Challenging gamma ray spectrum analysis from environmental samples

Problem in U-238 (Pa-234m) determination

Roy Pöllänen

In some cases we have observed that the results of U-238 determined from the peaks of Th-234 (63 keV) and Pa-234m (1001 keV) may notably differ. Sometimes happens that the result from the 1001 keV peak gives larger result compared with that of 63 keV peak (even if we assume that there is Th-232 counts in the 63 keV peak).

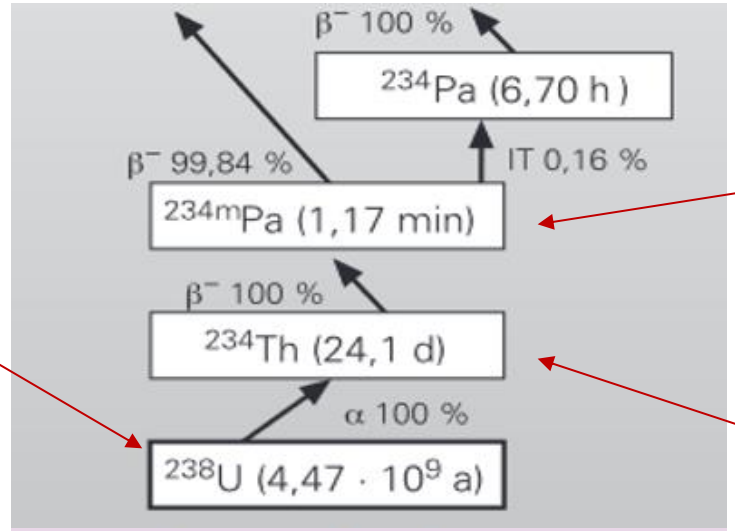
What has happened?

1. Introduction

Let's look at the situation through an example:

- Determination of U-238 is mainly done by using Pa-234m peak of 1001 keV. The daughter nuclide Th-234 can also be used for U-238 determination but there are some problems...
- Basic assumption: There is activity equilibrium between U-238→Th-234→Pa-234m.

This is difficult to directly determine by using gamma ray spectrometry



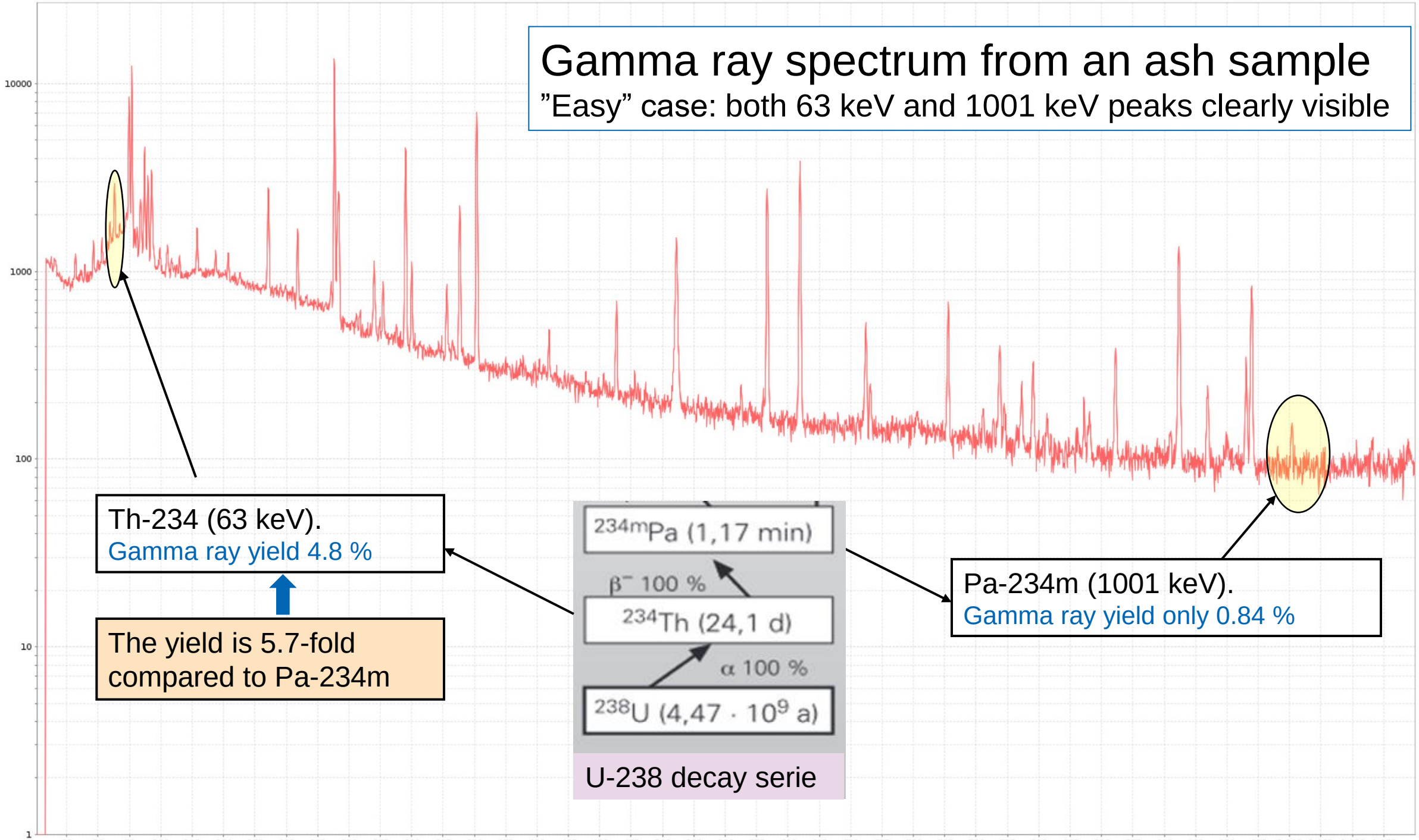
U-238 decay serie

This is easy to determine if there is 1001 keV peak in the spectrum

This is easy to determine if there is 63 keV peak in the spectrum (but take Th-232 into account!)

