Some aspects on analysis of mixed U/Pu particles by different mass-spectrometric techniques

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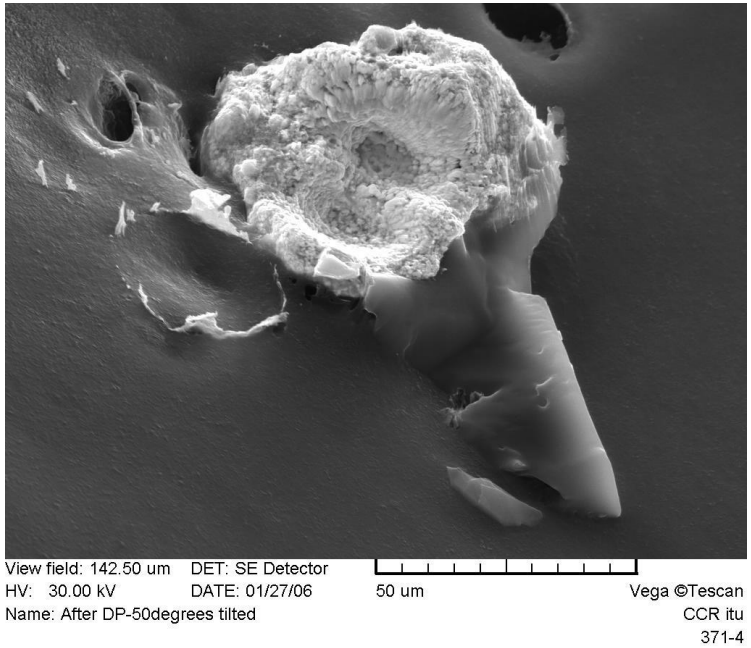
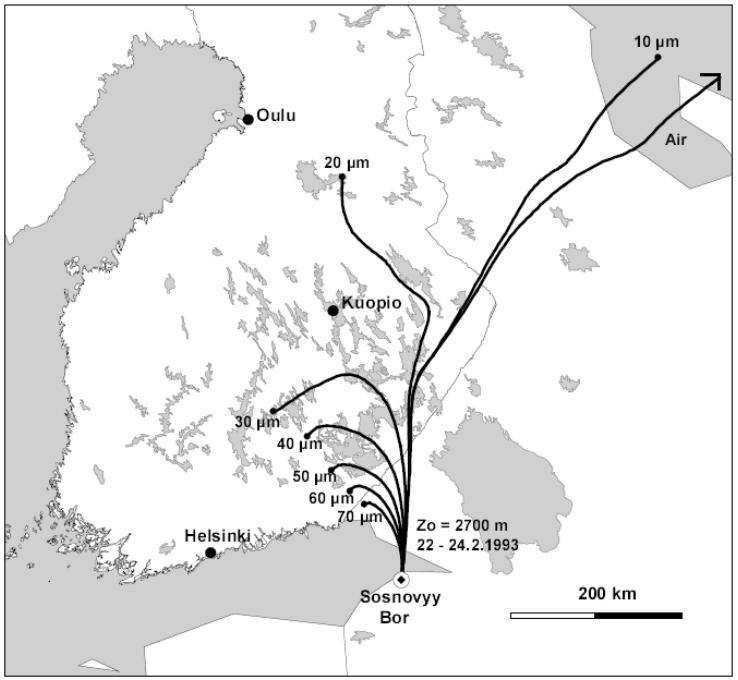


Why study large particles

- Formed in events involving explosions (e.g. the Chernobyl and the Thule accidents) and at nuclear installations (fuel fabrication, power and reprocessing plants)
- The fingerprint can reveal the source terms
- They carry the main portion of the mass released, however they are very rare, leading to a heterogeneous activity distribution
- Mostly a close-in fallout problem
- Contain geochemical “memory”
- Potential radiation hazard as they may lead to a high local absorbed dose



R.Pöllänen. Ph.D thesis, 2002

Bulk versus particle analysis

Safeguard perspective

- It is the particles originating from the nuclear facility that are the fingerprints of the facility's activities - bulk material will blur and bias the information.

Radiological and Forensic perspective

- In nuclear events involving explosions or fire, most of the material will be released as particles.
- If several sources are present, the bulk sample will show the mean of the sources.
- Forensic parameters can be obtained easier from particles than from bulk samples

The safeguard perspective

In safeguards the uranium and plutonium isotopic compositions are used to check that member states follow the Non-Proliferation Treaty (NPT).

Different categories of U and Pu			
Category	$^{235}U/^{238}U$(%)	$^{240}Pu/^{239}Pu$ (%)	
Depleted uranium (DU)	< 0.71		
Natural uranium	0.71		
Low enriched uranium (LEU)	0.71-20 (usually 3-5)		
Highly enriched uranium (HEU)	> 20 (usually 90)		
Weapons-grade uranium (WGU)	> 90		
Reactor-grade plutonium (RGPu)		> 19	
Fuel-grade plutonium (FGPu)		7-19	
Weapon-grade plutonium (WGPu)		< 7	
Super-grade plutonium (SGPu)		< 3	

