(Gamma spectrometric) Analysis of natural series using UniSampo-Shaman – case studies and considerations

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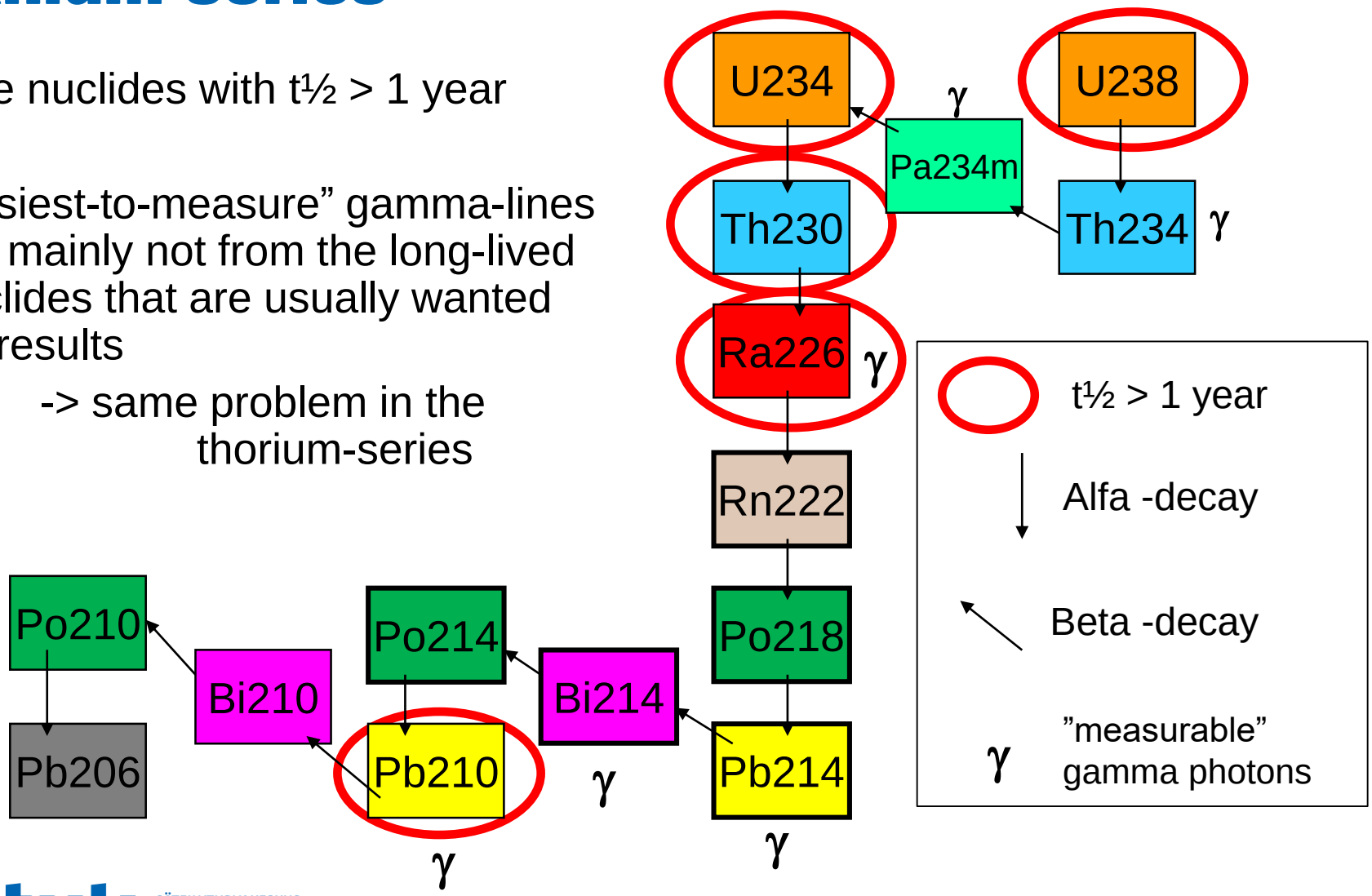
- Considerations for using USS in the analysis of natural series spectra

Uranium series

- Five nuclides with t½ > 1 year
- ”easiest-to-measure” gamma-lines are mainly not from the long-lived nuclides that are usually wanted for results

  -> same problem in the thorium-series



Measurement of natural radioactivity

Reporting	Measurement	Energies
K-40	K-40	1460.8 keV
Cs-137	Cs-137	661.7 keV
Be-7	Be-7	477.6 keV
Ra-228 →	Ac-228	338.3 keV, 911.2 keV
Pb-210	Pb-210	46.5 keV
Ra-226 Rn	Bi-214, Pb-214, Ra-226	609.3 keV, 351.9 keV, 186.2 keV
Th-228 Rn	Pb-212, Tl-208**	238.6 keV, 583.2 keV, 2614.5 keV
Th-232* Rn	Ac-228, Pb-212, Tl-208**	<1% <5%
U-238 →	Pa-234m, Th-234, (U-238)	1001.0 keV,63.3 keV,92.6 keV,49.6 keV
U-235	U-235	185.7 keV, 143.8 keV, 163.4 keV
(U-234)	U-234	53.2 keV, 120.9 keV <0,2%

"easy"