Gamma ray spectrum from an ash sample

”Easy” case: both 63 keV and 1001 keV peaks clearly visible



Th-234 (63 keV).
Gamma ray yield 4.8 %

The yield is 5.7-fold compared to Pa-234m

^{234m}Pa (1,17 min)

β^- 100 %

^{234}Th (24,1 d)

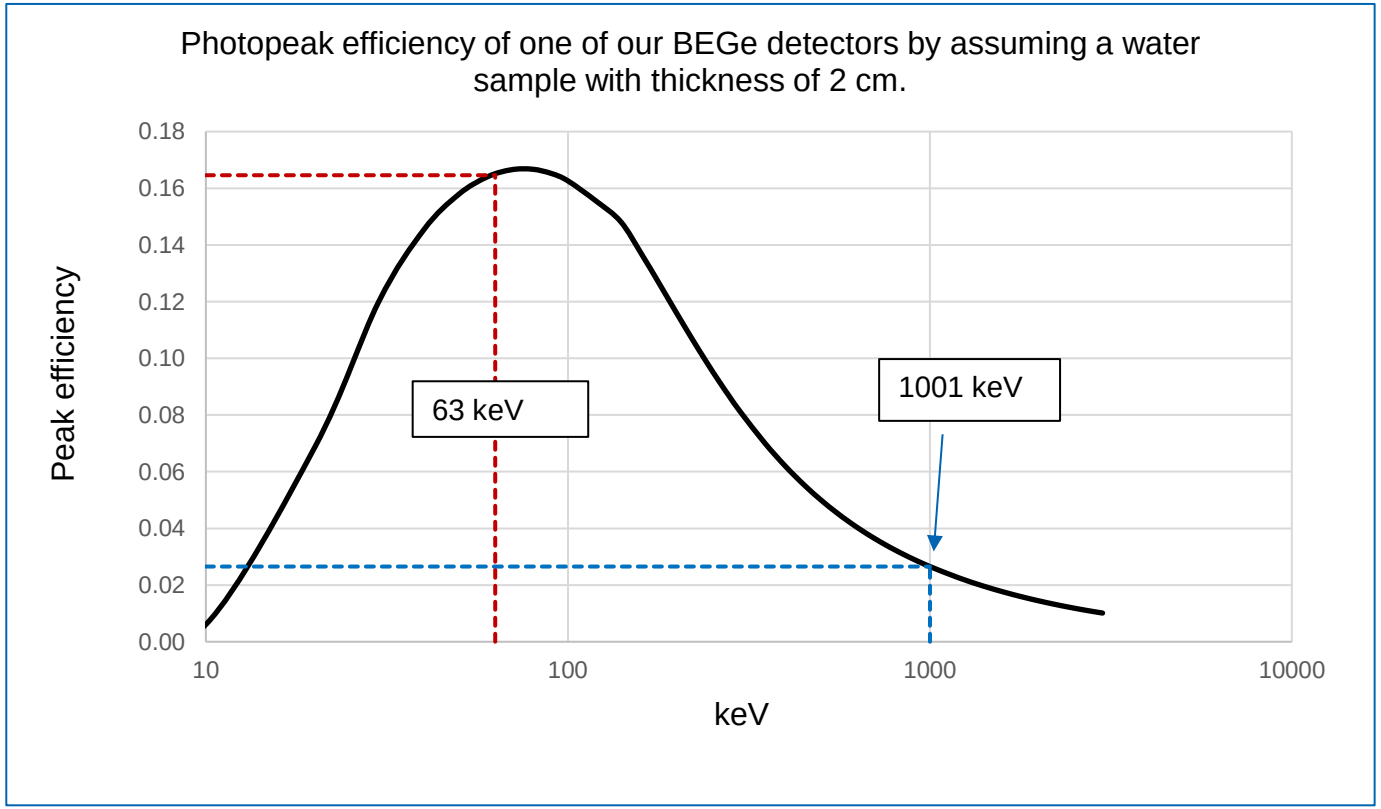
α 100 %

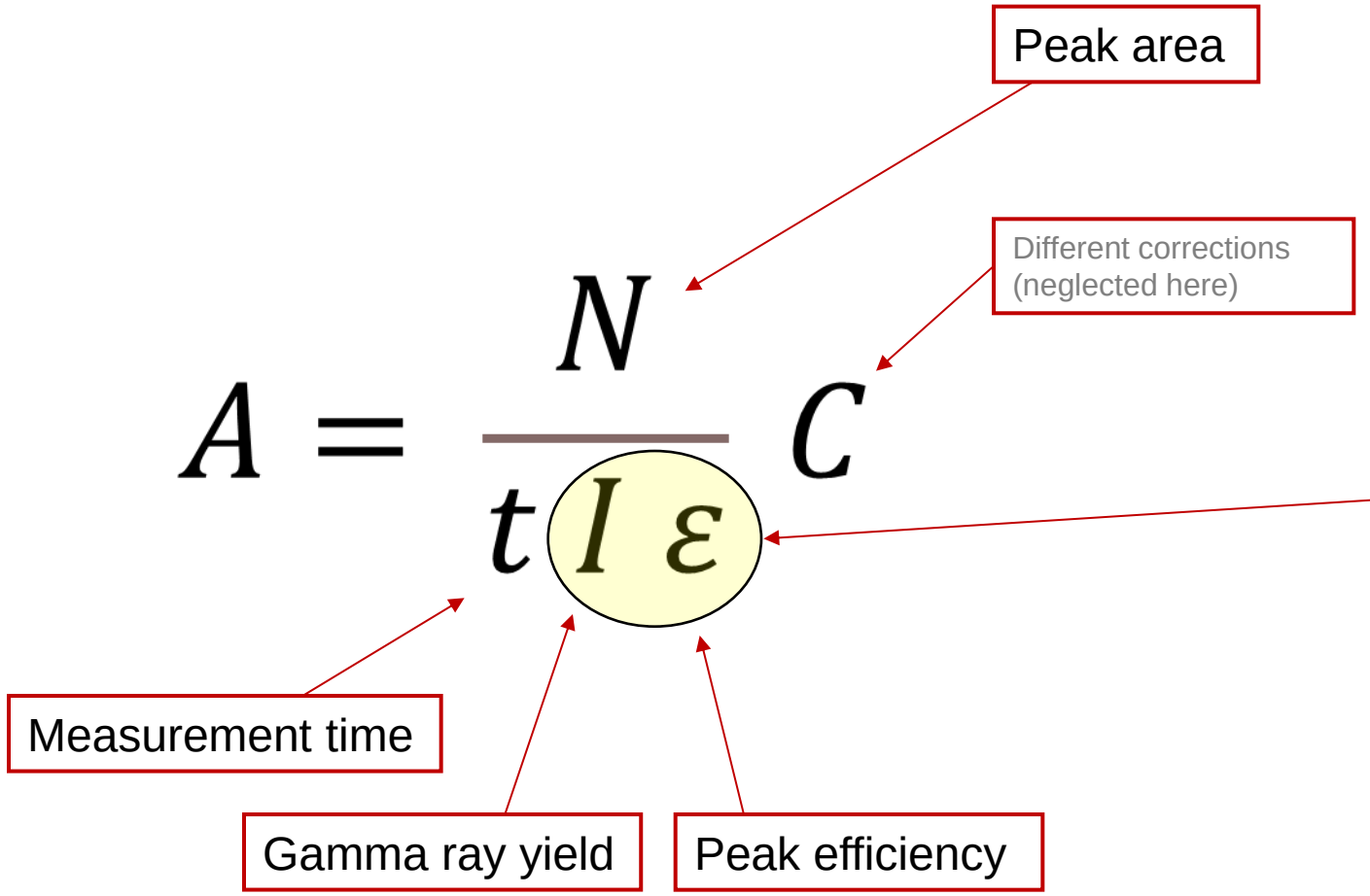
^{238}U (4,47 · 10^9 a)

