



Italian National Agency for New Technologies,  
Energy and Sustainable Economic Development

## Triskem Users Meeting 2022

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# Radioanalytical determination of actinides in biological samples by extraction chromatography and alpha spectrometry

**Dolores Arginelli – Radiation Protection Institute – Integrated Laboratory of  
Radioactivity Measurement and Monitoring - CR Saluggia (VC) - Italy**  
*[dolores.arginelli@enea.it](mailto:dolores.arginelli@enea.it)*



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# IRP MIR laboratories



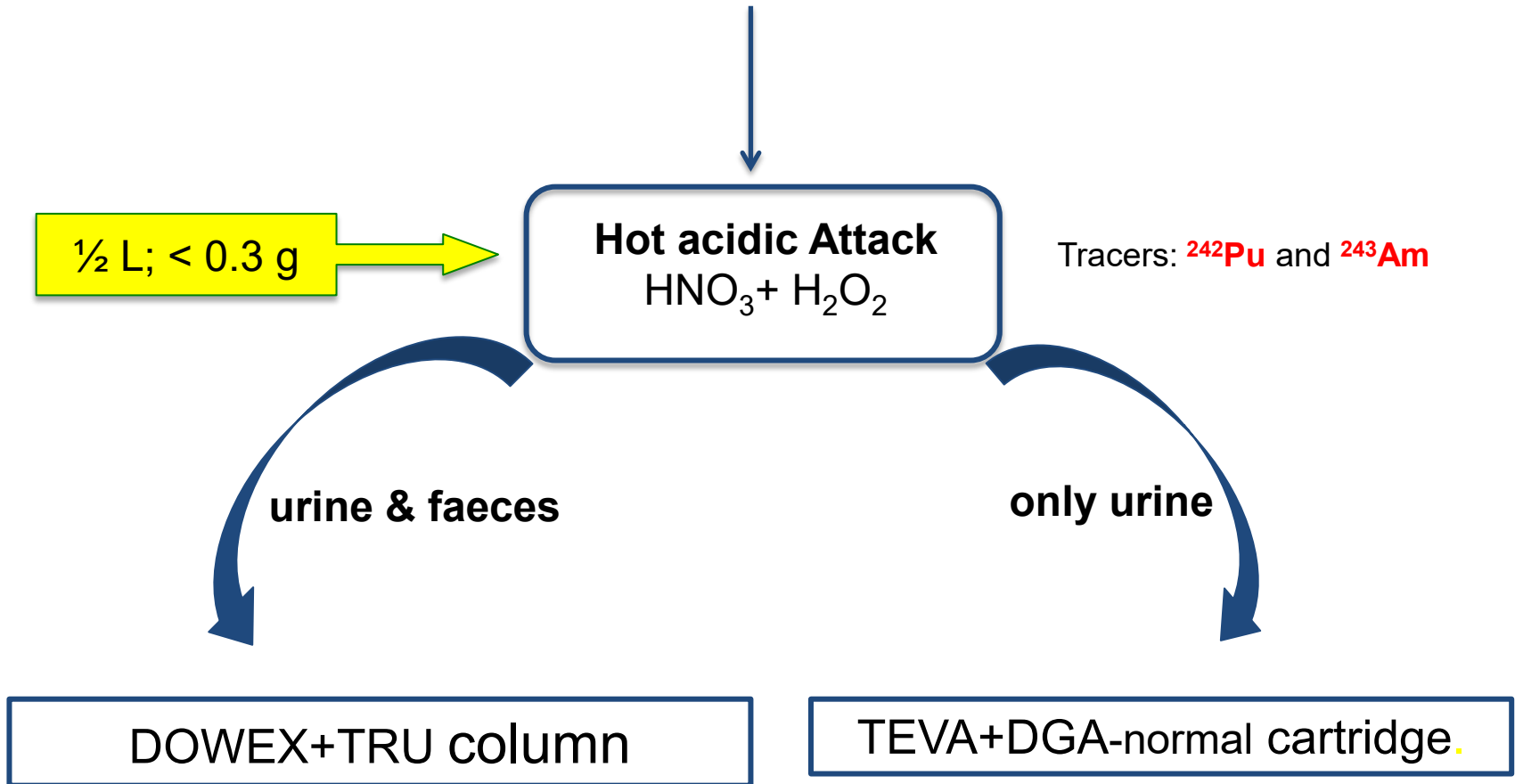
# Tasks of the Integrated Laboratory

- Physical surveillance for the decommissioning of past Italian NPP towards human health and the environment
- radiotoxicological analyses (Saluggia & Casaccia)
- Determination of Pu, Am and Cm in biological samples (urine and faeces)

# Routine bioassay analyses

- Very low levels of detection (LLD);
- Accuracy and reliability of measurement data;
- Good separation factors from chemical and radiochemical interferences;
- Development of selective, accurate, sensitive procedures