Thin geometry

Vacuum pack

Overlapping energies

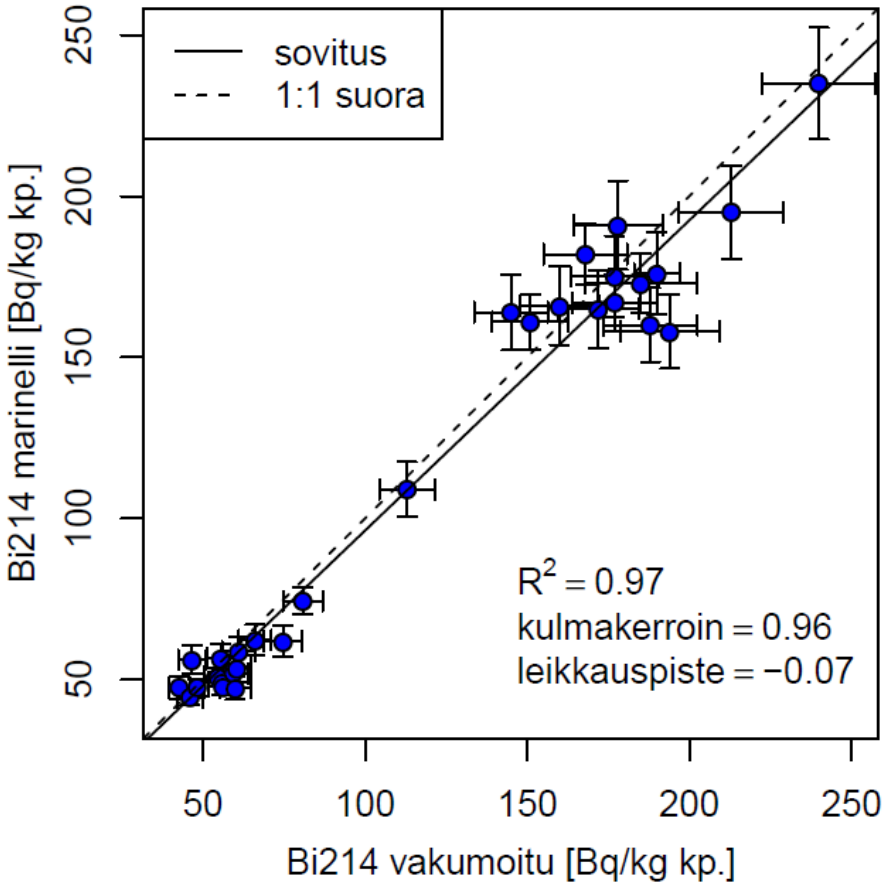
Low photon yield => longer measurements

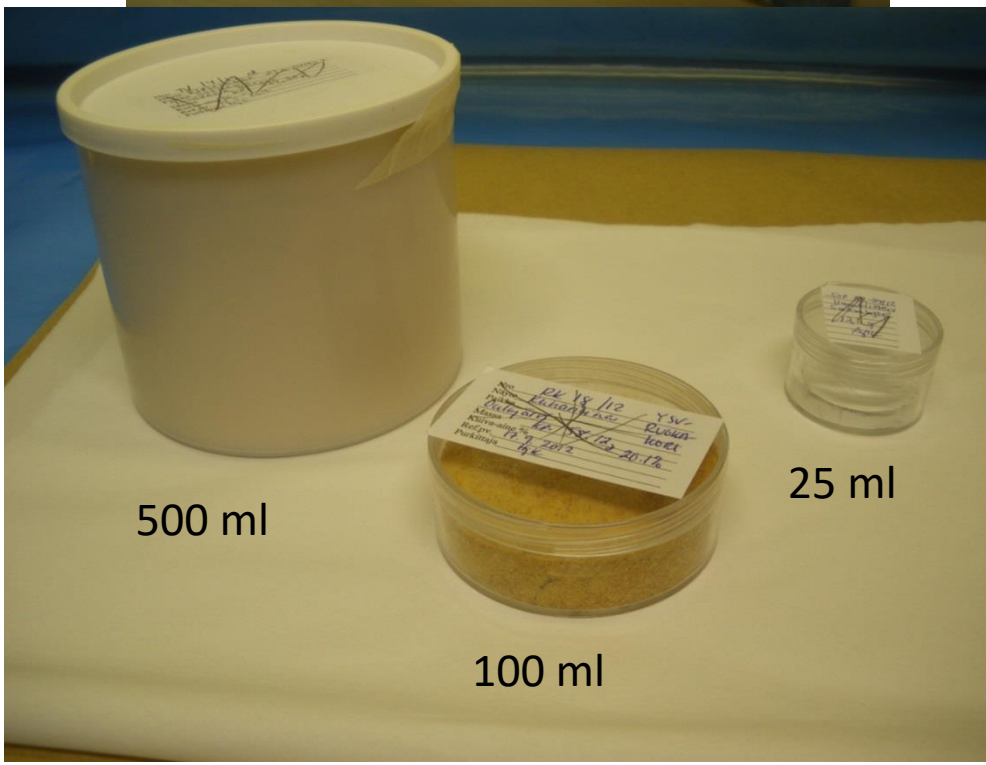
*Th-232 result can only be given if the series is in equilibrium!

**Tl-208 nuclide result multiplied with 2.7832 if used for Th-228 (36% branch of Bi-212)

Measurement geometry

No radon-loss seen from ash in marinelli (?)





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Optional approach: ”3-step procedure”

- **Step 1**: Thin sample, for Pb-210
- Can be measured immediately
- If there are suspicions of disequilibrium, move to steps 2 & 3
- Thin samples have been used for sediment Pb210-dating, and compared with radiochemical Pb-210 results with success

- **Step 2**: Vacuum-packed sample to prevent Radon-loss
- Needs three weeks of waiting time, not good if results are needed urgently
- Disequilibrium can be identified (decay or ingrowth)

- **Step 3**: if there is disequilibrium in the thorium-series, make other measurements to get Th232 (e.g. ICPMS where U238 can be measured at the same time)

UniSampo-Shaman (USS)

- Gamma spectrometric software from Baryon Oy, originally made for the monitoring of airborne radioactivity from aerosol filters
- Runs in linux

- USS has been used at STUK for many years for airfilter spectra, and since 2017 as the main gamma-software for all types of samples in combination with NAMIT-interface and LINSSI-database

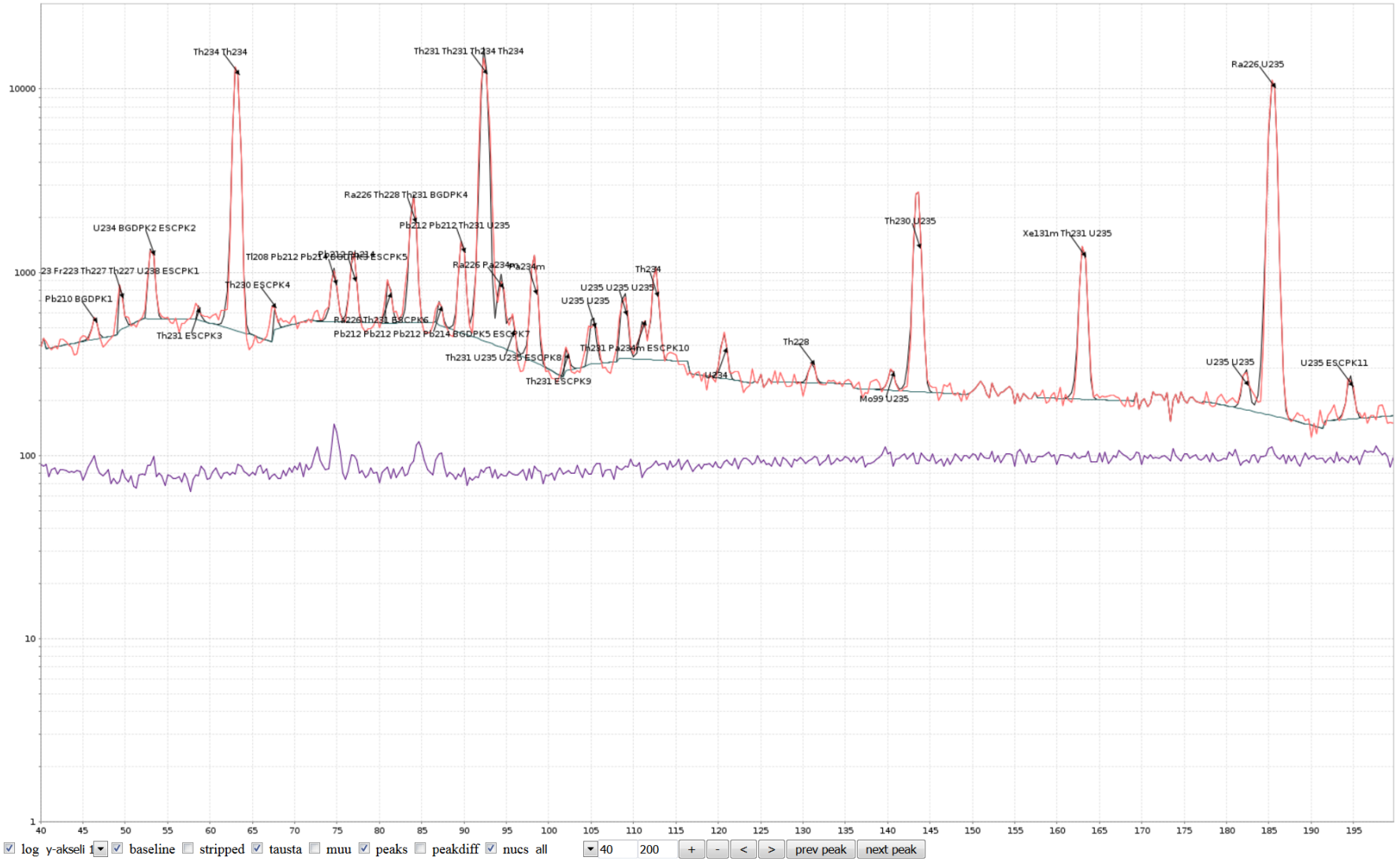
- Shaman library has around 3600 nuclides and 80 000 gamma and X-ray lines (ENSDF and NUDAT databases, latest DDEP update is underway)
- Shaman library is big, so it is used in binary format to make it faster – updates cannot be done by the user

UniSampo-Shaman (USS)