U-238 decay serie

Pa-234m (1001 keV).
Gamma ray yield only 0.84 %

Comparison of peak efficiency between Th-234 (63 keV) and Pa-234m (1001 keV): At the energy of 63 keV the efficiency is by a factor of 6.2 higher than at the energy of 1001 keV.





Determination of U-238 activity by using Th-234 (63 keV) peak could be more sensitive (e.g. 5.7 × 6.2 = 35) compared to Pa-234m (1001 keV) peak.

However, the background is notably higher at low energies compared to high energies!

2. The problem …

- A few years ago STUK participated in a proficiency test in which we determined too high value for U-238 (soil sample).
- By using ICP-MS we got correct value, by why not by using gamma ray spectrometry ?

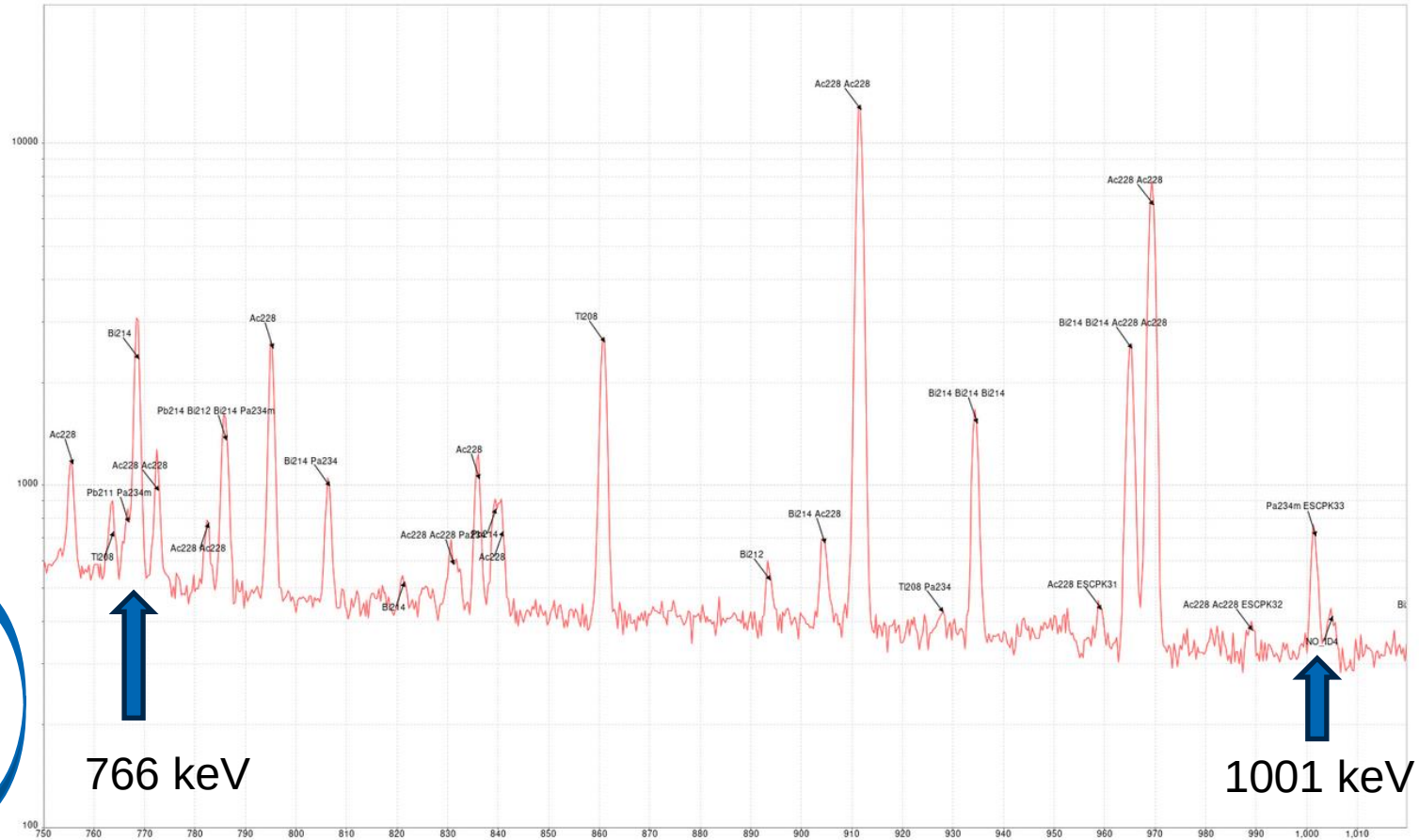
TABLE 4. Evaluation Results for Sample 3