# Urine/Faecal ash



# Pre - treatment of samples (DOWEX + TRU column)

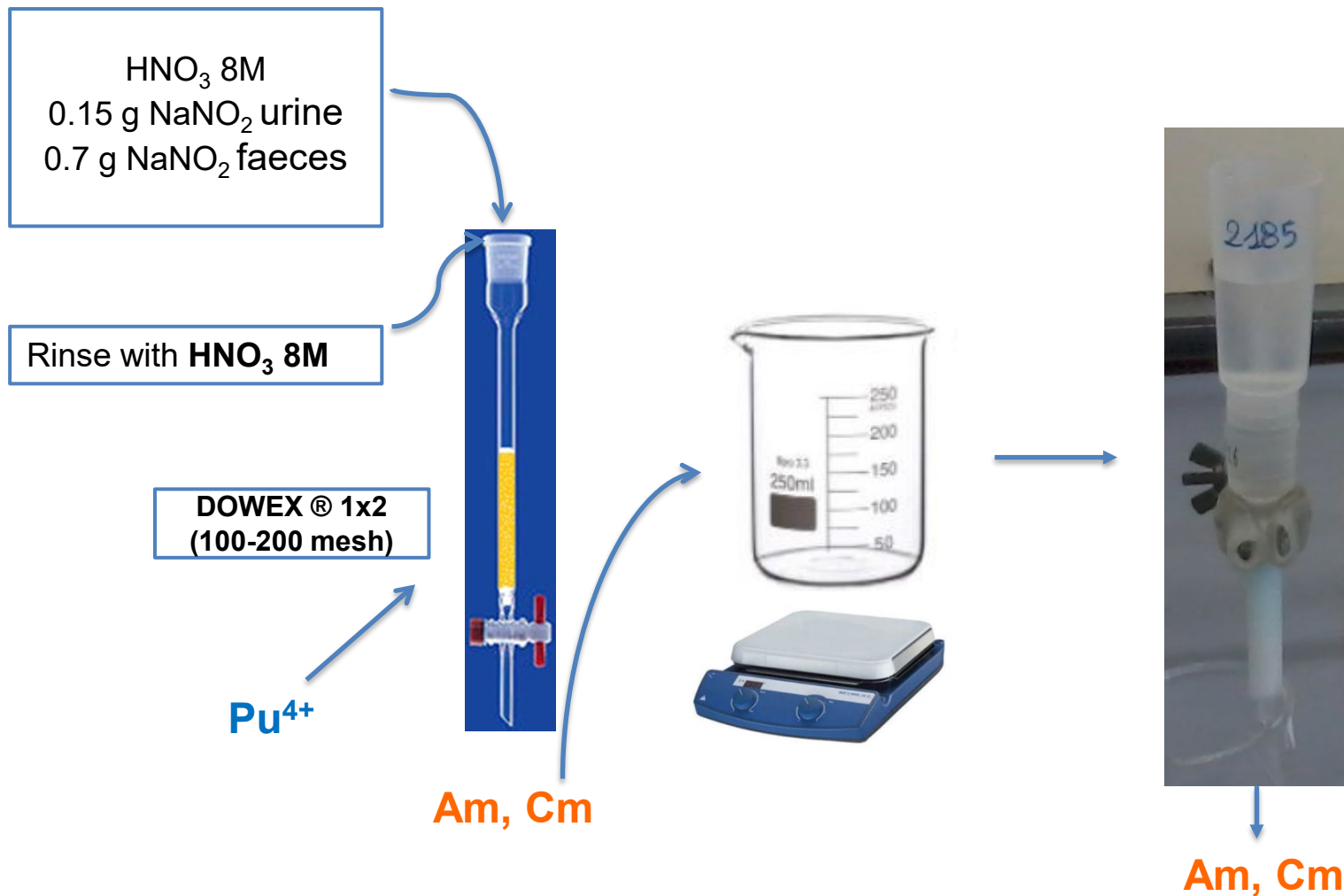
## URINE

1.  $\frac{1}{2}$  L sample + HNO<sub>3</sub> (120 mL) + H<sub>2</sub>O<sub>2</sub> (5mL)
2. **Spiking** with <sup>242</sup>Pu <sup>243</sup>Am tracers
3. **Mineralization** at 98°C under stirring for 2h, till clear yellow solution
4. Ca(NO<sub>3</sub>)<sub>2</sub> 3M (2 mL) + H<sub>3</sub>PO<sub>4</sub> (5 mL)
5. pH 8.5 - 9 with NH<sub>3</sub>
6. 1 night **digestion, centrifugation, dissolution** in HNO<sub>3</sub> and **mineralisation** with HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>
7. **dissolution** with 8M HNO<sub>3</sub>  
+ 0.15 g NaNO<sub>2</sub>

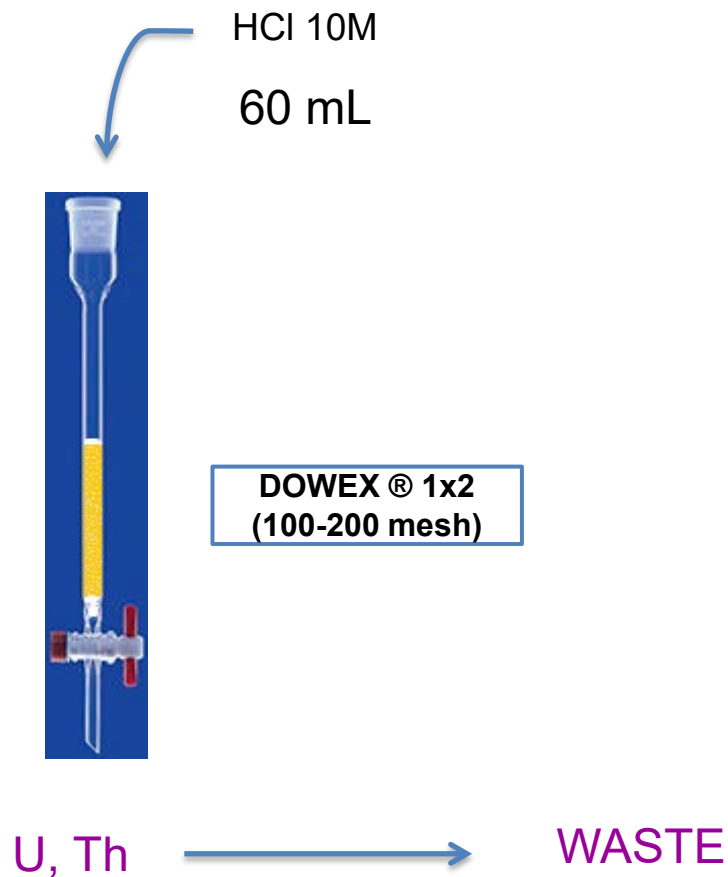
## FAECES

1. **Calcination** at 600°C for 7 h
2. **3 g faecal ash spiked with <sup>242</sup>Pu <sup>243</sup>Am tracers**
3. **Mineralization** of fecal ash with HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> let to dry and put in muffle at 500°, repeated steps until carbon free white residue
4. **dissolution** with 8M HNO<sub>3</sub>  
+ 0.7 g NaNO<sub>2</sub>