STUK USS:

- UniSampo is used for peak search and peak fitting, calibrations and peak data are fed into Shaman
- Shaman will try to find a complete explanation for the whole spectrum using a comprehensive library and rule based system
- Shaman calculates activities, will also try to calculate proportions for shared peaks based on other lines of the same nuclides
- ”Raw” activities from Shaman are used in NAMIT to calculate final results
- NAMIT = laboratory interface for USS and LINSSI developed at STUK

Case 1: Measurement of sludge



Case 1: Measurement 1 of sludge

Nuklidi	Aktiivisuus (LSQ)	Epävarm. % (LSQ)	Aktiivisuus (pri)	Epävarm. % (pri)	Havaitsemisraja	effHalfLife
U234	1118.2254	7.34	1062.208	13.1	116.6786	4.47E9 a U238
U238	789.8835	15.54	1002.6055	17.21	215.6884	4.47E9 a
Pa234m	655.3039	3.31	715.5094	6.8	30.4956	4.47E9 a U238
Th234	542.4284	3.82	510.6889	16.26	2.7609	4.47E9 a U238

Nuklidi	Energia	Peak	Merkittävyys	ExpLevel	Emissio tn	GC	Act	Unc %
Th234	63.29	5	196.469	1.06	0.048	1.0002	512.9235	16.26
Th234	92.38	13	118.494	0.48	0.028	1.000	1127.6185	12.24
Th234	92.8	13	119.365	0.48	0.028	1.0001	1127.6978	12.24
Pa234m	766.36	48	8.082	0.96	0.003	1.0003	681.6413	8.67
Pa234m	1001.03	51	21.488	0.92	0.008	0.9932	715.5094	6.8

Shaman user macro:

set user nuclide own_half_life ”90Th234 own_half_life \”Use own half life\””

Nuklidi	Aktiivisuus (LSQ)	Epävarm. % (LSQ)	Aktiivisuus (pri)	Epävarm. % (pri)	Havaitsemisraja	effHalfLife
U234	1088.3075	7.22	1032.7845	12.87	115.2435	246000.0 a
U238	819.762	13.62	1048.6814	16.29	205.7103	4.47E9 a
Pa234m	745.1628	3.5	1051.2664	6.8	44.395	24.1 d Th234
Th234	611.8819	3.81	734.1042	16.26	4.1139	24.1 d

Case 1: Issues with Shaman library 3.1.1

```
63.290 (+-  0.031601%)   4.800000 (+- 14.583332%)
73.920 (+-  0.027056%)   0.017200 (
83.300 (+-  0.060024%)   0.079000 (
92.380 (+-  0.010825%)   2.800000 (
92.800 (+-  0.021552%)   2.800000 (
103.350 (+-  0.096759%)   0.004200 (
112.810 (+-  0.044322%)   0.280000 (
```

Shaman Th-234

```
[Library 3.1.1] Search by nuclide (1) or by
```

Shaman Th-234 results need to be multiplied by 1.28 (with library 3.1.1)

5.2 Gamma Emissions

DDEP Th-234

	Energy keV	Photons per 100 disint.
$\gamma_{7,5}$(Pa)	20,01 (2)	0,0051 (21)
$\gamma_{3,2}$(Pa)	29,50 (2)	0,00123 (14)
$\gamma_{4,3}$(Pa)	62,88 (2)	0,0164 (28)
$\gamma_{5,3}$(Pa)	63,30 (2)	3,75 (8)
$\gamma_{1,0}$(Pa)	73,92 (2)	0,0133 (14)
$\gamma_{7,3}$(Pa)	83,31 (5)	0,061 (5)
$\gamma_{4,2}$(Pa)	92,38 (1)	2,18 (19)
$\gamma_{5,2}$(Pa)	92,80 (2)	2,15 (19)
$\gamma_{6,2}$(Pa)	103,35 (10)	0,0032 (10)
$\gamma_{7,2}$(Pa)	112,81 (5)	0,215 (22)

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Case 1: Measurement 1 corrected

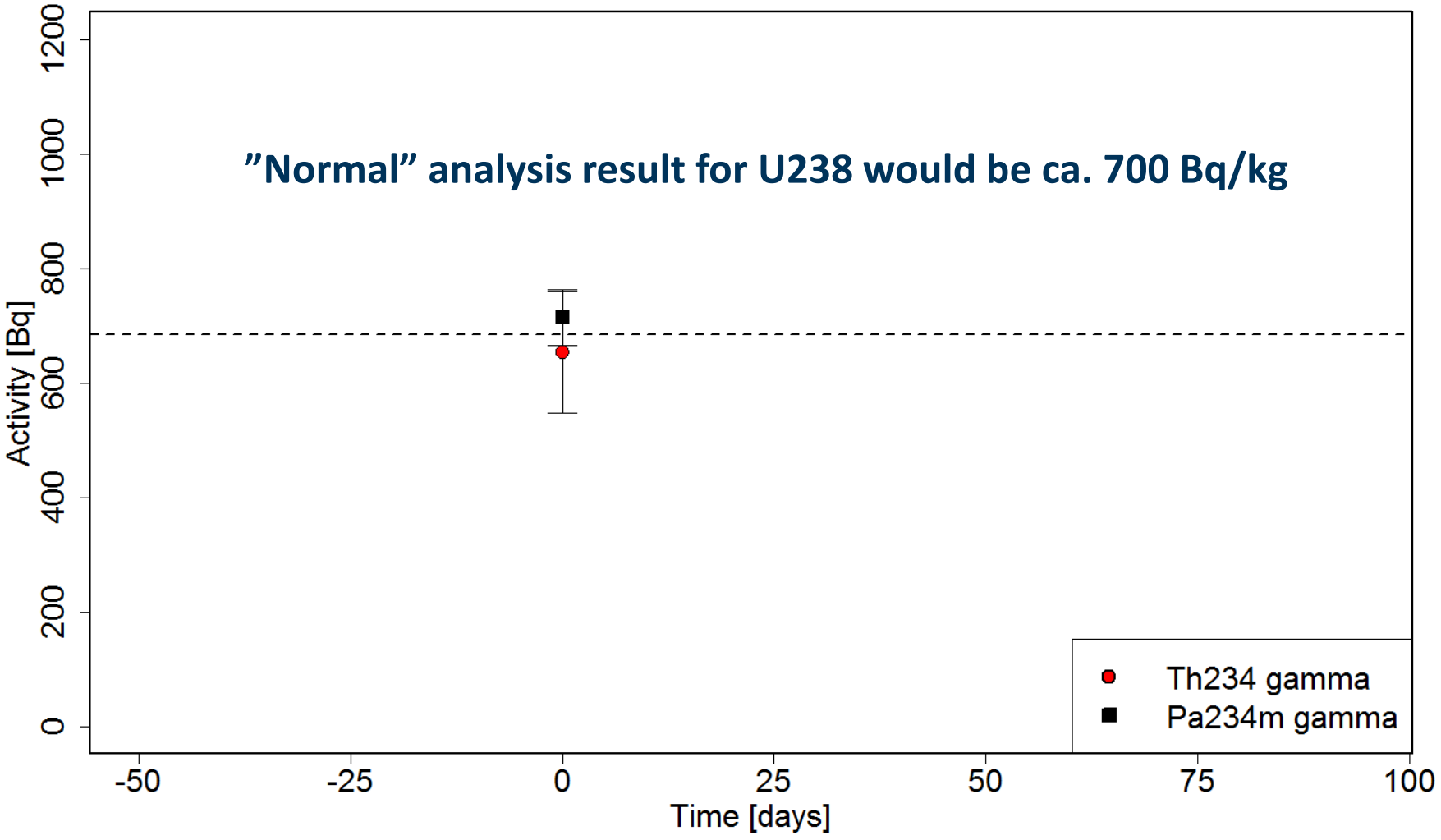
Nuklidi	Aktiivisuus (LSQ)	Epävarm. % (LSQ)	Aktiivisuus (pri)	Epävarm. % (pri)	Havaitsemisraja	effHalfLife
U234	1088.3075	7.22	1032.7845	12.87	115.2435	246000.0 a
U238	819.762	13.62	1048.6814	16.29	205.7103	4.47E9 a
Pa234m	745.1628	3.5	1051.2664	6.8	44.395	24.1 d Th234
Th234	611.8819	3.81	**940**	16.26	4.1139	24.1 d

- Now everything ok?