The radiological perspective

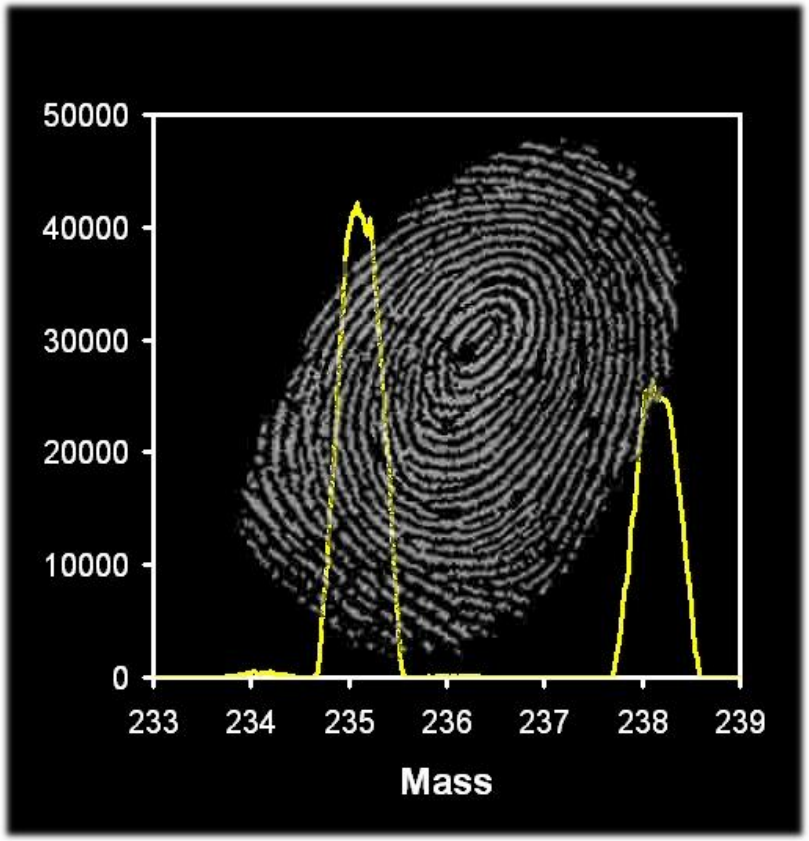
- With radiological studies** it is not only the elemental and isotopic composition that is of interest, but also the chemical form and radionuclide distribution. This information is essential for performing adequate dose assessments and for predicting the long term environmental behaviour of the contamination.

** (refers both to the radio-ecological and to the emergency preparedness studies in this talk)

Nuclear fingerprint

or

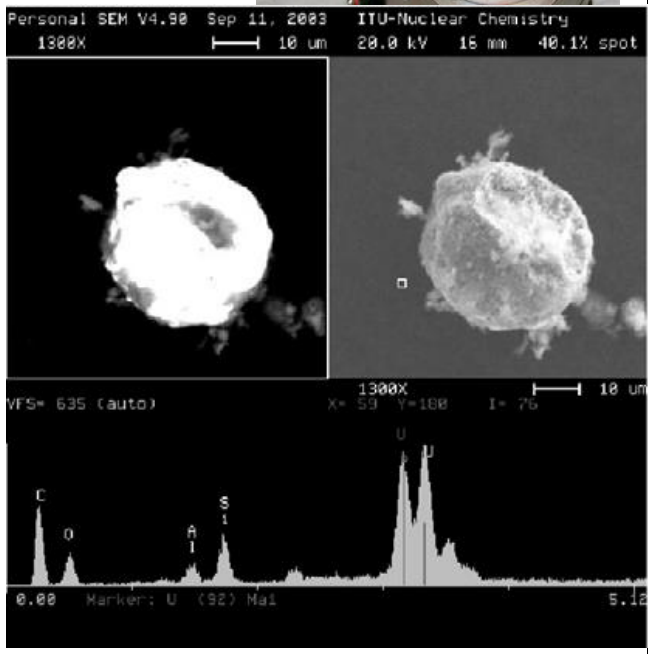
Nuclear material characteristic



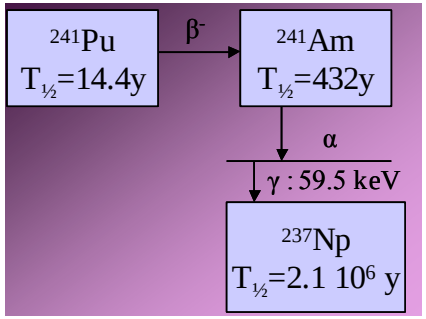
Trace of the source

Fingerprinting techniques applied to particles

- Finding and identification
  - Image techniques
    - (image plates, beta camera, SEM)
- Analytical techniques
  - Elemental and isotopic techniques:
    - SEM-EDX
    - Radiometric techniques:
      - (Gamma and alpha spectrometry)
    - **Mass-spectrometric techniques:**
      - **(ICP-MS, AMS, and SIMS**)
    - Synchrotron radiation techniques and PIXE
      - (µ-XRF, µ-XRF tomography, µ-XANES, µ-PIXE)