# DOWEX+TRU column

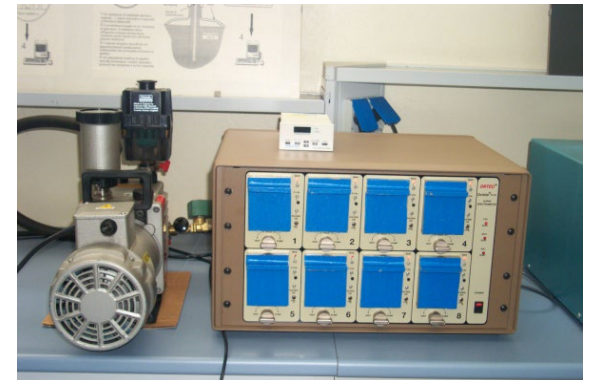
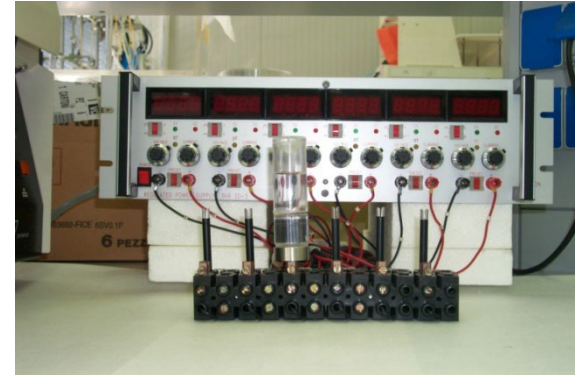
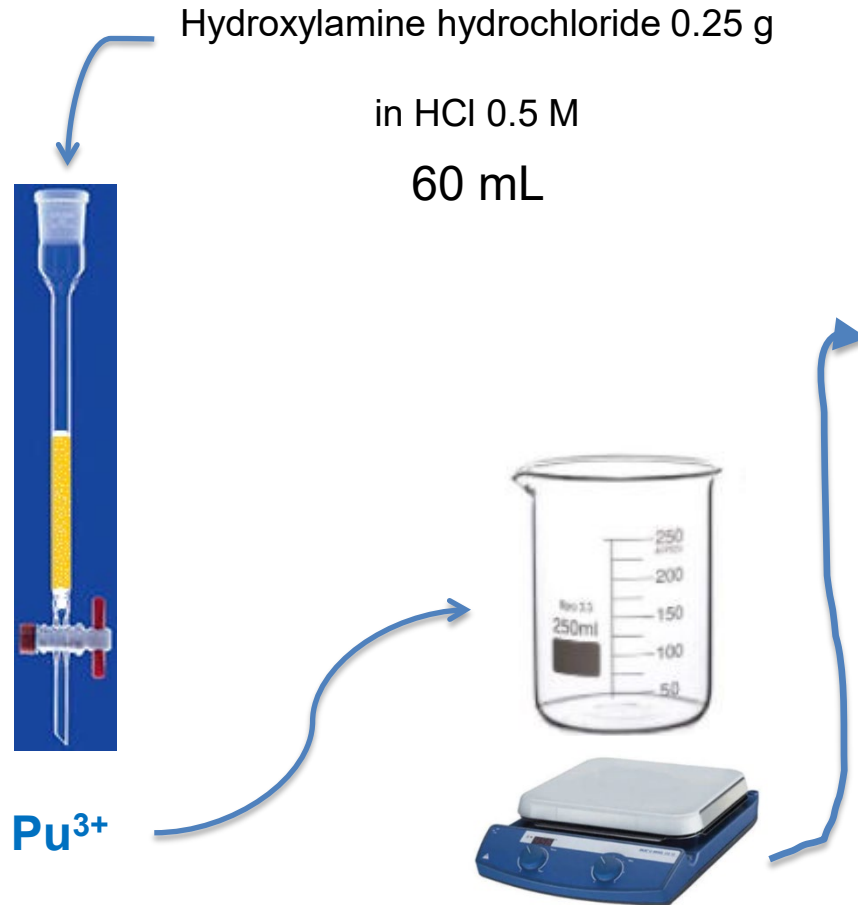


# DOWEX+TRU column





# DOWEX+TRU column



Alpha Spectrometry

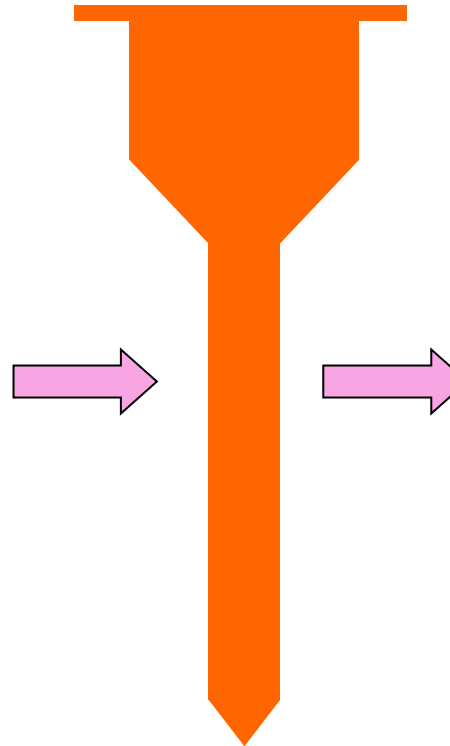
# Extraction of Am and Cm

## TRU COLUMN

0.6 cm I.D.

5 mL wet volume

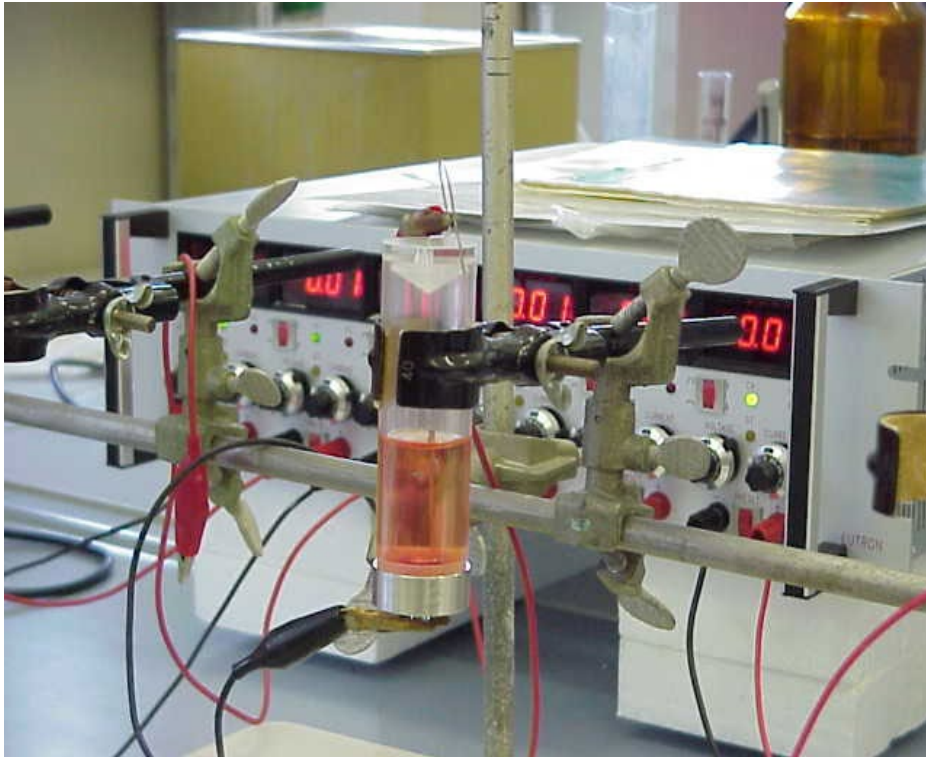
1. **Conditioning** with **2M HNO<sub>3</sub>**  
(10 mL);
2. **residue dissolution** in **2M HNO<sub>3</sub>**  
(15 mL ); **ascorbic acid** (0.1g) (II)
3. **Rinse** with **2M HNO<sub>3</sub>** (20 mL);
4. **Rinse** with **0.5 M HNO<sub>3</sub>** (5 mL);
5. **Elution of Am & Cm** with **9M HCl**  
(3 mL) and **4M HCl** (20 mL)



