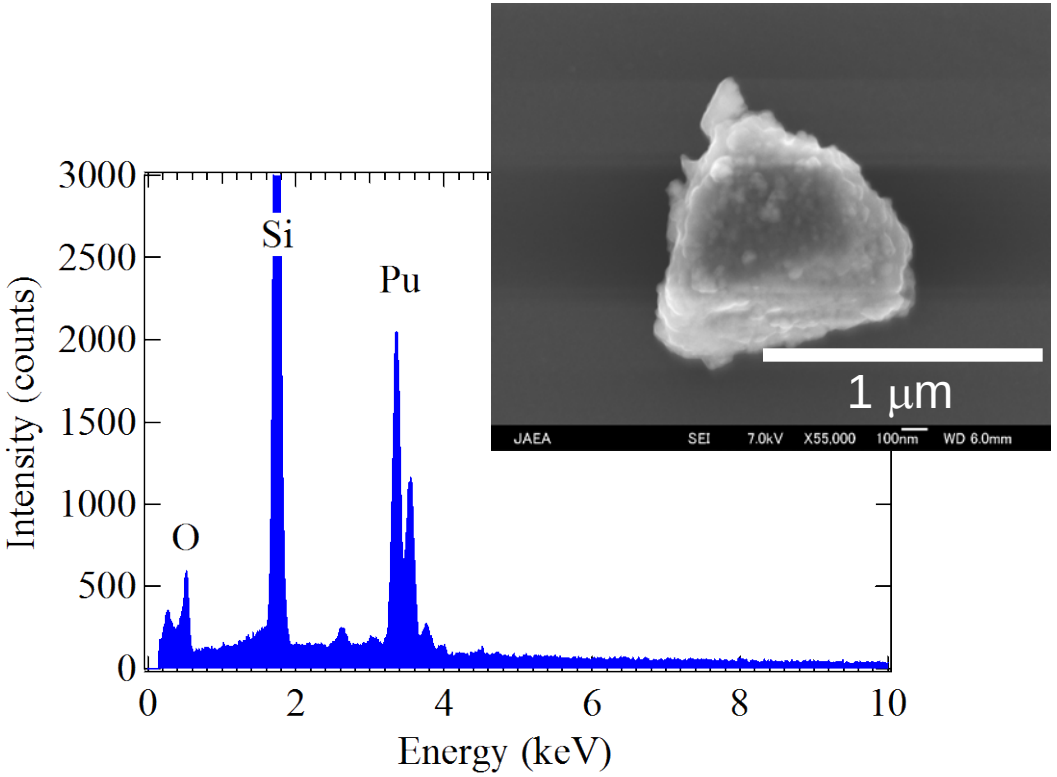
Sensitivity and samples

Count rates obtained by measuring NBL SRM 947 solution (5 ppt)

m/z	Counts / s	
	Without desolvation	desolvation
239	8775 ± 557	54393 ± 1078
240	2118 ± 129	13058 ± 279
241	388 ± 24	2376 ± 48
242	134 ± 10	835 ± 19