Analyte	Technique	Target Value	Target Unc.	MAB	Reported value [Bq/kg]	Reported uncertainty ($k = 1$) [Bq/kg]	Relative bias [%]	P-Test [%]	Trueness evaluation	Precision evaluation	Final Score
K-40	gamma	873.0	44.0	30	964.89	54.03	10.5	7.53	A	A	A
Pb-210	gamma	306.0	17.0	30	335.14	63.47	9.5	19.74	A	A	A
Ra-228	gamma	307.0	17.0	30	324.75	11.74	5.8	6.61	A	A	A
U-235	gamma	11.4	1.0	30	9.85	0.84	-13.6	12.23	A	A	A
U-238	gamma	246.0	11.0	30	337.25	16.25	37.1	6.57	N	N	N

- U-238 activity concentration was determined by using 1001 keV peak of Pa-234m (there was a ”mess” in the 766 keV peak).
- We later found that the 63 keV peak gave correct value.

Nuclide	Energy	Gamma ray yield	The peaks of other possible radionuclides (± 2 keV)
U-238	49.55 keV	0.064 %	Th-227 (49.89 keV, 0.57 %) Th-227 (50.13 keV, 8.0 %)
	113.5 keV	0.0102 %	Th-234 (112.81 keV, 0.277 %) Th-227 (113.159 keV, 0.65 %)
Th-234	62.86 keV	0.021 %	Th-227 (61.44 keV, 0.085%) Th-227 (62.45 keV, 0.19%) Pa-234 (62.70 keV, 1.5 %)
	63.29 keV	4.8 %	Ra-223 (63.2 keV, 0.055 %) Th-231 (63.825 keV,0.023%) Th-232 (63.83 keV, 0.263 %)
	92.38 keV 92.80 keV	2.81 % 2.77 %	Th → Pa $K_{\alpha 2}$ (92.282 keV, 0.5 %) Th-231 (93.063 keV, 0.045 %) Th-227 (93.93 keV, 1.37 %) U → Th $K_{\alpha 1}$ (93.35 keV, 0.03 %) Ac → Th $K_{\alpha 1}$ (93.35 keV, 3.19 %)
Pa-234m	1001.03 keV	0.837 %	Ac-228 (1000.69, 0.0054 %)
	766.38 keV	0.294 %	Pb-214 (765.96 keV, 0.078 %) Pb-211 (766.51 keV, 0.617 %) Bi-214 (768.356 keV, 4.94 %)

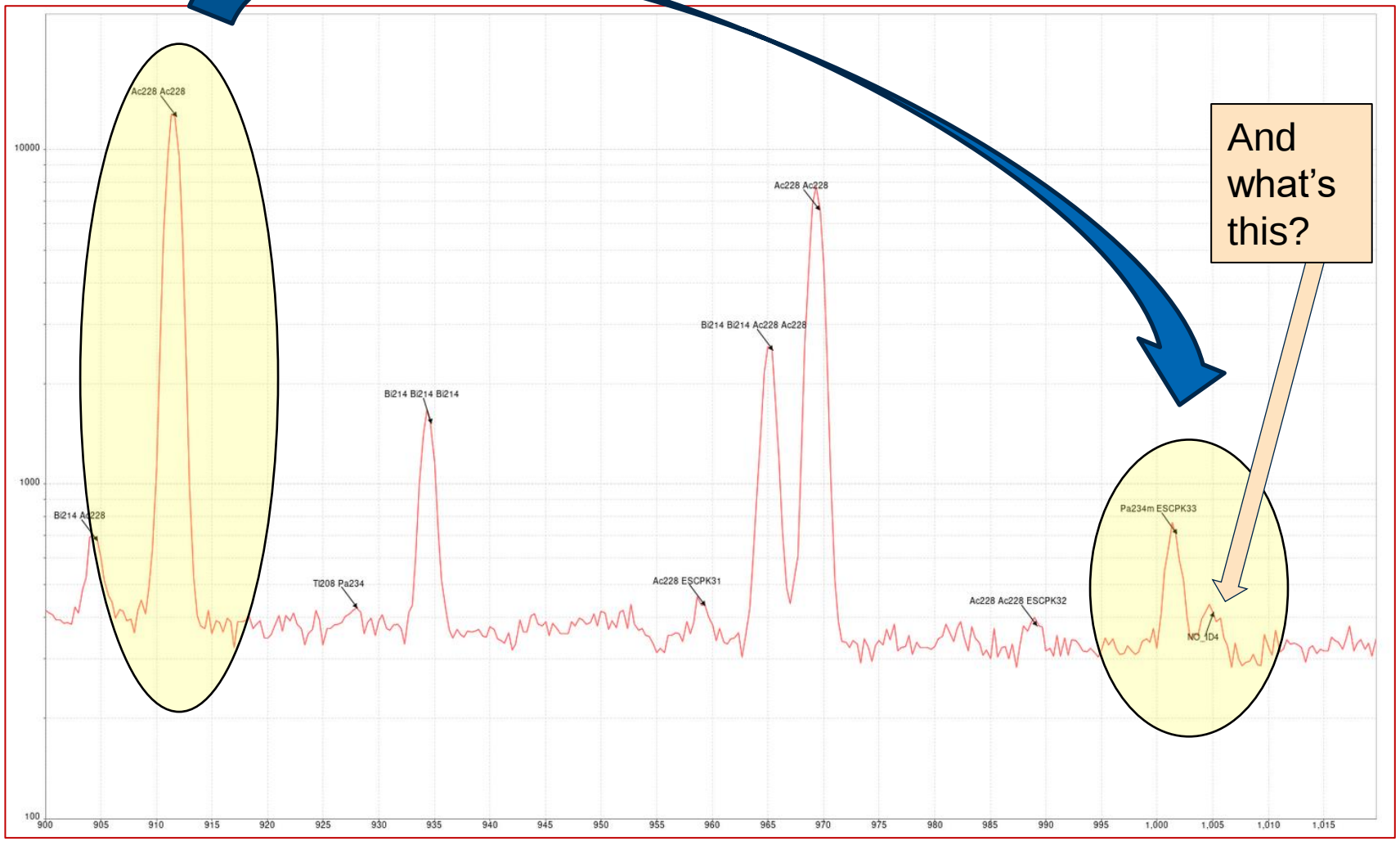
If the U-238 result is obtained from the 1001 keV peak, the contribution of Ac-228 peak at 1000.69 keV must be taken into account! But but …