**Electrodeposition** on  
stainless steel planchets  
at 0.75 A for 90'

High resolution **alpha**  
**spectrometry** (600000 s)

# Electrodeposition

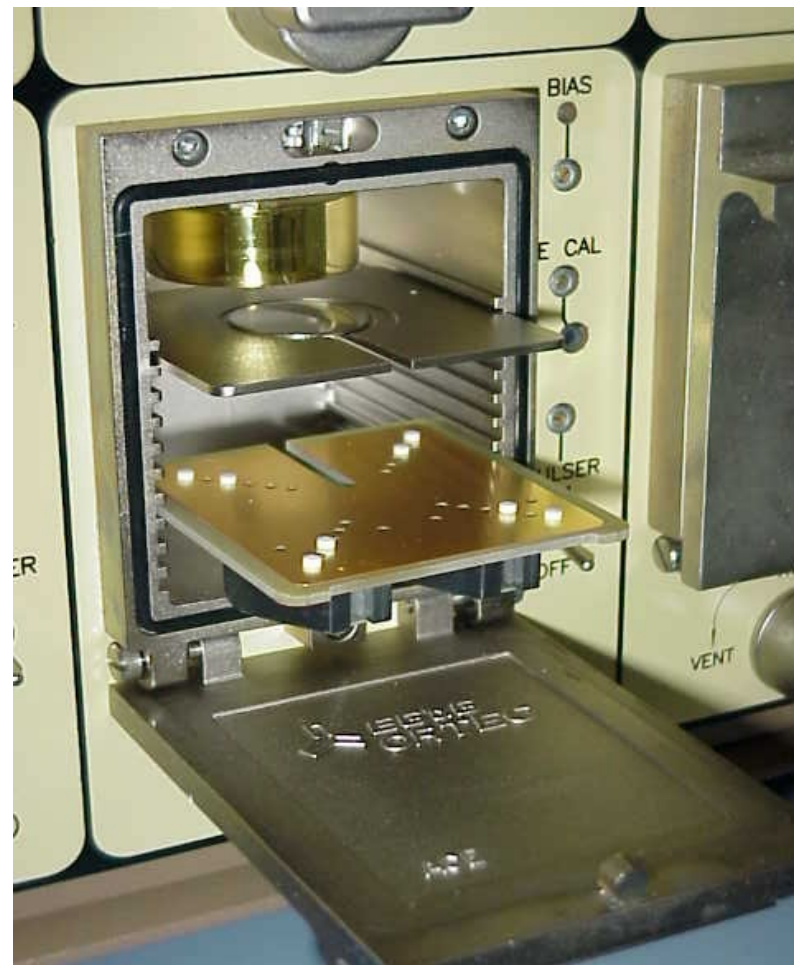


**Stable current at 0,75 A  
for 90'**



# High Resolution Alpha Spectrometry

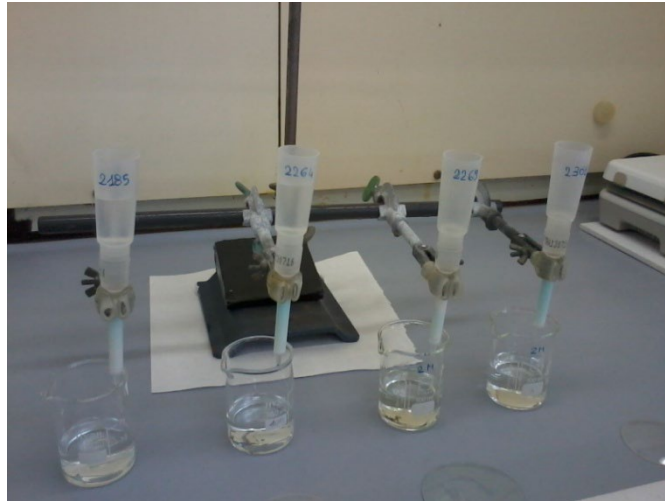
- **Passivated Implanted Planar Silicon Detectors (PIPS)**
- Detection **active** surface:  
**450 mm<sup>2</sup>**
- Efficiency **at 4.5 mm 25 %**  
**at 3 mm : 33 %**
- Energy resolution: **25 - 30 keV**  
**35 - 40 keV**
- keV/ch ratio: **5**
- **Counting Time: 600000 s**