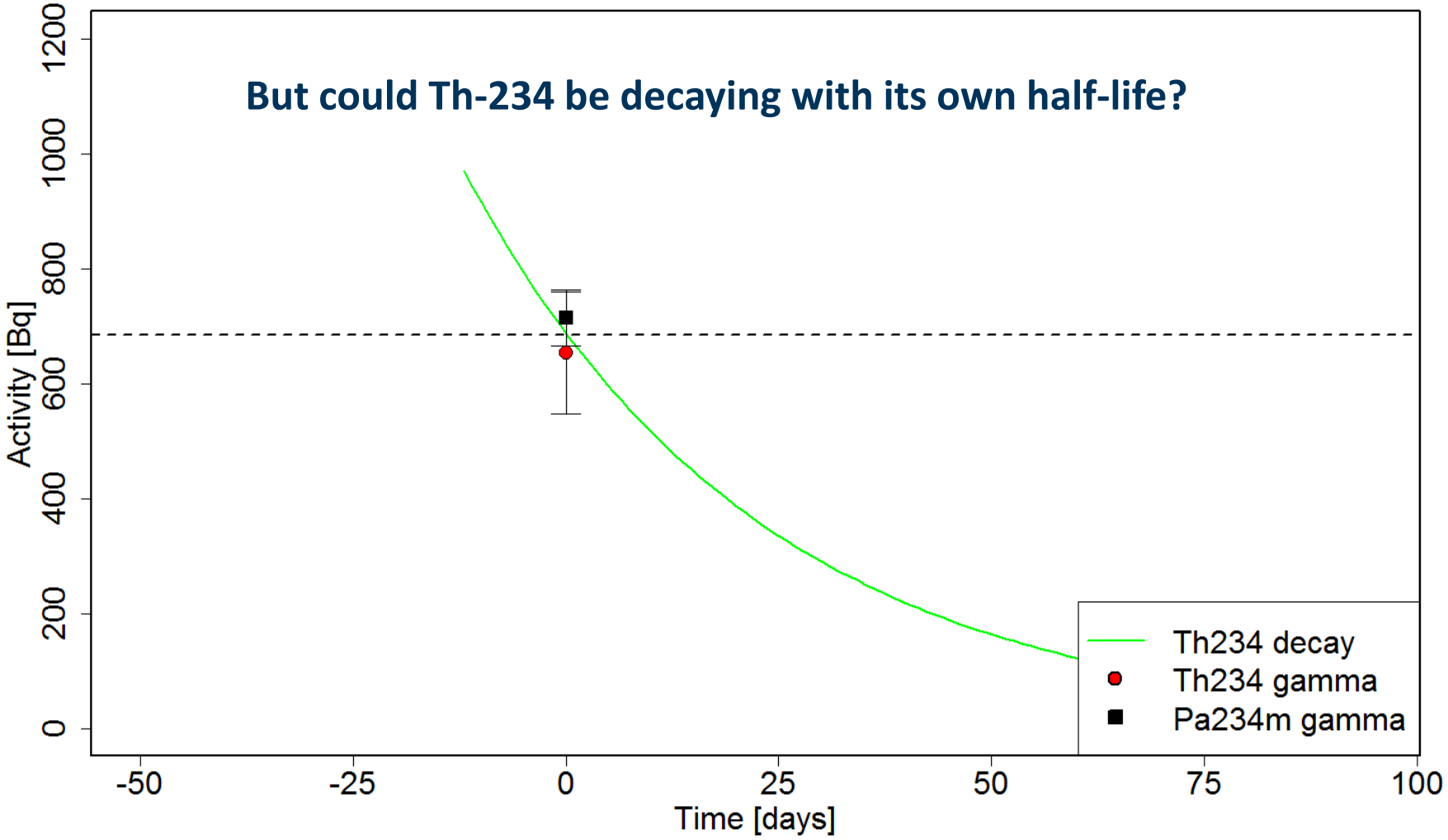
  NO!

  But how would you know if U238 and U234 were not directly detected?

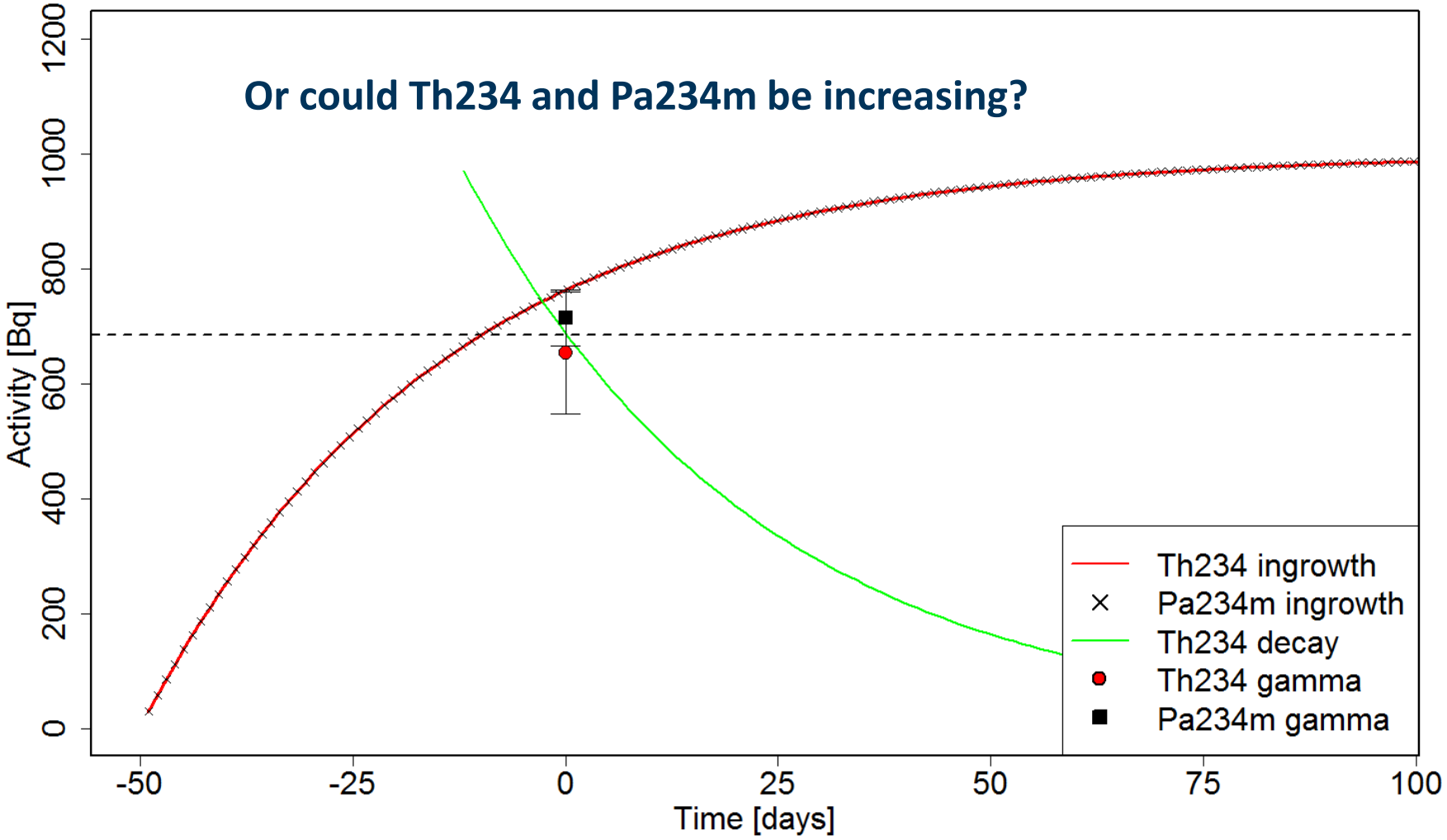
Case 1


”Normal” analysis result for U238 would be ca. 700 Bq/kg
Activity [Bq]
0
200
400
600
800
1000
1200
-50
-25
0
25
50
75
100
Time [days]
Th234 gamma
Pa234m gamma