Particle separation and localization techniques



Pu/U hot particle

Sampling splitting

↓

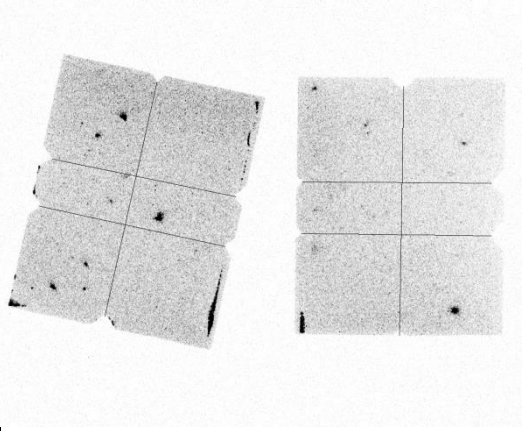
Fixation on adhesive carbon tape

↓

Measurements for identification

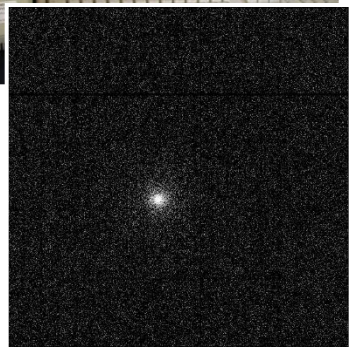
Impactor and SIMS for U particles

Tritium image plates



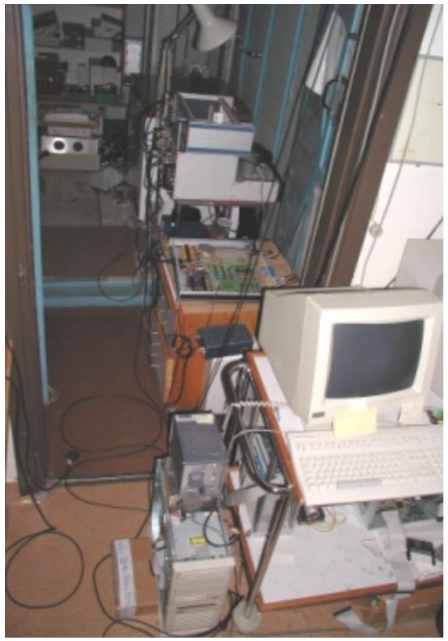
1 week exposure time

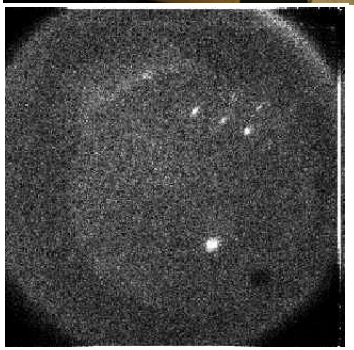
IDE Bioscope



20 h acquisition time

Beta camera



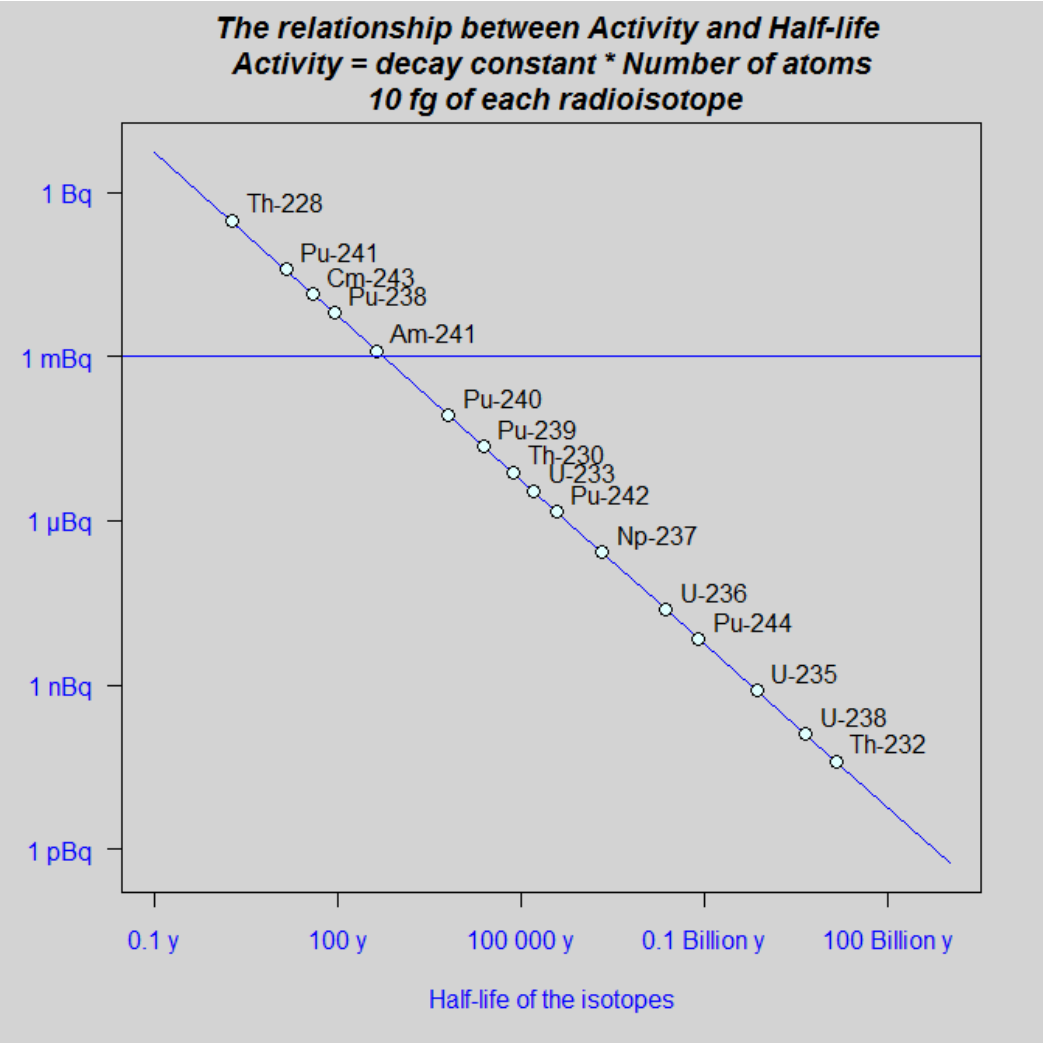


1 h acquisition time

Eriksson, et al. *Nucl. Instrum. Methods A* **2002**, *488*, 375–380.