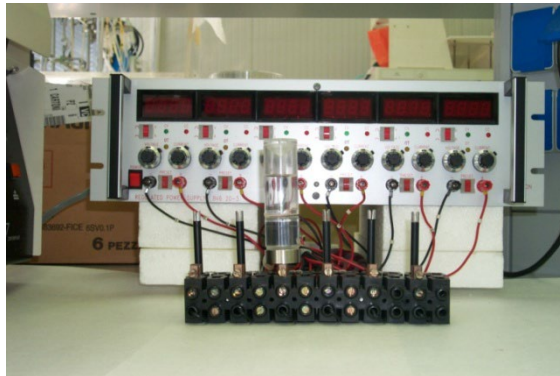
# Analytical techniques



**DOWEX  
+  
TRU  
columns**



**TEVA+DGA  
cartridges  
+ vacuum box**



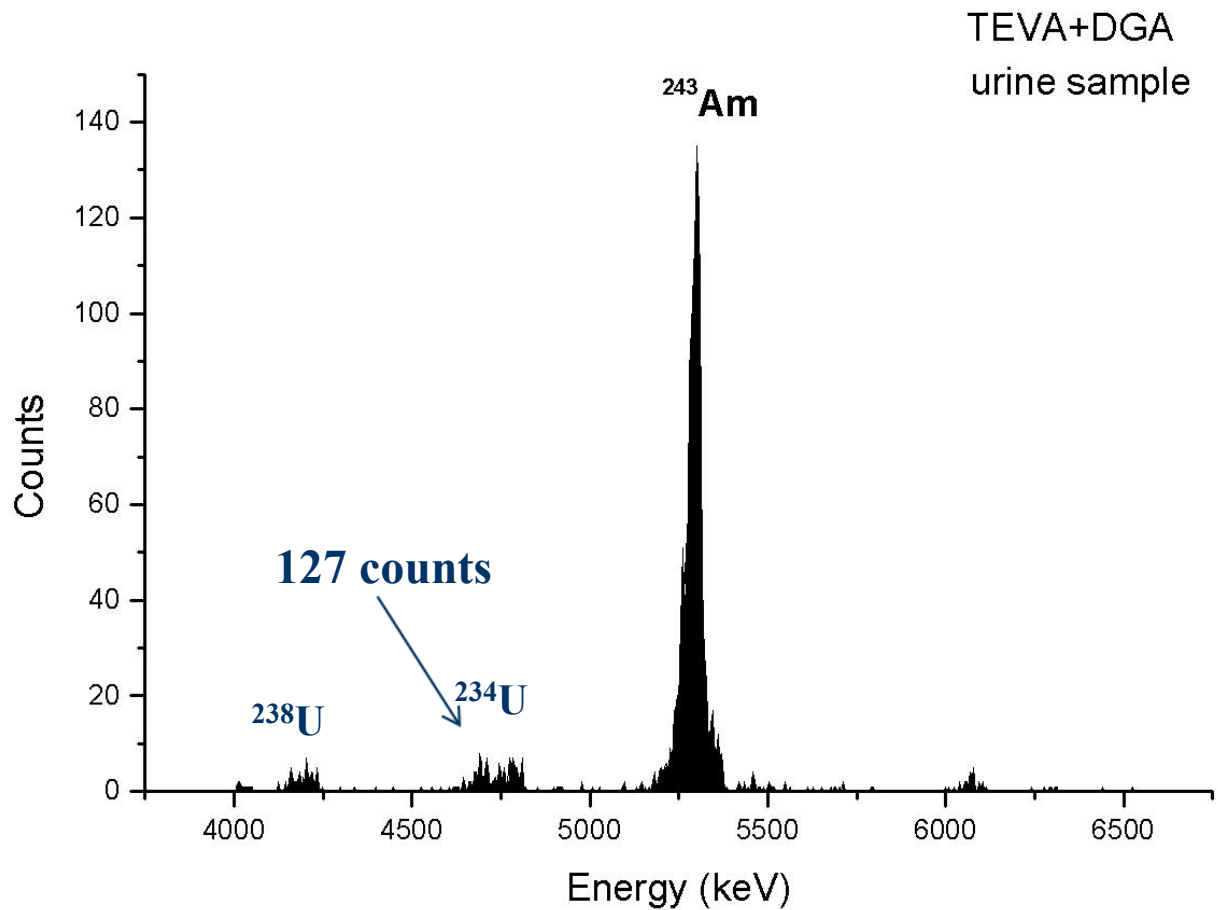
**Electrodeposition system**

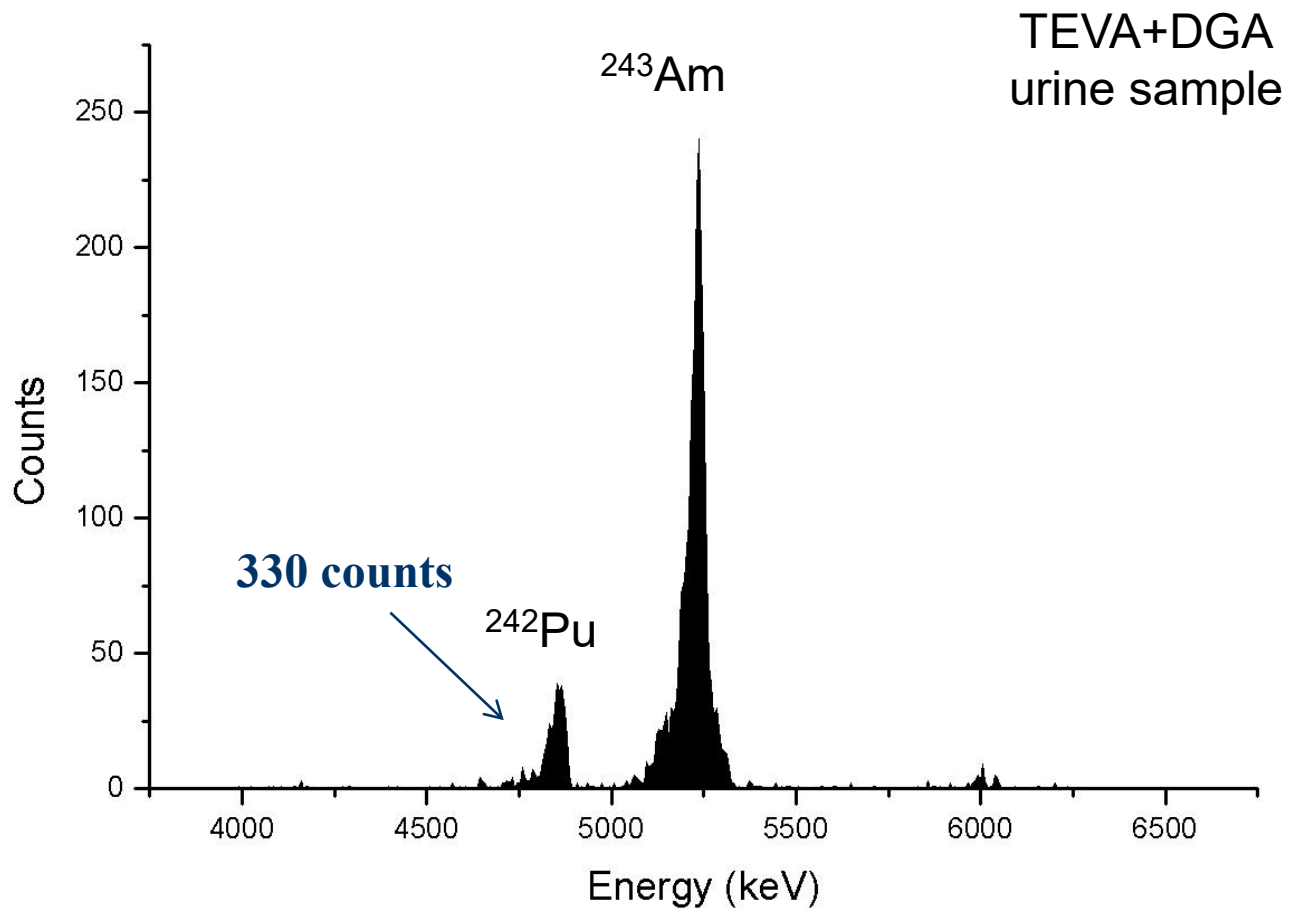


**High Resolution  
Alpha Spectrometry**

# Mean values of tracer recoveries (+/- 1SD)

	DOWEX+TRU ( <i>Saluggia</i> )		TEVA+DGA ( <i>Casaccia</i> )	
	Pu (N.samp.)	Am, Cm (N.samp.)	Pu (N.samp.)	Am, Cm (N.samp.)
<b>URINE</b>	<b>84 ± 12 (%) (36)</b>	<b>71 ± 8 (%) (36)</b>	<b>75 ± 21 (%) (47)</b>	<b>94 ± 4 (%) (53)</b>
<b>FAECES</b>	<b>87 ± 4 (%) (163)</b>	<b>68 ± 1 (%) (138)</b>	-	-