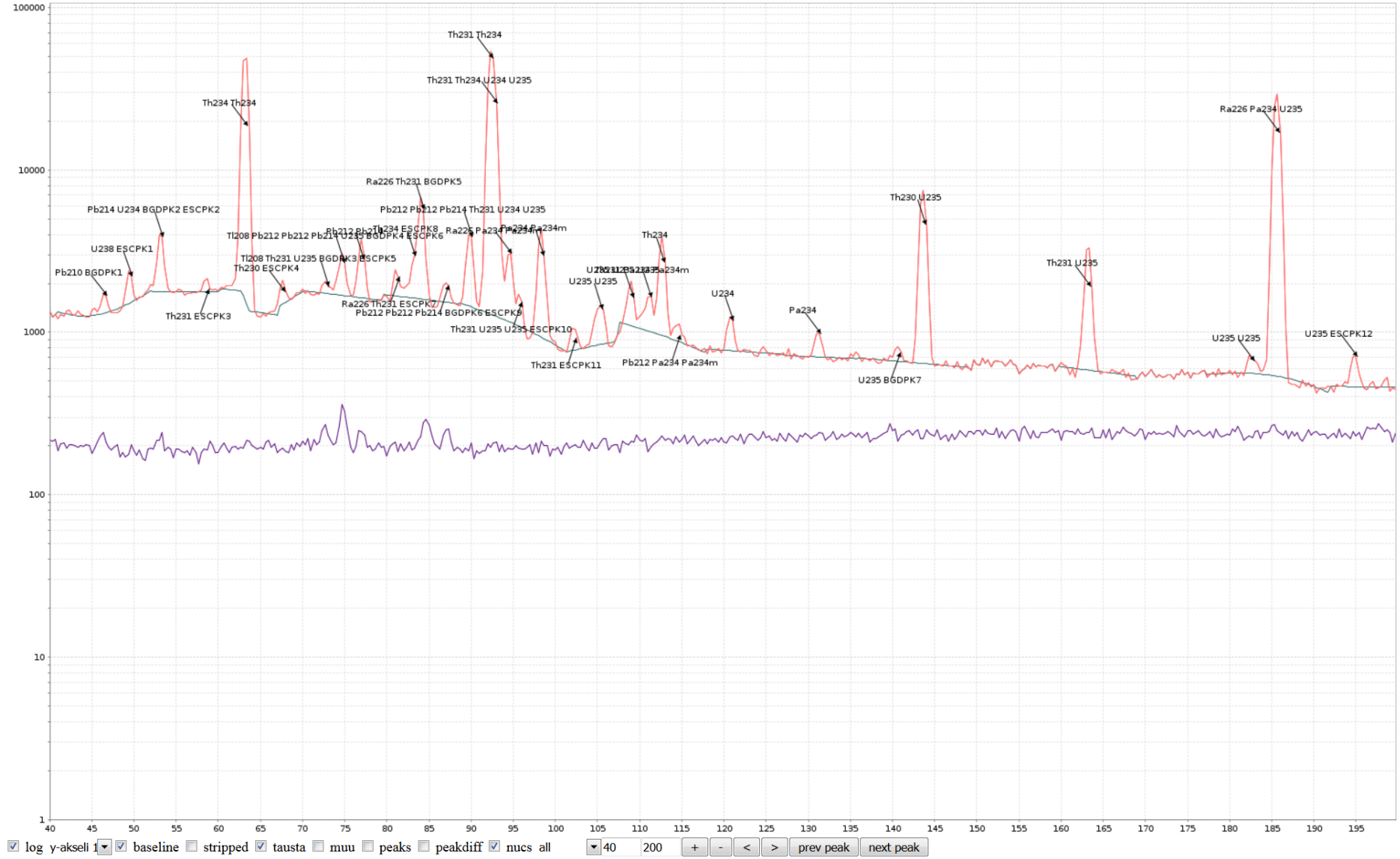
Case 1


But could Th-234 be decaying with its own half-life?
Activity [Bq]
0
200
400
600
800
1000
1200
-50
-25
0
25
50
75
100
Time [days]
Th234 decay
Th234 gamma
Pa234m gamma