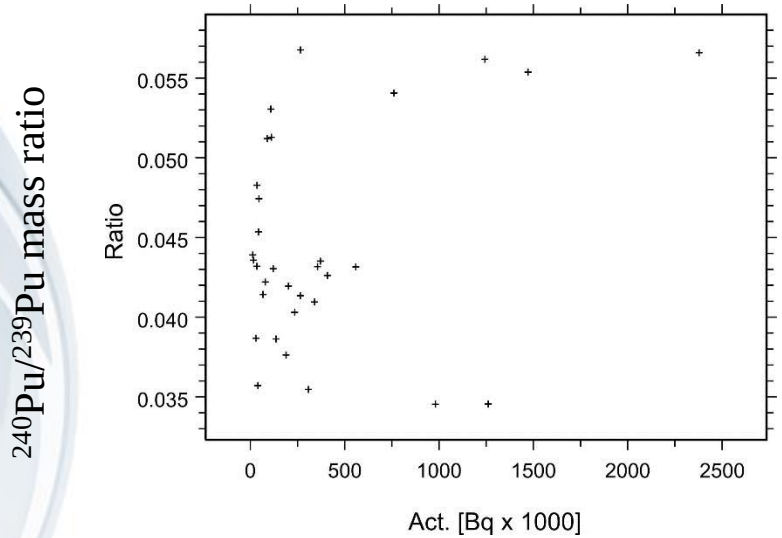
Mass-spectrometric techniques

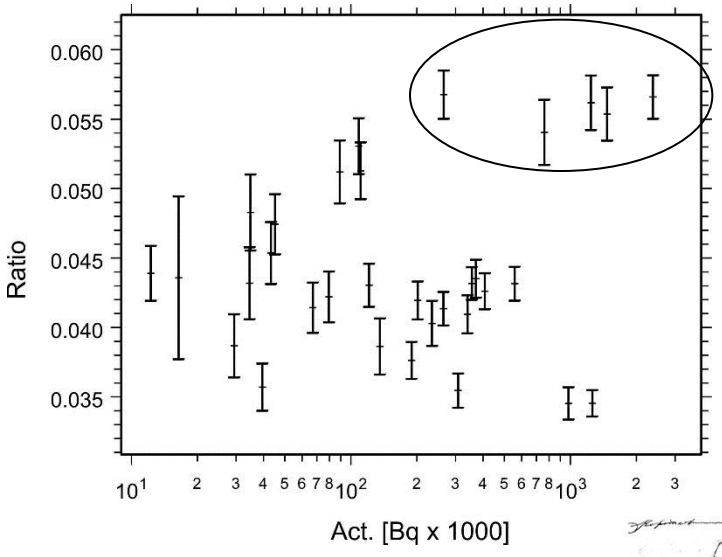
- Higher sensitivity to long lived radionuclides than radiometric techniques
- Isotopic ratios
- Mass spectra
- Depth profile (SIMS)



ICP-MS on bulk soil samples

Pu isotopic ratio results from Thule soil samples





In soil contaminated with U material it is very difficult to find the source U fingerprint from bulk soil sample analysis, as natural U is present everywhere causing a bias in the fingerprint.

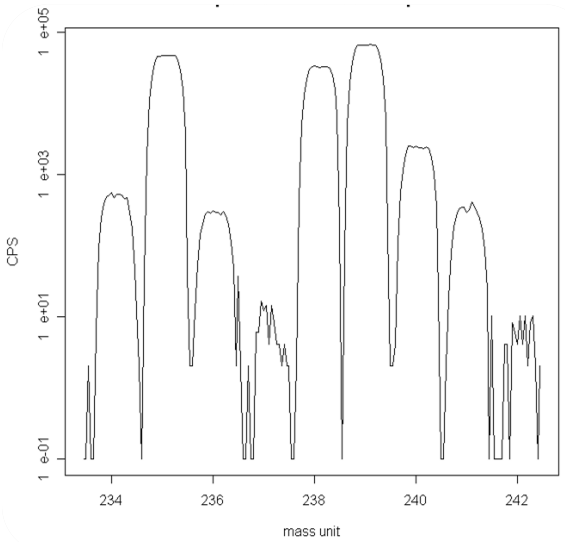
ICP-MS on particles

Radiochemistry: Risk for cross contamination especially from U

Particle dissolution in ultrapure acids:

* 30 x (3 drops HNO3 +1 drop HF)
* 30 drops HNO3 +8 drops in a teflon bomb for 16 hours

- no radiochemical separation after dissolution
- tracer -> Pu and U concentration can be determined simultaneously
- no correction for Hydrides (peak stripping) can de done
- (no real problems for the main isotopes but for the minor e.g. U-236)
- cross contamination, biasing ratios, mainly a problem for U



Eriksson et al 2008 Environ. Sci. Technol

TABLE 1. Pu Isotope Content and Ratios in the Particles on Mass and Activity Basis As Measured by HR-ICP-MS

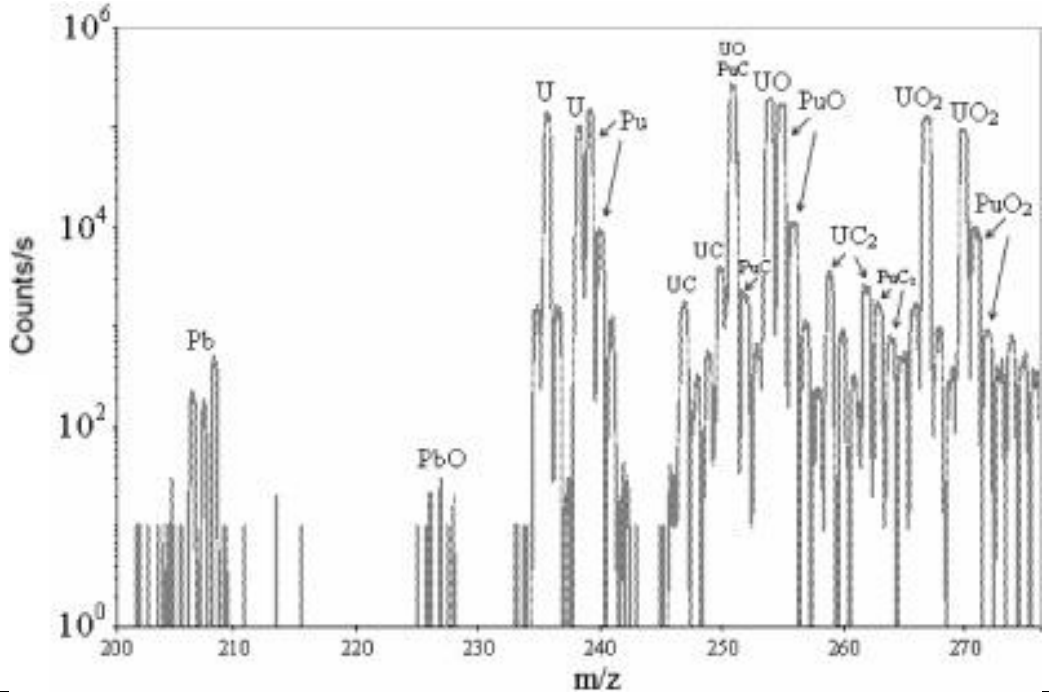
particle id	$^{239+240}$Pu (ng)	^{239}Pu (ng)	^{240}Pu (ng)	^{240}Pu/^{239}Pu atom ratio
TPA	2.51 ± 0.09	2.380 ± 0.088	0.133 ± 0.006	0.0544 ± 0.0017
TPB	4.37 ± 0.16	4.14 ± 0.15	0.232 ± 0.009	0.0558 ± 0.0013
TPC	10.66 ± 0.39	10.10 ± 0.37	0.559 ± 0.022	0.0559 ± 0.0011
TPD	28.9 ± 1.1	27.4 ± 1.0	1.521 ± 0.060	0.0554 ± 0.0012
TPE	32.2 ± 1.2	30.5 ± 1.1	1.709 ± 0.067	0.0541 ± 0.0011