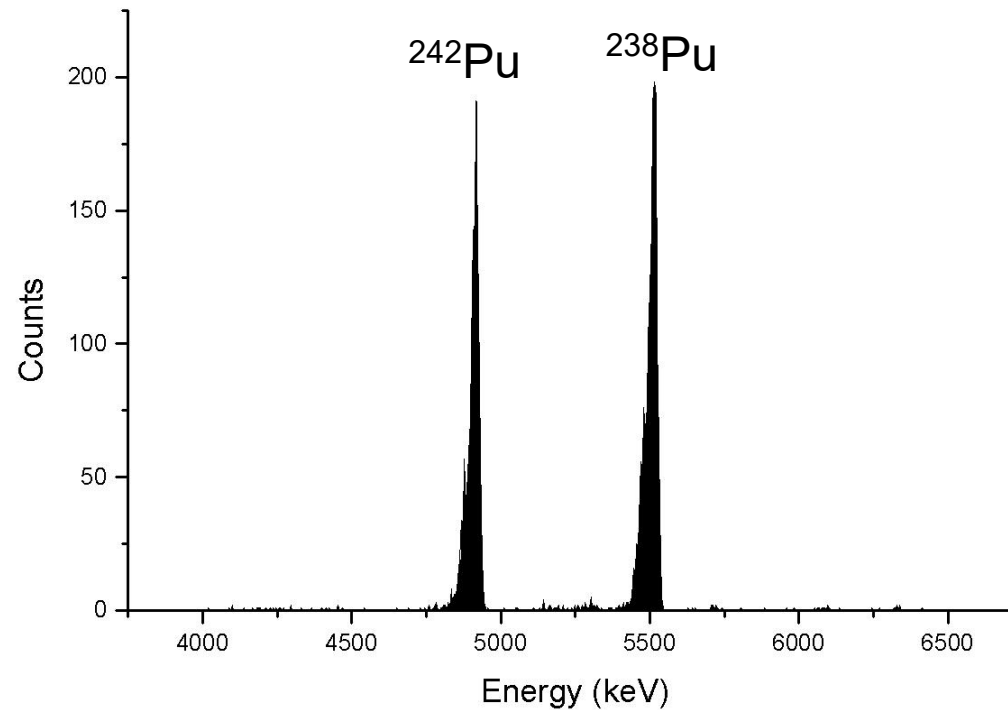






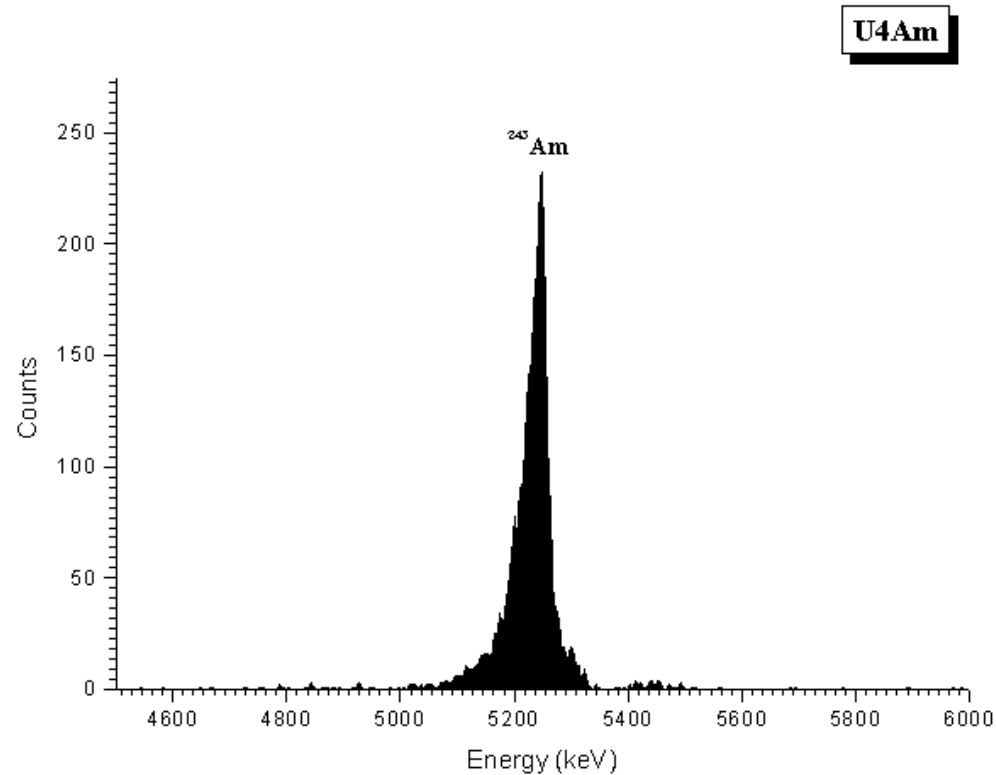
# Sequential separation of Pu/Am Pu fraction in urine (DOWEX)

(I)



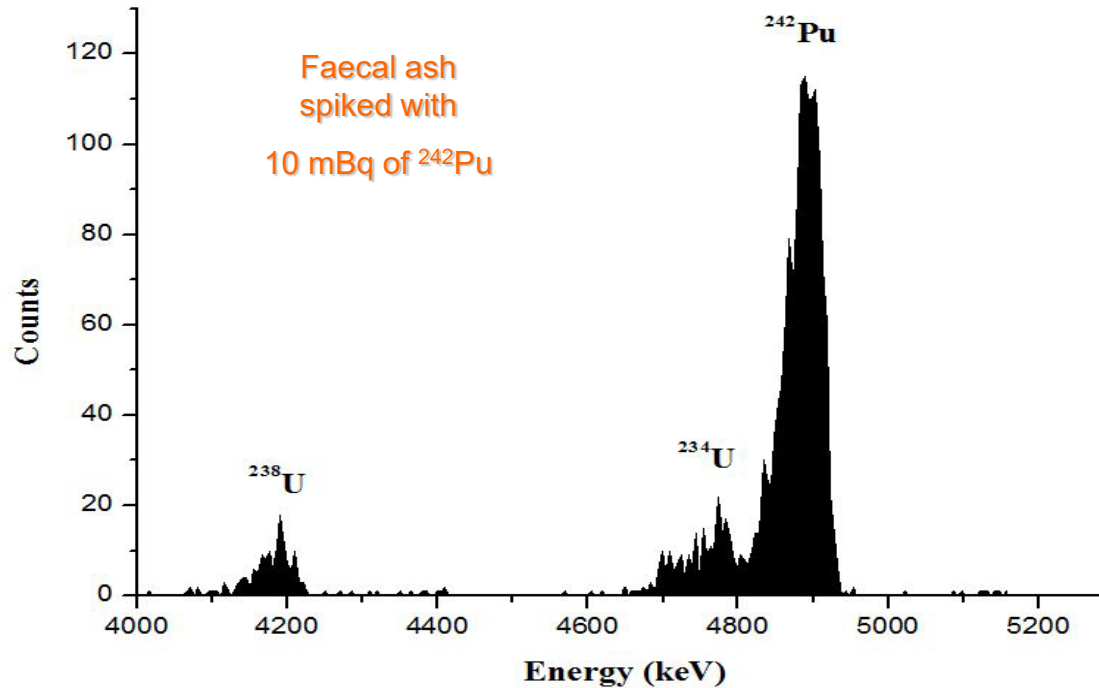
# Sequential separation of Pu/Am Am fraction in urine (TRU col.)