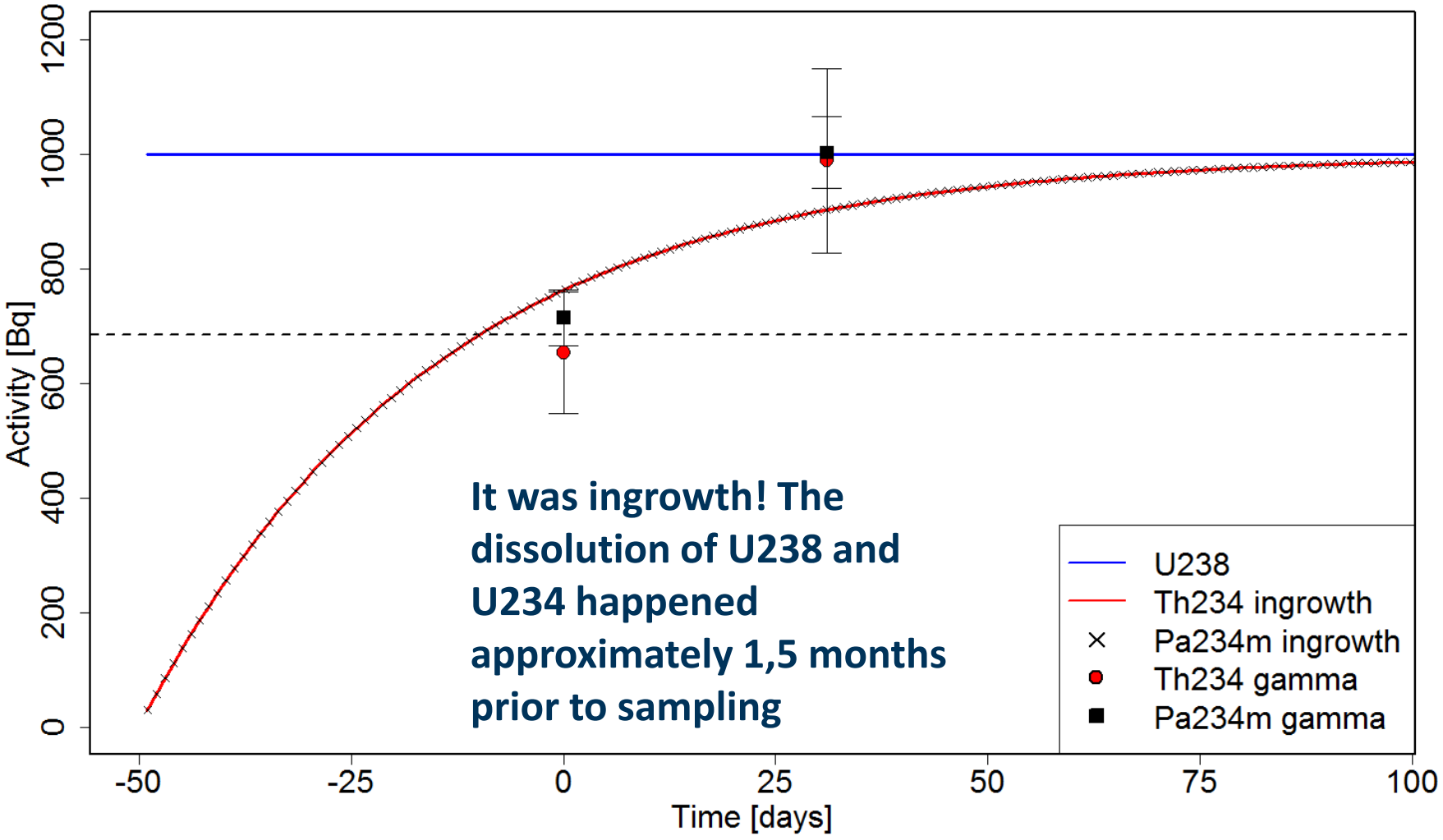
Case 1


Or could Th234 and Pa234m be increasing?
Activity [Bq]
0
200
400
600
800
1000
1200
-50
-25
0
25
50
75
100
Time [days]
Th234 ingrowth
Pa234m ingrowth
Th234 decay
Th234 gamma
Pa234m gamma

Case 1: 2nd measurement after 1 month

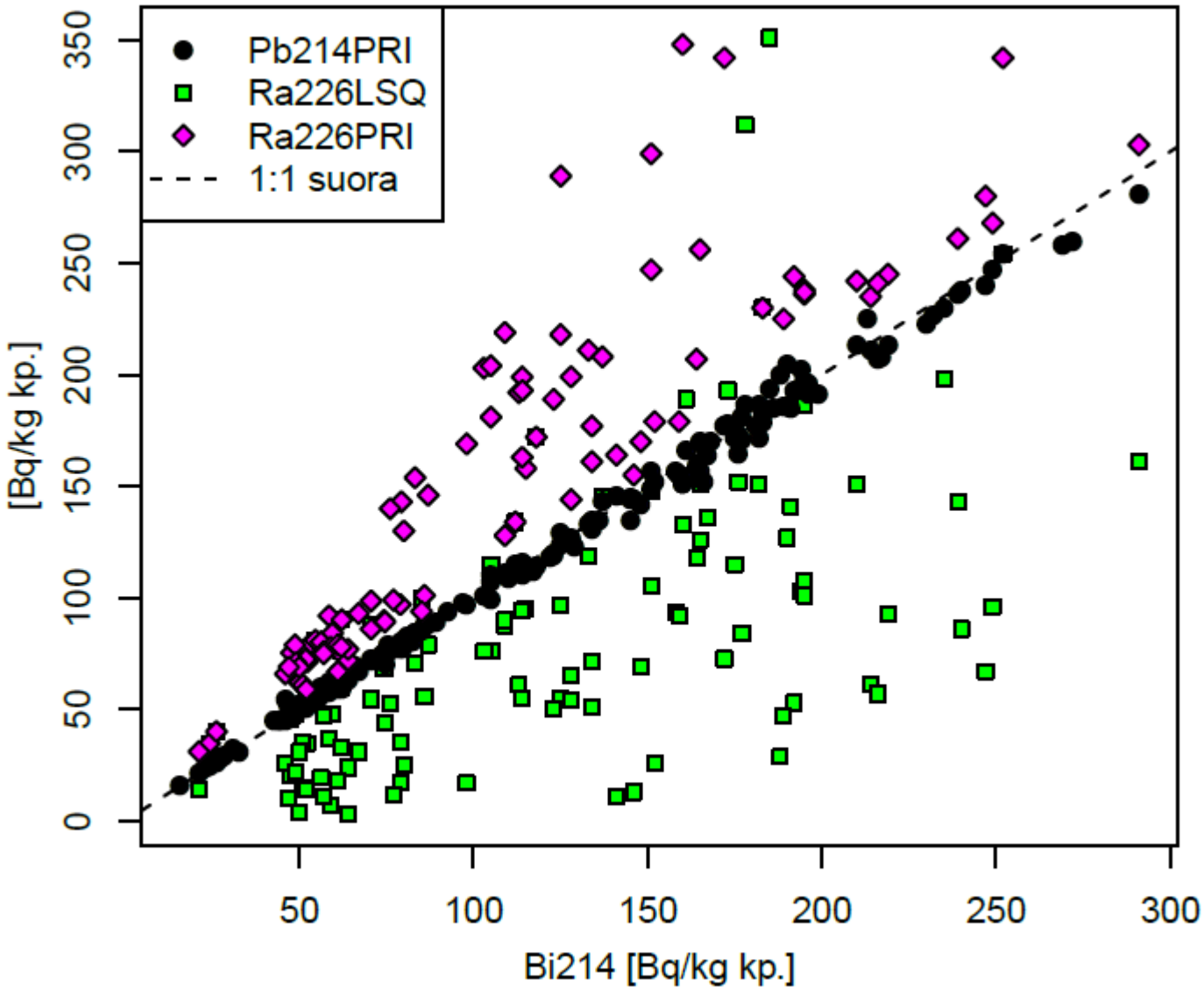


Case 1: Measurement 2 included



Case 2: Shaman PRI and LSQ results

- ~180 ash samples, where U238,U234 and Ra226 are in disequilibrium
- Ra226 primary peak (186 keV) gives too high results as expected
- LSQ-results are not correct! The shares of U-235 and Ra-226 from Shaman are not acceptable