3. … and how to solve it

Could Ac-228 (because of the high number of counts in the 911 keV peak) cause the problem?

Let's zoom the spectrum presented above



Validated DDEP data of Ac-228 shows large number of gamma transitions

2.2 Gamma Transitions and Internal Conversion Coefficients

	Energy keV	$P_{\gamma+ce} \times 100$	Multipolarity	α_K	α_L	α_M	α_T
$\gamma_{28,27}$(Th)	18,415 (12)	0,142 (30)	E1		3,82 (6)	2,00 (3)	6,46 (10)
$\gamma_{38,35}$(Th)	42,440 (16)	0,43 (14)	M1		35,0 (5)	8,43 (13)	46,3 (7)
$\gamma_{31,29}$(Th)	56,861 (15)	8 (8)	E1+[M2]		260 (160)	70 (50)	360 (220)
$\gamma_{1,0}$(Th)	57,759 (4)	72,5 (28)	E2		112,2 (16)	30,7 (5)	153,2 (22)
$\gamma_{20,17}$(Th)	77,358 (9)	0,027 (6)	E1		0,1747 (25)	0,0426 (6)	0,232 (4)
$\gamma_{29,27}$(Th)	99,495 (8)	6,10 (21)	M1		2,90 (4)	0,699 (10)	3,84 (6)
$\gamma_{18,15}$(Th)	100,424 (8)	0,114 (6)	E1+M2		2,27 (4)	0,615 (9)	3,10 (5)
$\gamma_{35,29}$(Th)	114,480 (13)	0,102 (46)	M1+E2	5 (5)	3,2 (13)	0,8 (4)	9 (4)
$\gamma_{2,1}$(Th)	129,064 (6)	11,85 (36)	E2	0,264 (4)	2,54 (4)	0,697 (10)	3,74 (6)
$\gamma_{23,17}$(Th)	135,548 (11)	0,024 (6)	E1	0,185 (3)	0,0401 (6)	0,00971 (14)	0,238 (4)
$\gamma_{31,28}$(Th)	137,941 (17)	0,239 (34)	M1	6,00 (9)	1,146 (16)	0,276 (4)	7,52 (11)
$\gamma_{6,4}$(Th)	141,013 (12)	0,055 (11)	E1	0,1690 (24)	0,0362 (5)	0,00876 (13)	0,217 (3)
$\gamma_{20,15}$(Th)	145,848 (8)	0,169 (6)	E1	0,1562 (22)	0,0332 (5)	0,00803 (12)	0,200 (3)
$\gamma_{18,12}$(Th)	153,983 (8)	0,754 (23)	E1	0,1375 (20)	0,0289 (4)	0,00698 (10)	0,1757 (25)
$\gamma_{49,43}$(Th)	168,35 (6)	0,0093 (46)	M1+E2	1,8 (16)	0,70 (7)	0,18 (3)	2,7 (15)
$\gamma_{25,22}$(Th)	168,69 (5)	0,0127 (31)	M1+E2	1,8 (16)	0,70 (7)	0,18 (3)	2,7 (15)
$\gamma_{19,13}$(Th)	173,968 (17)	0,036 (5)	M1+E2	1,6 (15)	0,63 (5)	0,162 (22)	2,5 (14)
$\gamma_{19,12}$(Th)	184,499 (11)	5,5 (29)	E0+M1	80 (30)			100 (40)
$\gamma_{4,2}$(Th)	191,356 (11)	0,236 (14)	E2	0,1710 (24)	0,443 (7)	0,1209 (17)	0,776 (11)
$\gamma_{20,12}$(Th)	199,407 (7)	0,299 (23)	E1	0,0752 (11)	0,01502 (21)	0,00362 (5)	0,0950 (14)
$\gamma_{24,15}$(Th)	204,038 (9)	0,114 (8)	M2	7,26 (11)	2,51 (4)	0,653 (10)	10,65 (15)
$\gamma_{5,2}$(Th)	209,255 (6)	4,31 (14)	E1	0,0672 (10)	0,01333 (19)	0,00321 (5)	0,0848 (12)
$\gamma_{19,9}$(Th)	214,89 (7)	0,047 (8)	E2	0,1399 (20)	0,274 (4)	0,0746 (11)	0,514 (8)
$\gamma_{28,23}$(Th)	223,829 (12)	0,058 (6)	M1+E2	1,48 (4)	0,286 (5)	0,0688 (10)	1,85 (4)
$\gamma_{22,10}$(Th)	231,19 (5)	0,026 (4)	E2	0,1211 (17)	0,199 (3)	0,0539 (8)	0,392 (6)
$\gamma_{27,21}$(Th)	257,471 (19)	0,0286 (19)	M1	1,029 (15)	0,194 (3)	0,0466 (7)	1,285 (18)
$\gamma_{27,20}$(Th)	263,604 (8)	0,0451 (31)	E1	0,0397 (6)	0,00760 (11)	0,00182 (3)	0,0498 (7)
$\gamma_{3,1}$(Th)	270,244 (6)	3,72 (10)	E1	0,0376 (6)	0,00716 (10)	0,001717 (24)	0,0470 (7)
$\gamma_{27,19}$(Th)	278,512 (12)	0,038 (6)	E2	0,0843 (12)	0,0937 (14)	0,0252 (4)	0,212 (3)
$\gamma_{19,8}$(Th)	278,994 (21)	0,33 (9)	M1+E2	0,5 (4)	0,12 (3)	0,031 (6)	0,6 (4)