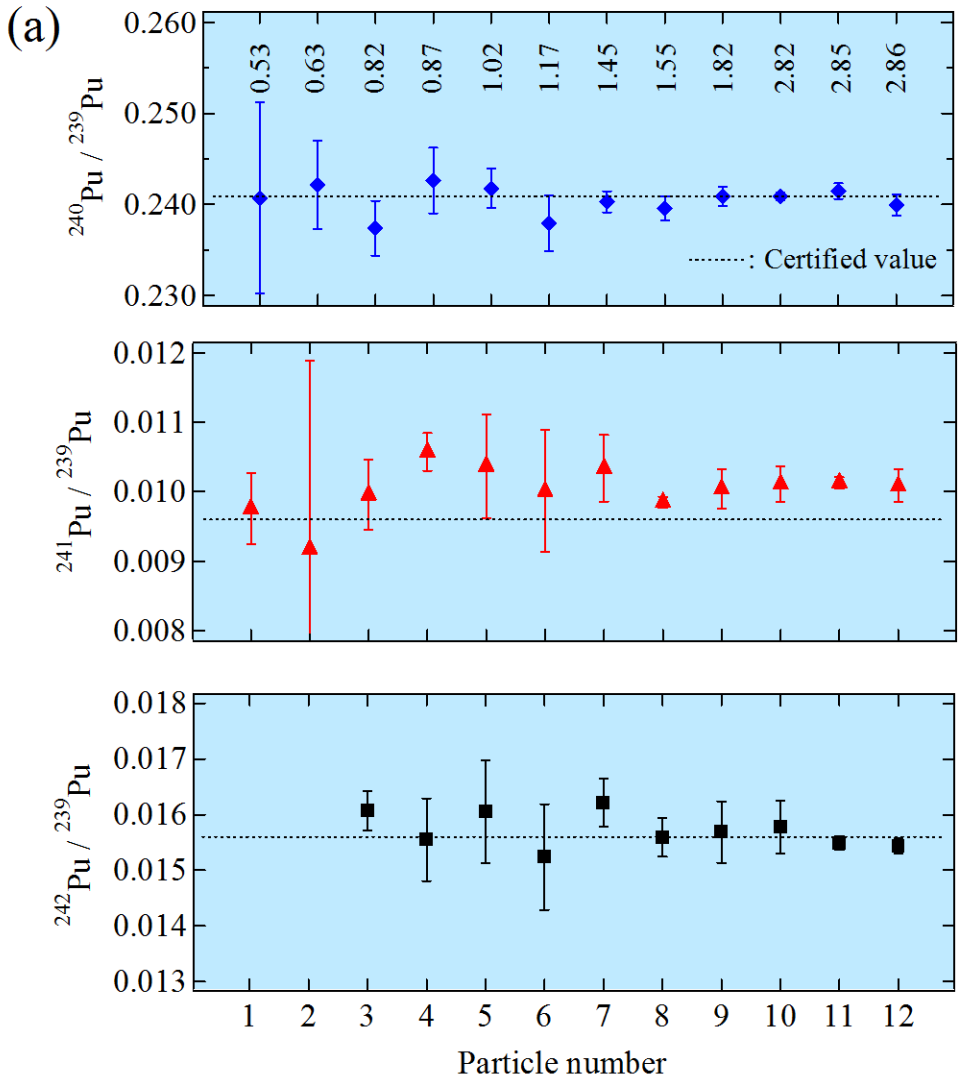
Without desolvation: 1700 cps/ppt
With desolvation: 10600 cps/ppt

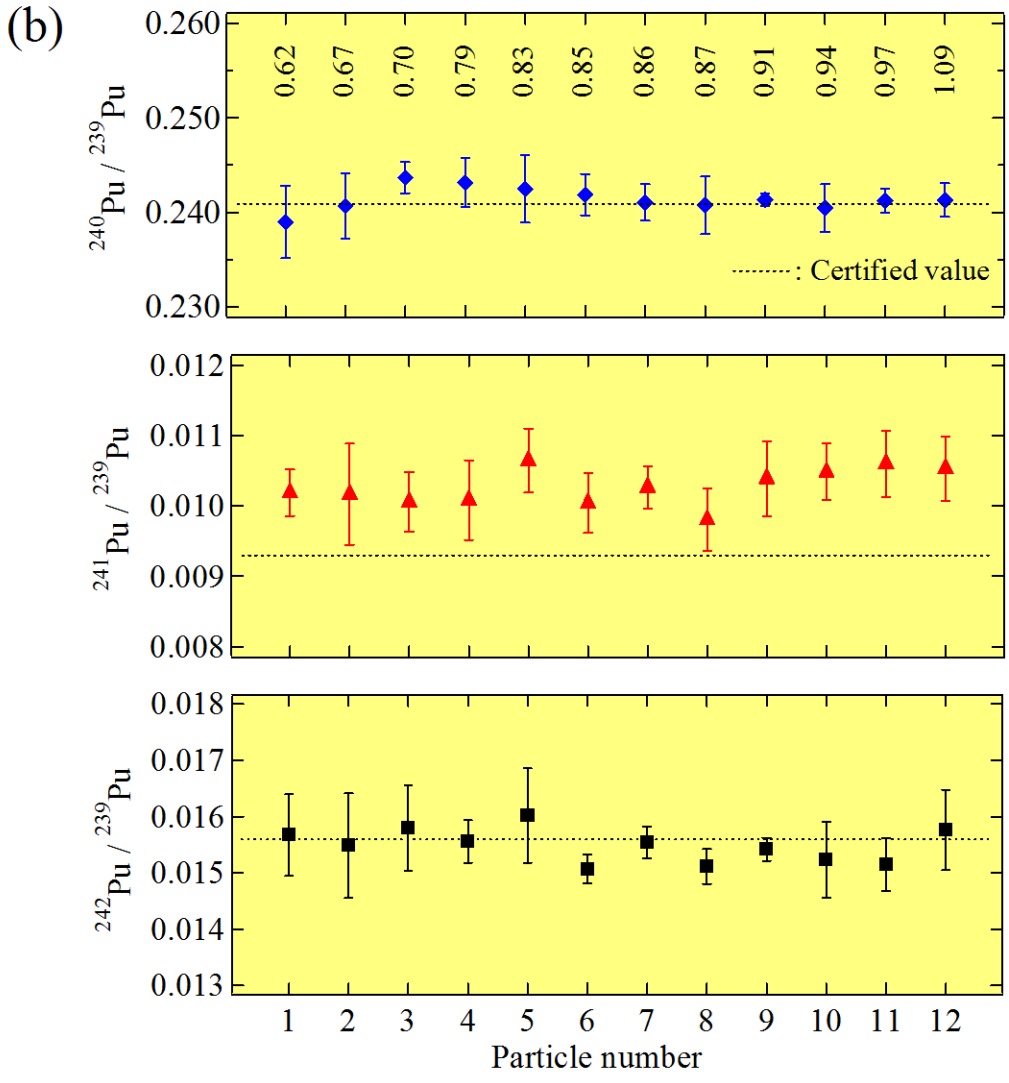
Plutonium oxide particles prepared from NBL SRM 947 standard material