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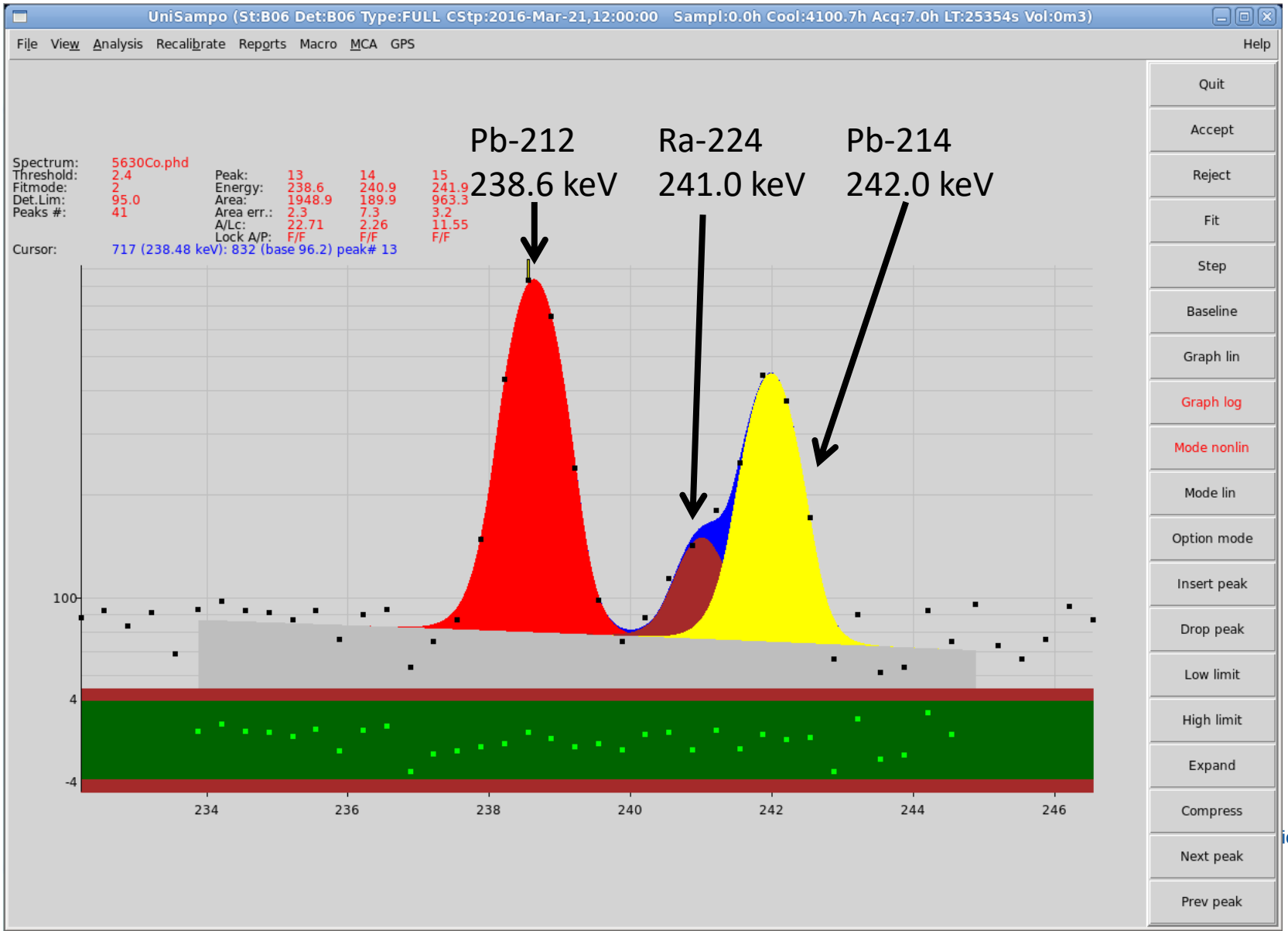
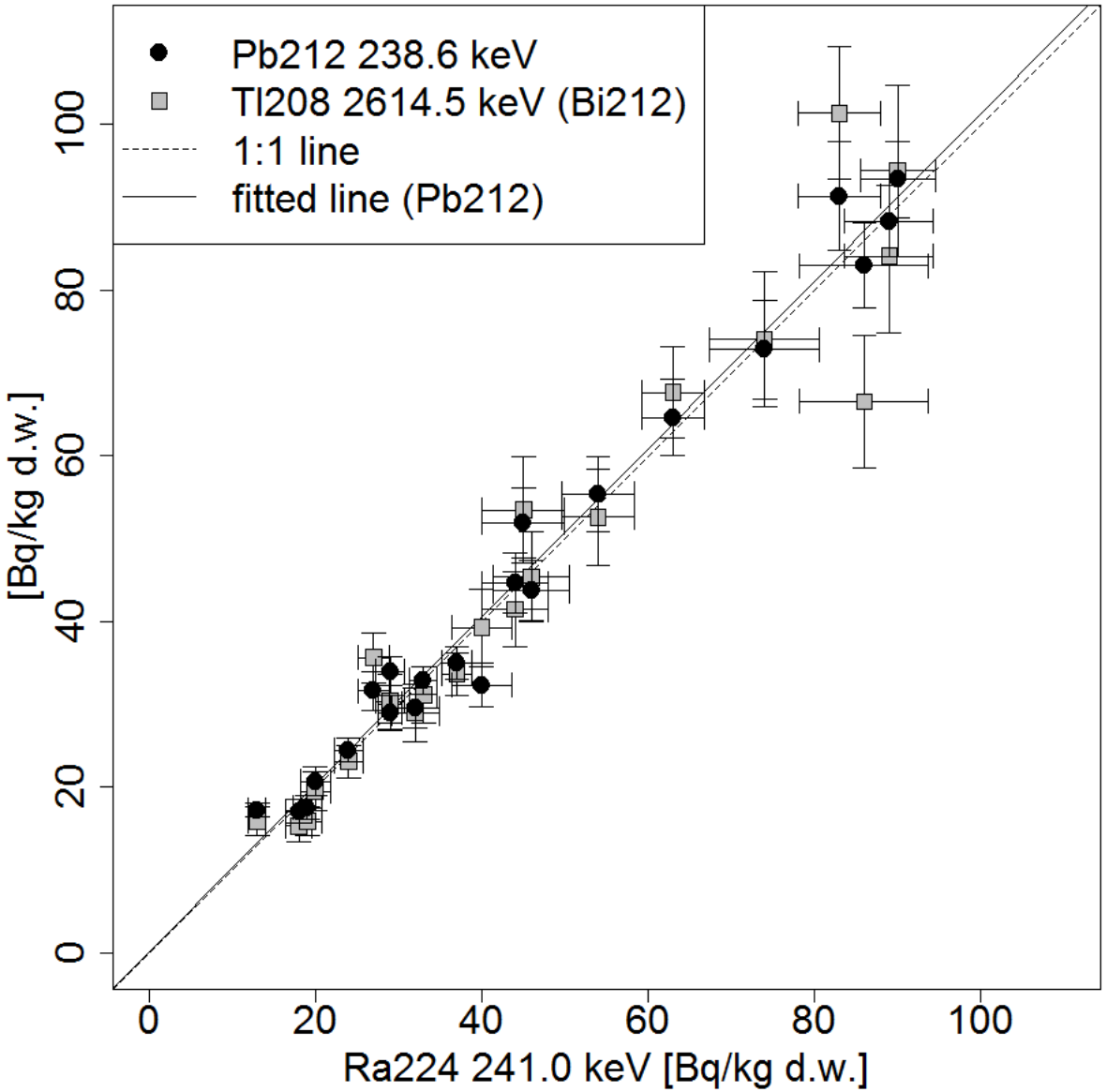
Case 3: Ra-224 with USS



Case 3: Ra-224

- Ash samples, thorium-series in equilibrium, low activity concentrations

- USS Ra-224 results compare well with Pb-212 and Tl-208, when analysis is done manually (interactive mode) to check fitting of overlapping peaks



USS: considerations for natural series

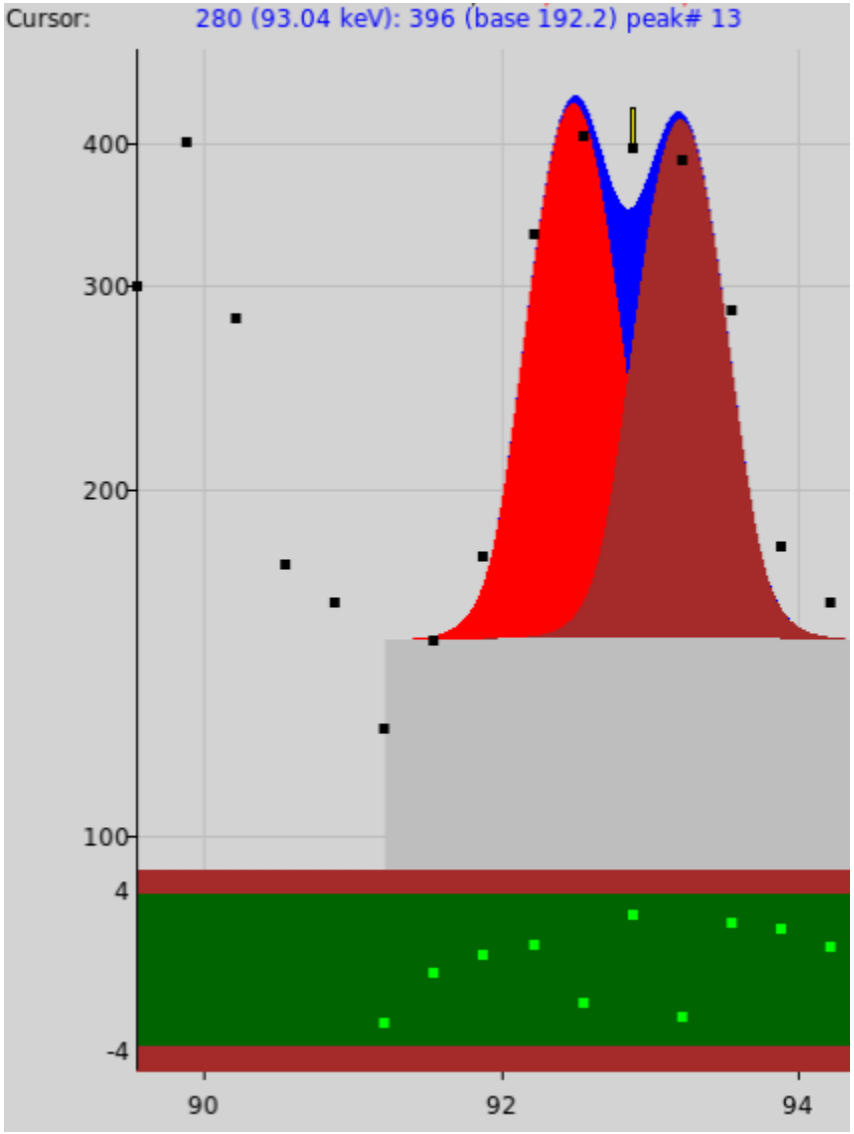
- UniSampo is good for fitting partially overlapping peaks
  - 241 keV Ra224 between Pb-212 and Pb-214 works well
  - 92.4 & 92.8 keV Th234 doublet