stuk
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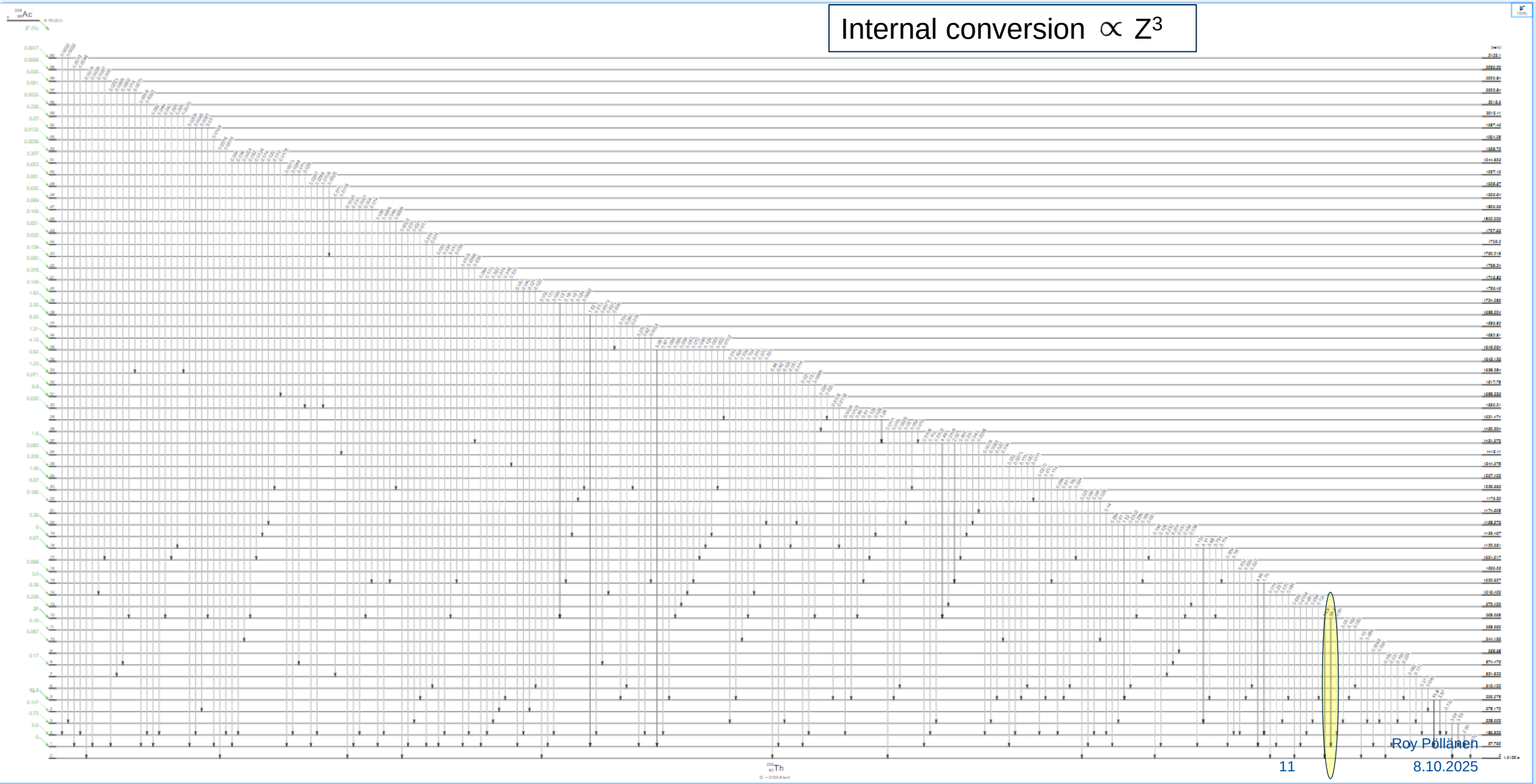
Internal conversion $\propto Z^3$