Particle	^{235}U/^{238}U	^{235}U/^{238}U (first run)
TPA	1.112	0.653
TPB	0.832	0.343
TPC	0.858	0.355
TPD	1.143	0.493
TPE	1.148	0.029

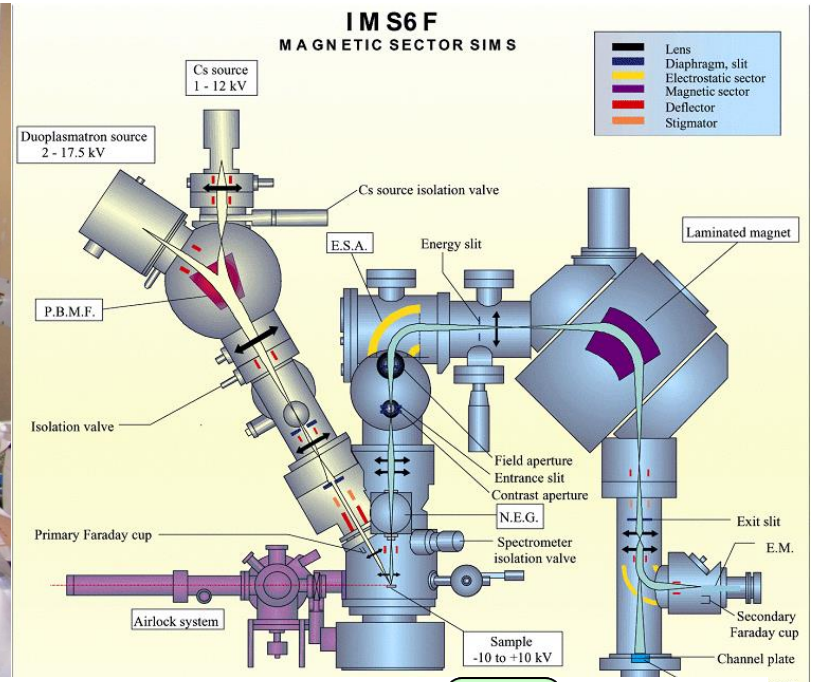
particle id	^{235}U (ng)	^{238}U (ng)	^{235}U/^{238}U atom ratio	^{235}U/^{239}Pu mass ratio	sampling date
TPA	9.28 ± 0.63	8.34 ± 0.57	1.112 ± 0.005	3.90 ± 0.30	1979−8−23
TPB	10.00 ± 0.68	12.02 ± 0.82	0.832 ± 0.003	2.41 ± 0.19	1984−8−11
TPC	13.98 ± 0.95	16.29 ± 1.11	0.858 ± 0.004	1.38 ± 0.11	1984−8−11
TPD	74.65 ± 5.06	65.34 ± 4.44	1.143 ± 0.004	2.73 ± 0.21	1979−8−23
TPE	34.75 ± 2.36	30.27 ± 2.07	1.148 ± 0.006	1.14 ± 0.09	1997−8−25