SEM image and EDX spectrum of a Pu particle.

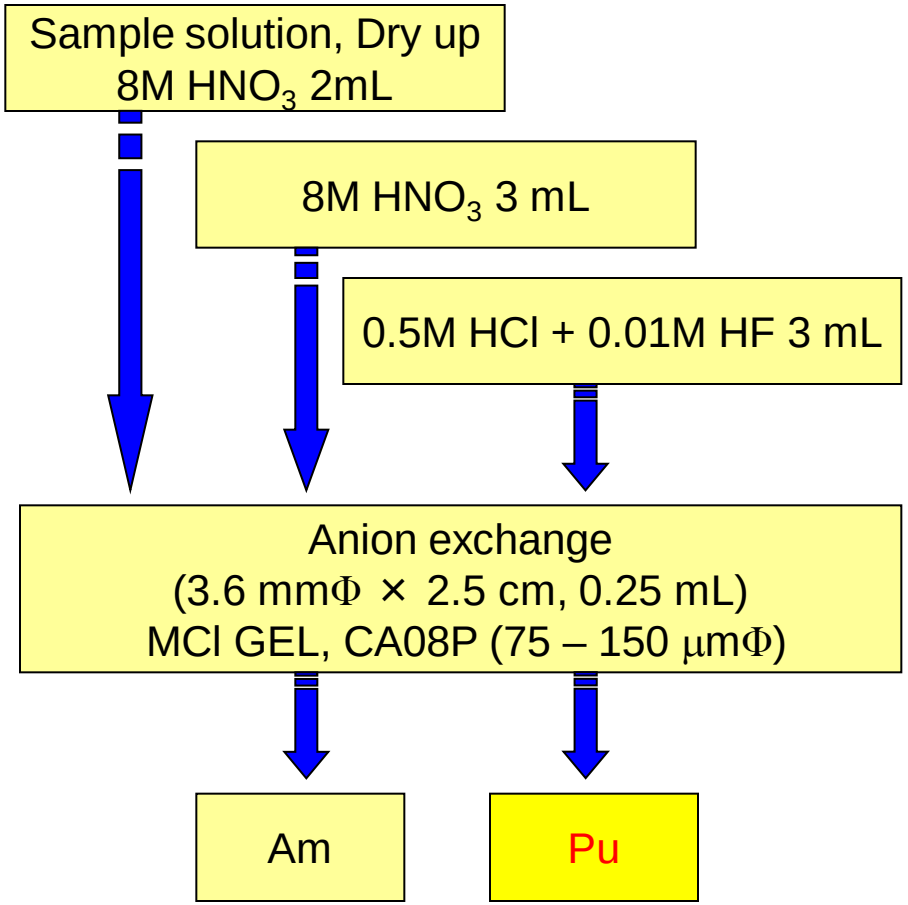
Results of isotope ratio analysis without chemical separation