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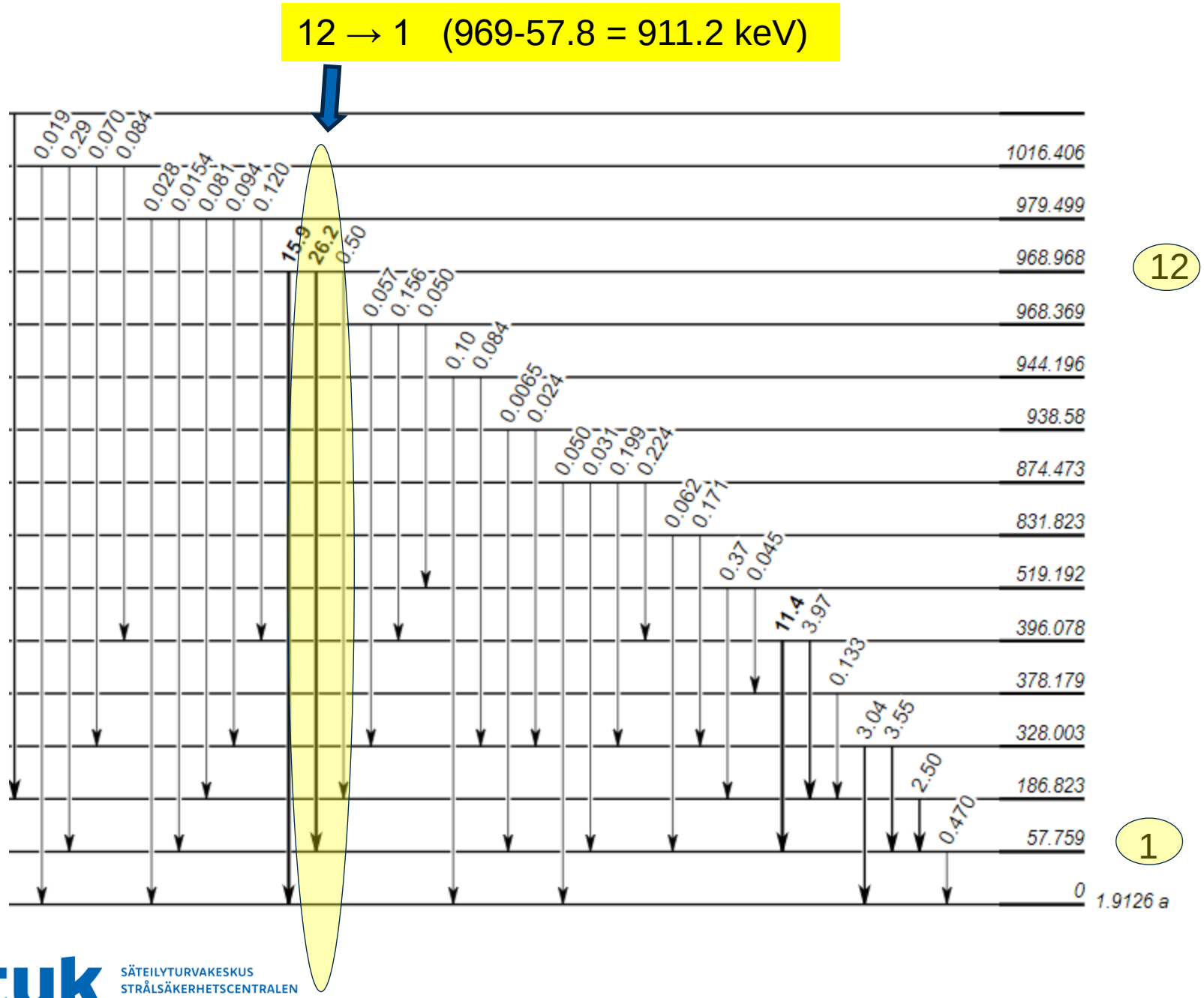
$\gamma_{19,8}$(Th)	278,994 (21)	0,33 (9)	M1+E2	0,5 (4)	0,12 (3)	0,031 (6)	0,6 (4)

I looked DDEP-data and searched those states that have

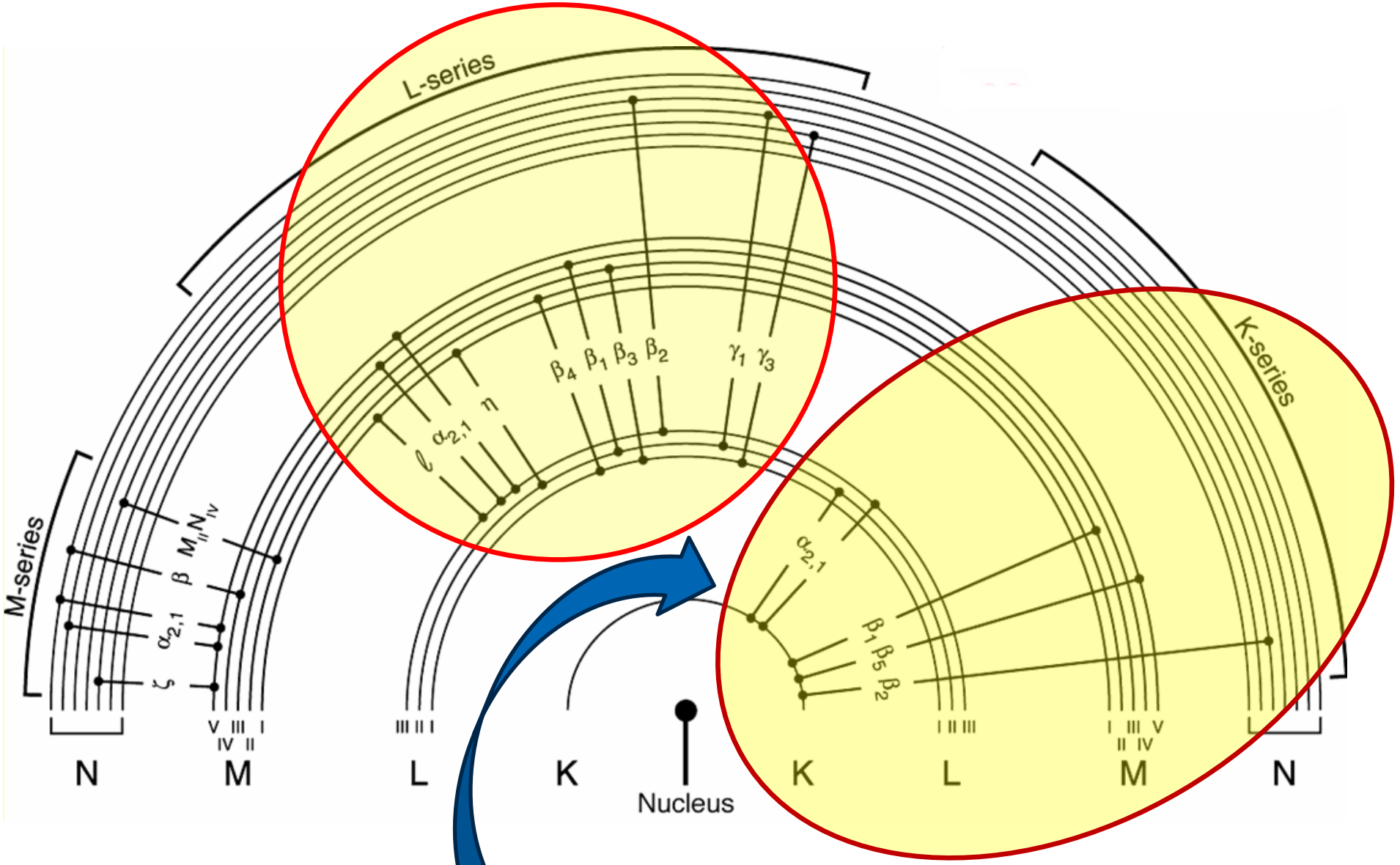
1) large conv.coefficient
2) transition to state 12
3) large enough $P_{\gamma+ce}$

$$\alpha_K = \frac{I_{ce_K}}{I_\gamma}$$



Transition from state 19 -> 12 has large K-conversion coefficient α_k= 80 ja $P_{\gamma+ce}$= 5,5%.