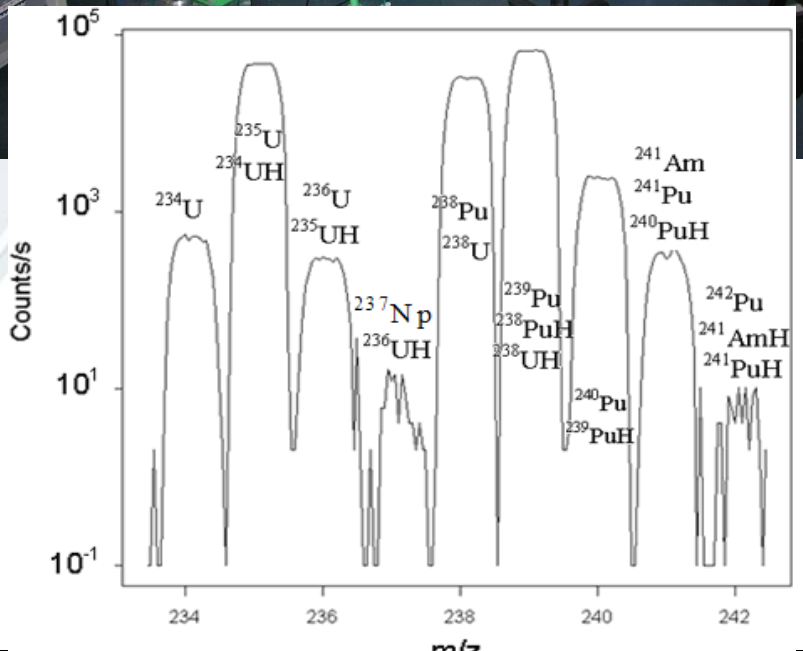
SIMS

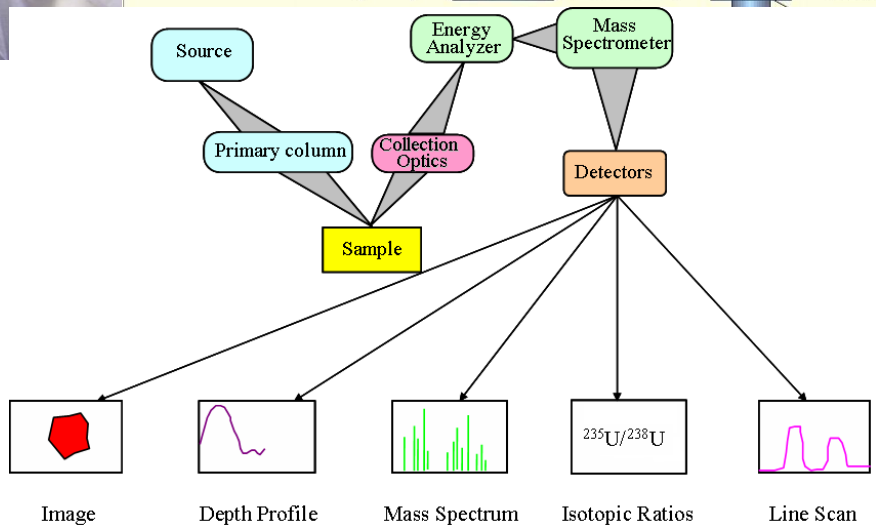
- no chemical treatment
- no problem with cross-contamination
- U and Pu isotopes can be measured simultaneously, however no information on the relative elemental ratio (rsf)
- hydrides a problem



The SIMS technique







SIMS Results-Isotopic Ratio

Nuclear fingerprints of the Thule accident

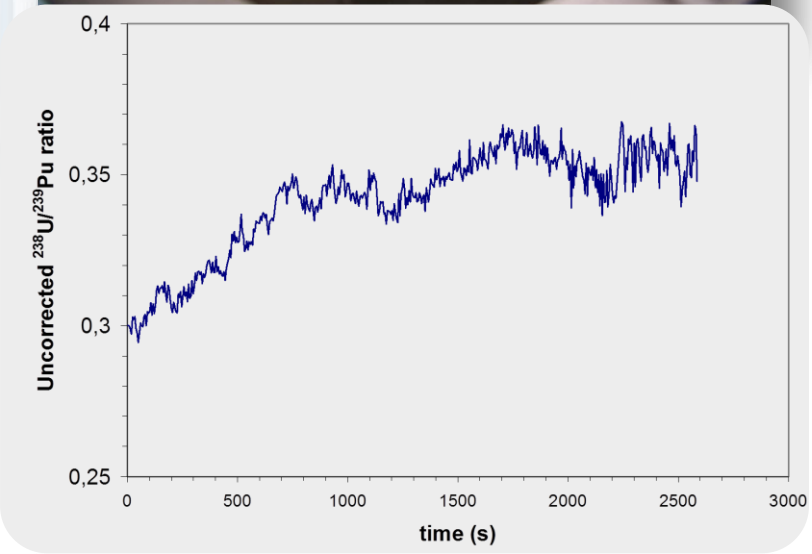
	$^{234}U/^{235}U$	$^{236}U/^{235}U$	$^{235}U/^{238}U$	$^{240}Pu/^{239}Pu$	$^{242}Pu/^{239}Pu$	$(^{241}Pu+^{241}Am)/^{239}Pu$
Thule68−1	0.0108± 0.0002	0.0090± 0.0004	1.355± 0.006	0.0578± 0.0005	0.00018± 0.00002	0.0082± 0.0002
Thule68−2	0.0108± 0.0001	0.0129± 0.0003	0.893± 0.002	0.0457± 0.0004	0.00011± 0.00003	0.0034± 0.0001
Thule68−3	0.0111± 0.0003	0.0142± 0.0004	1.199± 0.006	0.0580± 0.0006	0.00028± 0.00003	0.0099± 0.0002
Thule79−4	0.0107± 0.0002	0.0048± 0.0002	1.440± 0.006	0.0364± 0.0004	0.00008± 0.00002	0.0052± 0.0002
Thule79−5	0.0112± 0.0004	0.0104± 0.0003	1.302± 0.010	0.0631± 0.0008	0.00045± 0.00006	0.0062± 0.0002
Thule79−6	0.0107± 0.0008	0.0103± 0.004	1.032± 0.012	0.0284± 0.0004	0.00003± 0.00002	0.0024± 0.0001
Thu975380−5nr1	0.0109± 0.0003	0.0102± 0.001	1.376± 0.009	0.0580± 0.0007	0.00017± 0.00004	0.0106± 0.0003
Ratio range	0.0107-0.011	0.0048-0.0129	0.893-1.440	0.0364-0.0631	0.00003-0.00045	0.0034-0.0106