(II)



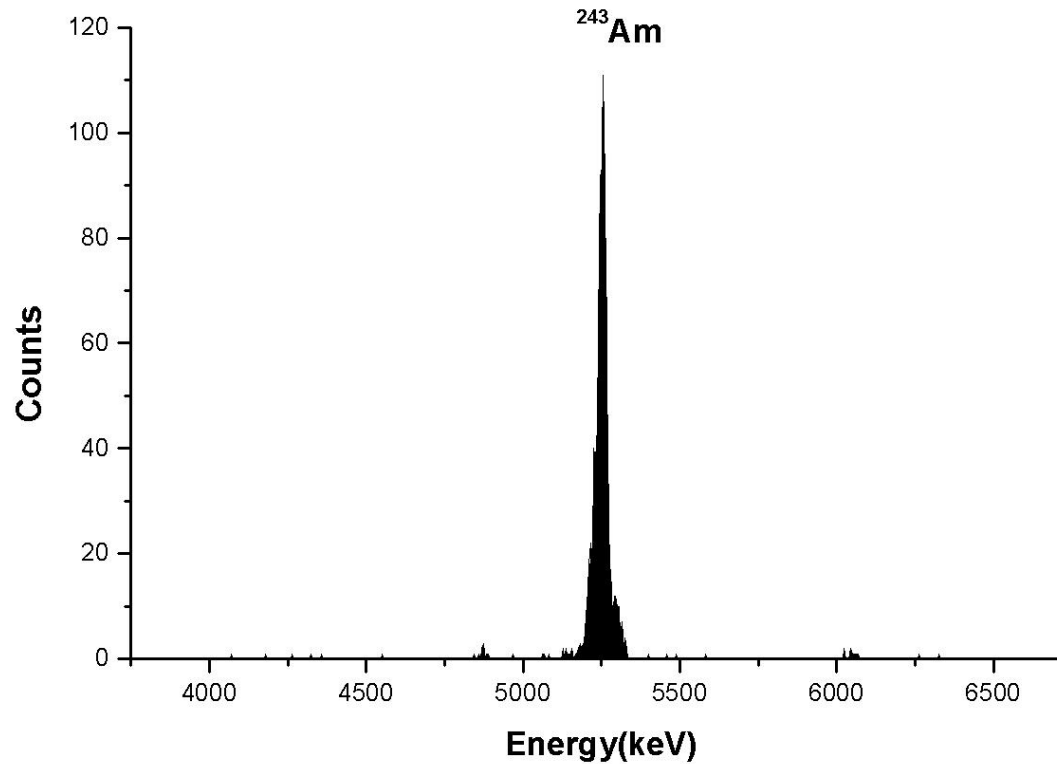
# Sequential separation of Pu/Am Pu fraction in faeces (ionic resin)

(III)

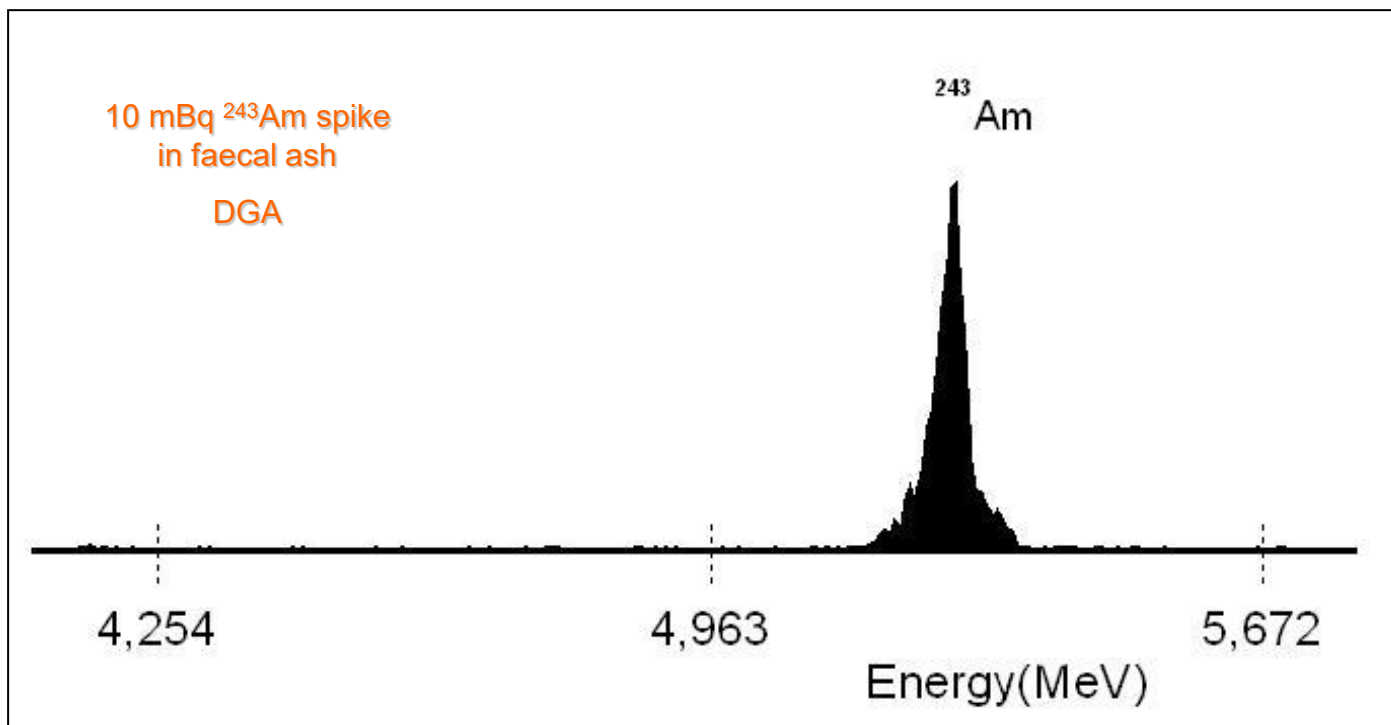


- Separation of Pu via AG 1-X2 before Am/Cm extraction
- In faeces the presence of uranium could be more important than in urine