So, in practice there is no 184.5 keV gamma emission. Instead there is emission of conversion electrons and K- x-rays.



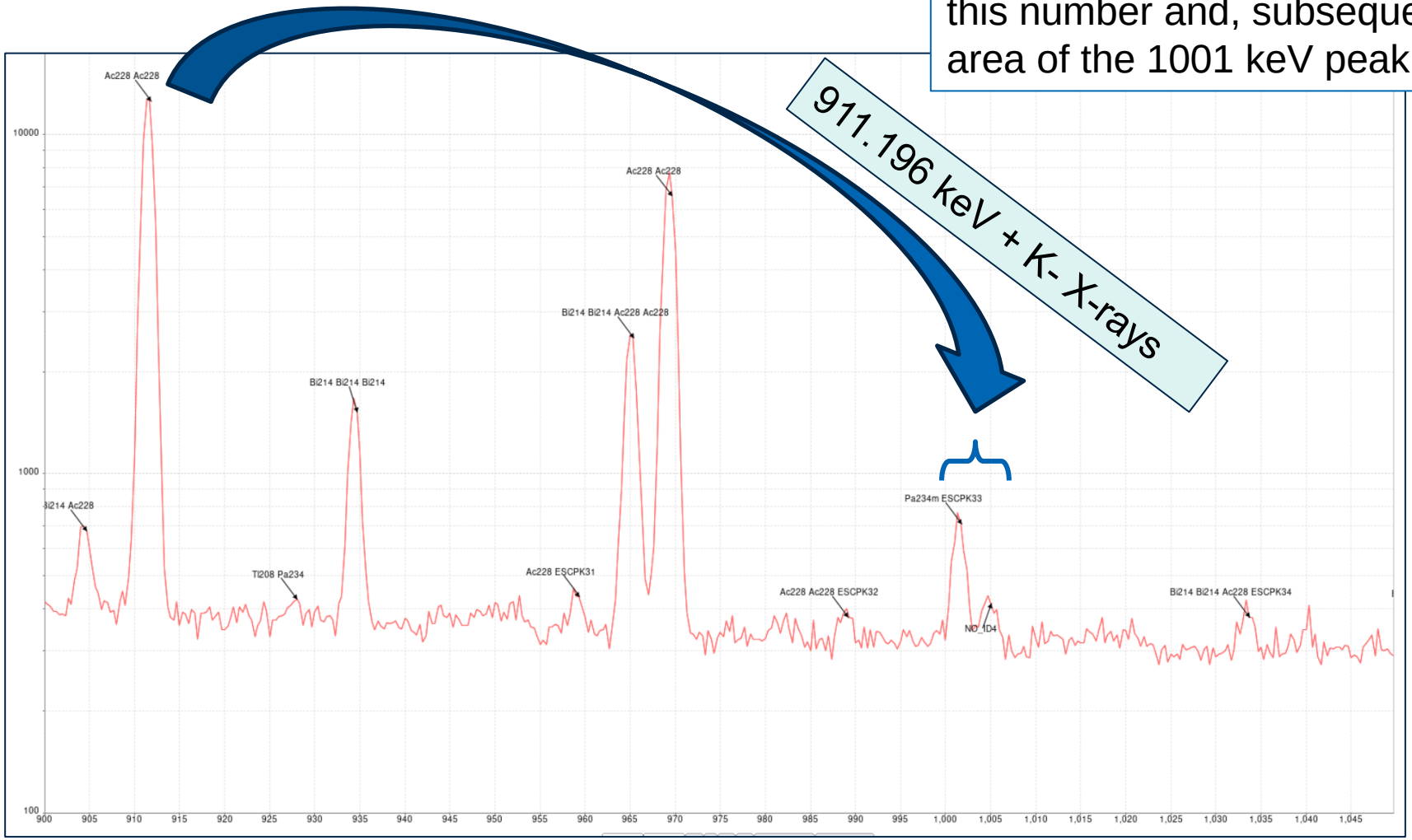
$X_{Kα2}$
$X_{Kα1}$

Ac-228 data from DDEP site

Energy (keV)	Intensity (%)*	Type	Origin*	Levels Start*	Levels End*	Possible coincidence with (keV) / Possible sum of (levels)	Parent
15.311 (-)	37 (4)	X_L	Th				Ac-228
89.954 (-)	2.5 (7)	$X_{K\alpha 2}$	Th				Ac-228
93.351 (-)	4.1 (11)	$X_{K\alpha 1}$	Th				Ac-228
105.554 (-)	1.5 (4)	$X_{K'\beta 1}$	Th				Ac-228
108.9687 (-)	0.49 (13)	$X_{K'\beta 2}$	Th				Ac-228

911.196 + 89.984 = 1001.18keV
911.196 + 93.351 = 1004.55keV

Intensity ratio 2.5/4.1 = 0.61. So, you must multiply the area of 1004 keV peak area to this number and, subsequently, reduce the area of the 1001 keV peak.



Note! Take into account also Ac-228 peak of 1001.69 keV and possible escape peaks.

Roy Pöllänen
8.10.2025

4. Comment

- After above-mentioned correction the 1001 keV peak gave correct value for the U-238 activity concentration!
- So, when determining U-238 activity concentration, please take care possible Ac-228 X-ray coincidences.
- Note: Other explanations might be possible, too.

I contacted a NPL specialist, who has evaluated the DDEP data. We agreed to study this issue and he promised to do some measurements to check the validity of above-mentioned interpretation.

Comments, please!