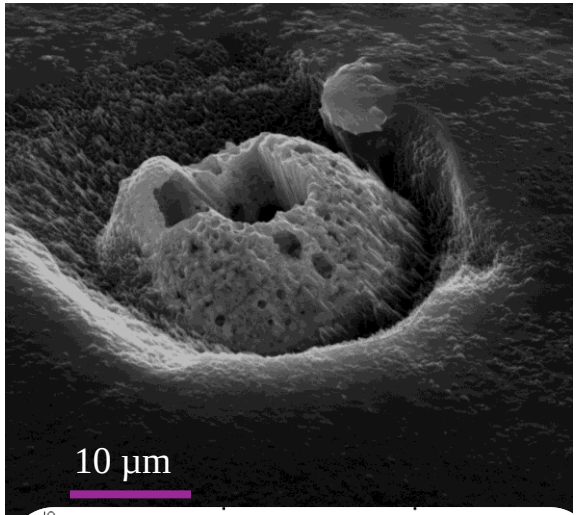
WGU | WGPu

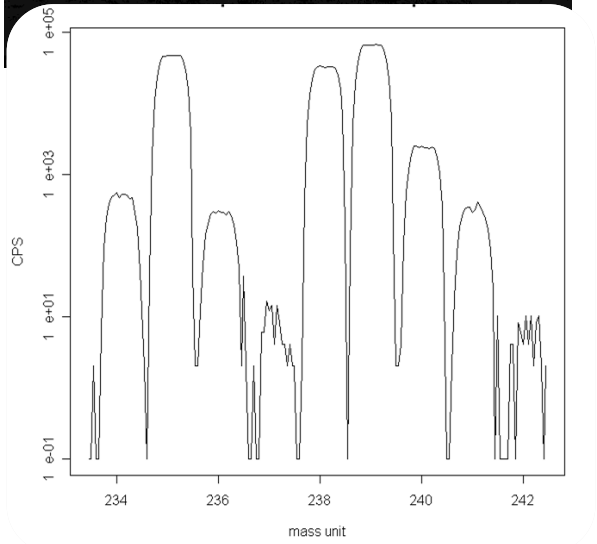
The different ratios indicate that the particles originated from different weapon components involved in the Thule accident