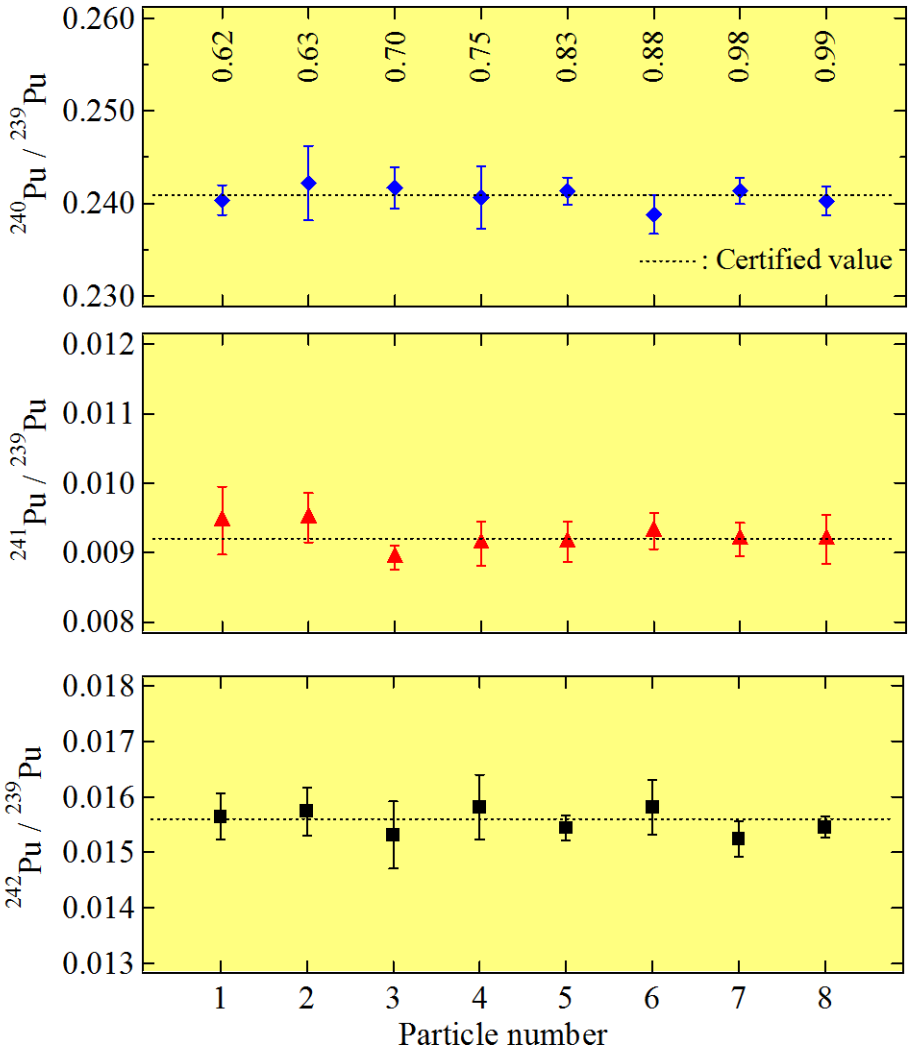


Isotope ratios of individual Pu particles measured by ICP-MS without (a) and with (b) desolvation sample introduction.

Results of isotope ratio analysis after chemical separation



Procedure of chemical separation



Isotope ratios of individual Pu particles measured by ICP-MS after chemical separation.

Conclusions

- SIMS and FT-TIMS techniques are successfully used for uranium particle analysis as a member of IAEA-NWALs.

- We have developed an analytical method for individual plutonium particles by a combination of chemical separation and ICP-MS.
- Accurate and precise isotope ratio results can be obtained, even if the particle size is less than 1 μm.

- This method is going to be applied to age determination of individual plutonium particles. ($^{241}Am/^{241}Pu$ ratio)

- Feasibility study will be carried out for age determination of (individual) uranium particles. ($^{230}Th/^{234}U$ ratio ???)