# Sequential separation of Pu/Am (IV) Am fraction in faeces



# Separation of Am (DGA)



DGA resin shows great selectivity for Am

# DL - Detection Limit - mean value

	DOWEX+TRU				TEVA + DGA			
	<sup>239</sup> Pu	<sup>238</sup> Pu	<sup>241</sup> Am	<sup>244</sup> Cm	<sup>239</sup> Pu	<sup>238</sup> Pu	<sup>241</sup> Am	<sup>244</sup> Cm
<b>URINE (mBq/L)</b>	0.2	0.2	0.2	0.1	0.2	0.2	0.1	0.1
<b>FAECES (mBq/sample)</b>	0.2	0.1	0.3	0.1				

# PROCORAD Intercomparison 2019 & 2021

## Actinides in urines and faeces

	URINES samples						FAECAL samples						
2019	A BIAS (%)		B BIAS (%)			C	A BIAS (%)				C BIAS (%)		B
	<sup>239</sup> Pu	<sup>241</sup> Am	<sup>238</sup> Pu	<sup>239</sup> Pu	<sup>241</sup> Am	Blank	<sup>238</sup> Pu	<sup>239</sup> Pu	<sup>241</sup> Am	<sup>244</sup> Cm	<sup>241</sup> Am	<sup>244</sup> Cm	Blank
TEVA+ DGA	3.4	-5.5	-3	4.1	-0.5	ND							
DOWEX +TRU	2	-10	-6	-1	-6	ND	-3	-4	-2	-5	-5	5	ND

TOP LAB

	URINES samples					FAECAL samples					
2021	A BIAS (%)	B BIAS (%)			C	A BIAS (%)			B BIAS (%)		C
	<sup>239</sup> Pu	<sup>238</sup> Pu	<sup>239</sup> Pu	<sup>241</sup> Am	Blank	<sup>239</sup> Pu	<sup>241</sup> Am	<sup>244</sup> Cm	<sup>238</sup> Pu	<sup>244</sup> Cm	Blank
TEVA+ DGA	-4.4	-3.1	4.2	6.7	ND						
DOWEX +TRU	-2	-4	-2	-7	ND	-5	-11	-9	4	-8	ND

# Conclusion (I)

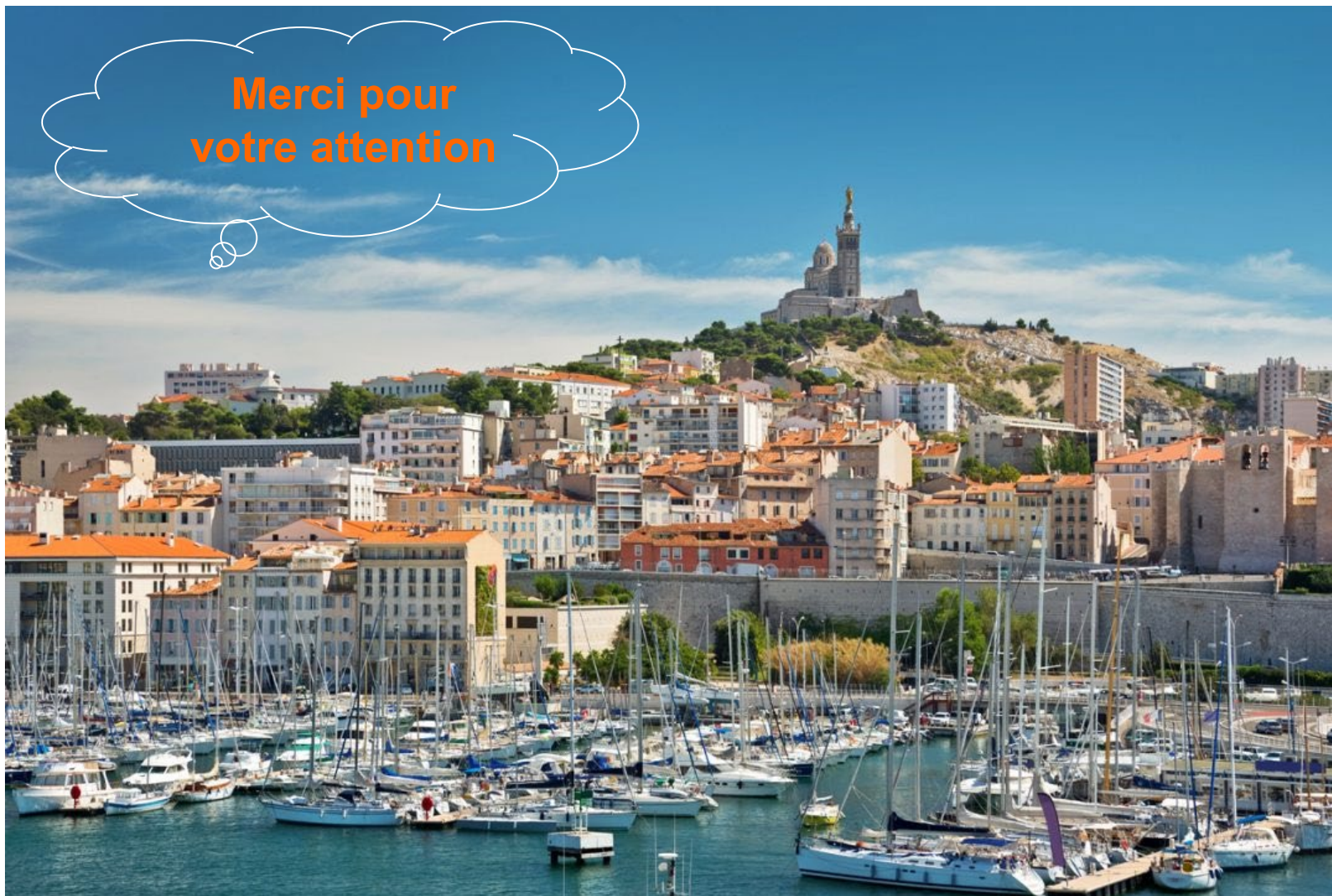
- Internal contamination analyses of actinides in biological samples based on two steps:
- Use of anionic resin (**DOWEX**) or extraction chromatography (**TEVA**) for isolation of **Pu** and for purification from **U** and **Th interferences**
- Use of **TRU** resin or **DGA** for **extraction of Am/Cm**
- Both methods of **Am/Cm extraction** are sufficiently selective, accurate and sensitive.



# Conclusion (II)

- TEVA+DGA requires shorter times and small volumes, but only for urine at the moment
- Pu/Am separation not always satisfactory
- DOWEX+TRU both for urine and for faecal ash
- DOWEX+DGA as well

**Merci pour  
votre attention**



dolores.arginelli@enea.it



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