Ranebo et al 2007 Microsc. Microanal

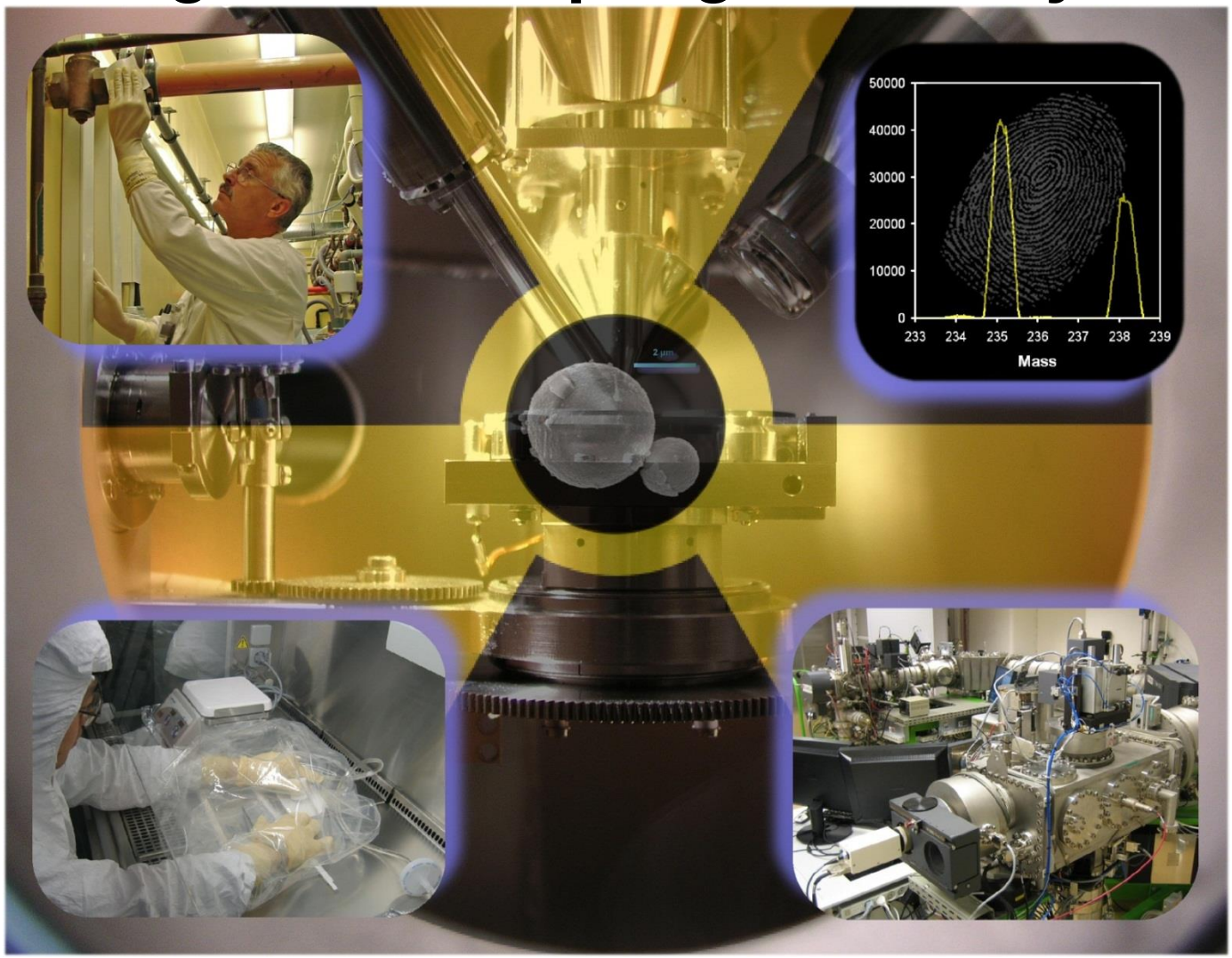
SIMS depth profile





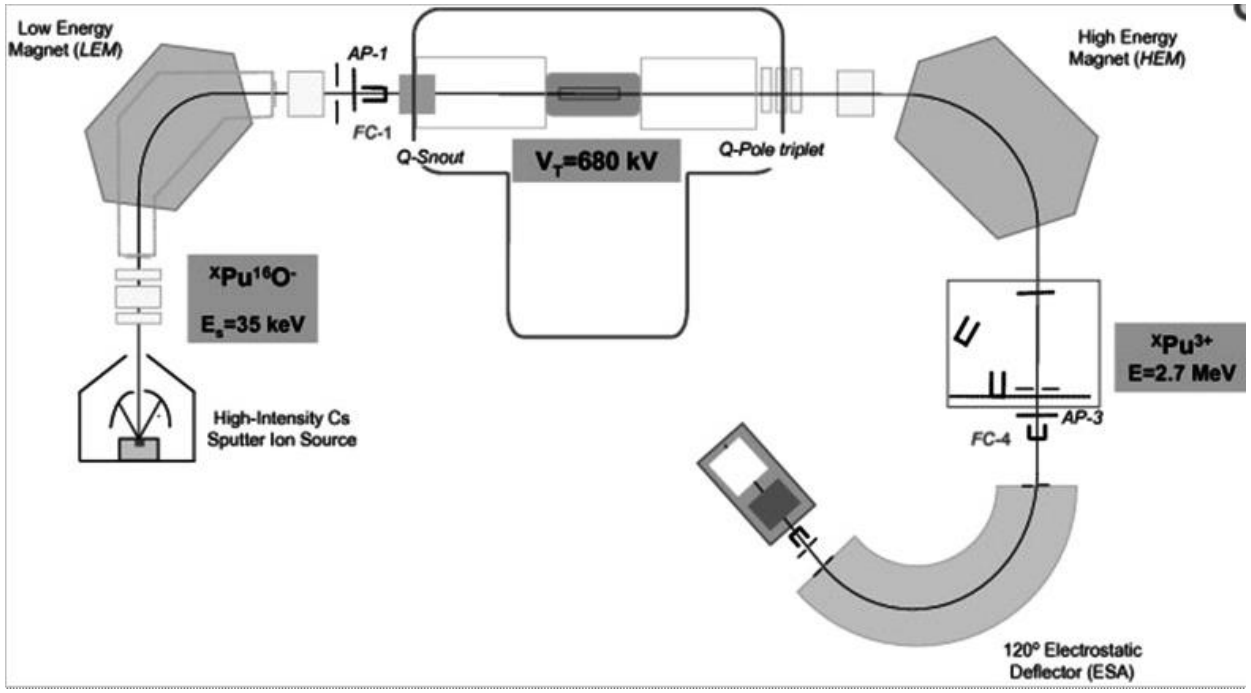


Safeguards sampling and analysis

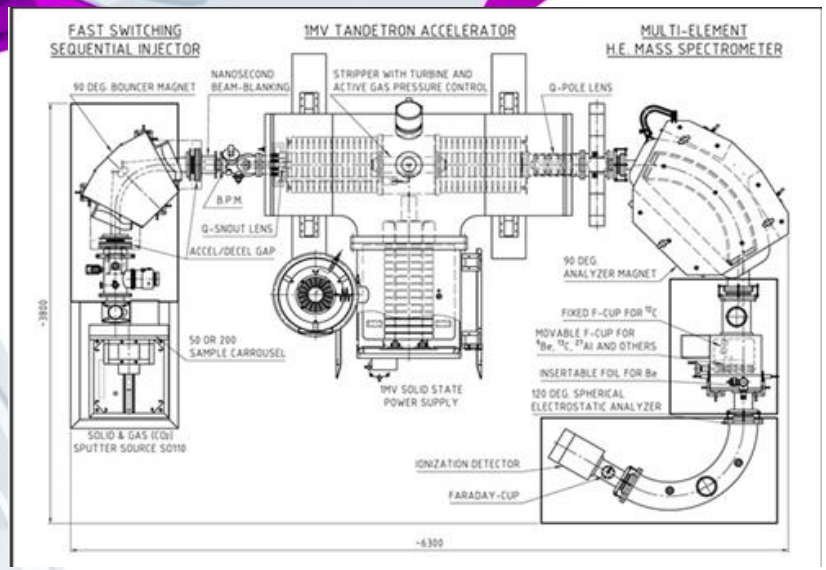


AMS

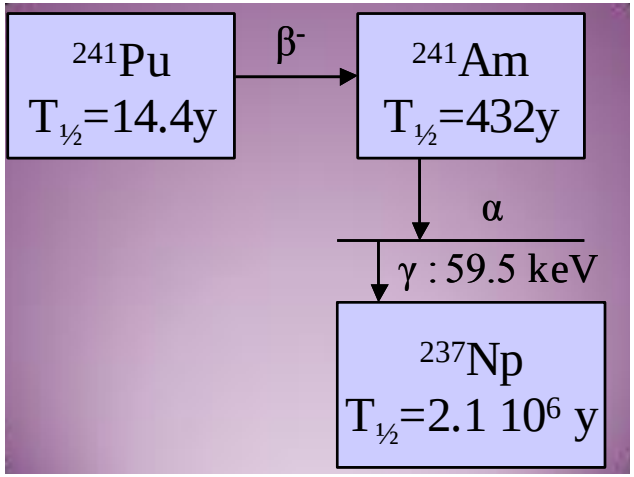
- Particle dissolution followed be radiochemical separation of U and Pu
- source preparation (cathode)
- no problem with hydrides and polyatomic interferences



AMS on particles



- Minor isotops determination
- Age



Summary

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- - tracer -> Pu and U concentration can be determined simultaneously
- - no correction for Hydrides (peak stripping) can de done (no real problems for the main isotopes but for the minor e.g. U-236
- - cross contamination, biasing ratios, mainly a problem for U

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