- Baseline can be difficult to ”shape” using UniSampo, especially in the low-energy part of the spectrum which has complicated baseline but is important for natural series peaks

- Care is needed even when using ”good” daughter peaks like Pa234m 1001 keV and Th-234 63 keV – disequilibrium checks and thinking about the nature of the sample!

USS: considerations for natural series

- UniSampo makes a gaussian fit with exponential tails for all detected peaks
- If double peaks are fitted (e.g. Th234 92.4 keV and 92.8 keV), and the nuclide is also present in the background spectrum, double peaks must also be fitted in the background spectrum
- If only one peak is present in the background, the background is subtracted from only one of the peaks in the spectrum
- Something to watch out for!



USS: considerations for natural series

- **Shaman library 3.1.1 is not up to date with Th234**

- Shaman LSQ-results cannot be used for natural series without careful checking, except in some equilibrium cases

- Shaman selection of primary peak depends on peak significance
  - ”primary peak” is not a universally robust way to select peaks for analysis of natural series
  - e.g. primary peak is 63 keV in one sample and 92.6 keV in another

- Manual peak selection and checking is needed from peak tables

- Tl208 result from Shaman is true Tl208 – user needs to calculate manually the branching of Bi212 decay if used for Th228

Case 2: Shaman PRI and LSQ results

- Need to calculate the ”true” Ra226 proportion from Shaman Ra226PRI (186 keV) result:

  = Bi214PRI/Ra226PRI (0.574 in the equilibrium case)

- The remaining share of 186 keV 1-(Bi214PRI/Ra226PRI) is multiplied with Shaman U235PRI to get ”true” U-235:

  U235 = U235PRI * [1-(Bi214PRI/Ra226PRI)]

- Sometimes one or the other is not detected by Shaman, depending on other peaks present – need one more calculation step if the detection cannot be forced manually
- U238/U235 is checked, (median) should be close to 21, but can vary in single measurements at least 10-30

- If U >> Ra, the 143 keV peak result can be used directly for U235 (in the equilibrium case multiplied by 0.72)

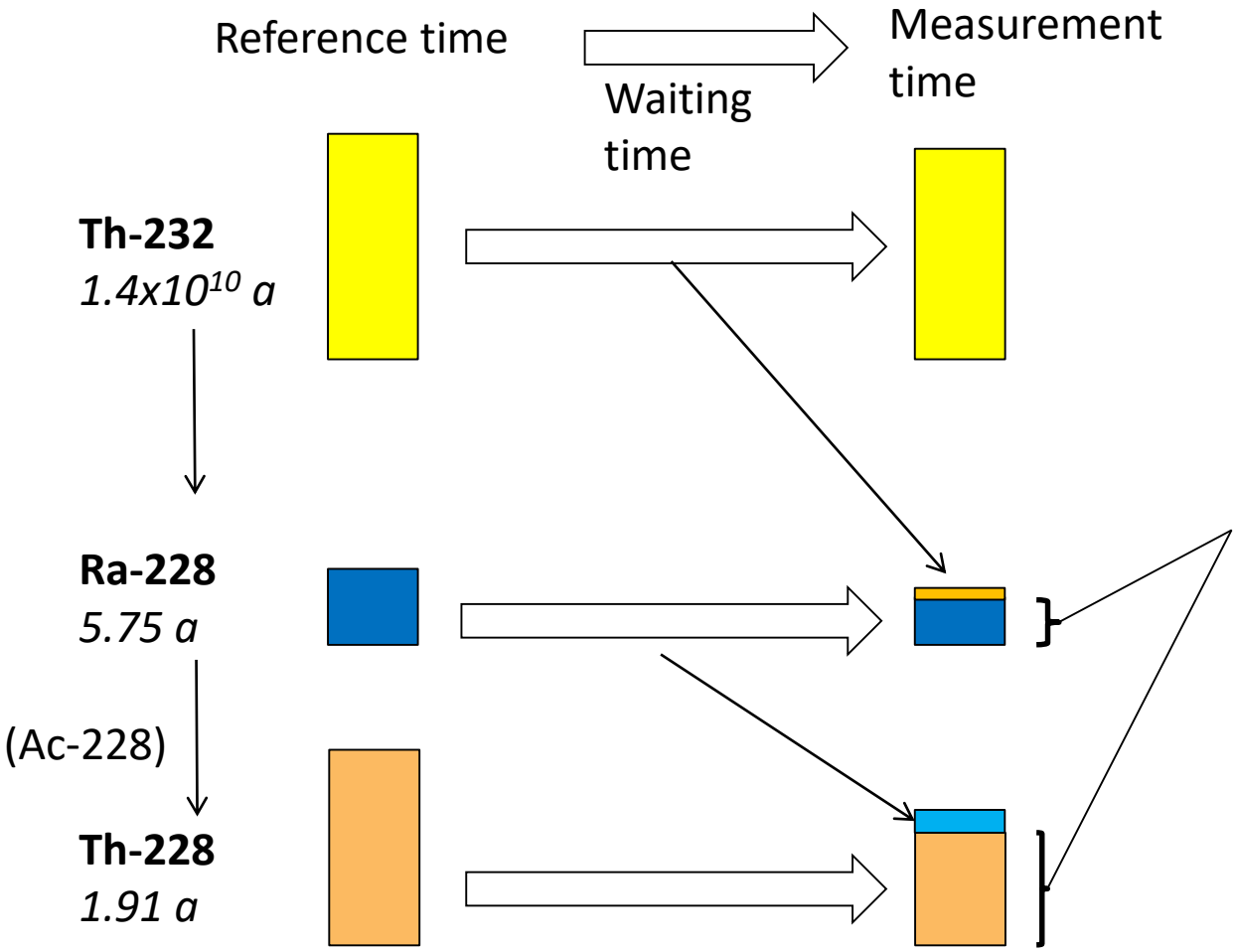
Problems with gammaspectrometric measurements of natural series

Conditions for a succesful measurement of natural series using gamma-spectrometry (in addition to a working detector, electronics, calibrations, coincidence correction, …):

Vacuum packed samples with 3 week waiting time

- Sample should stay inside the measuring geometry (radon)
- Photons should make it from the sample to the detector (Pb-210 photon self-absorption) **Thin samples or corrective calculation**
- Peaks should be distinguishable from background peaks (laboratory background) **Background measurements**
- Peaks should be resolvable from each other in order to calculate activities (interferences) **Resolution/fitting/deconvolution**
- Peaks should tell something about the nuclides that are actually of interest (decay series) **Daughter nuclides, equilibrium?**

Thorium-series disequilibrium



Thorium-series disequilibrium:

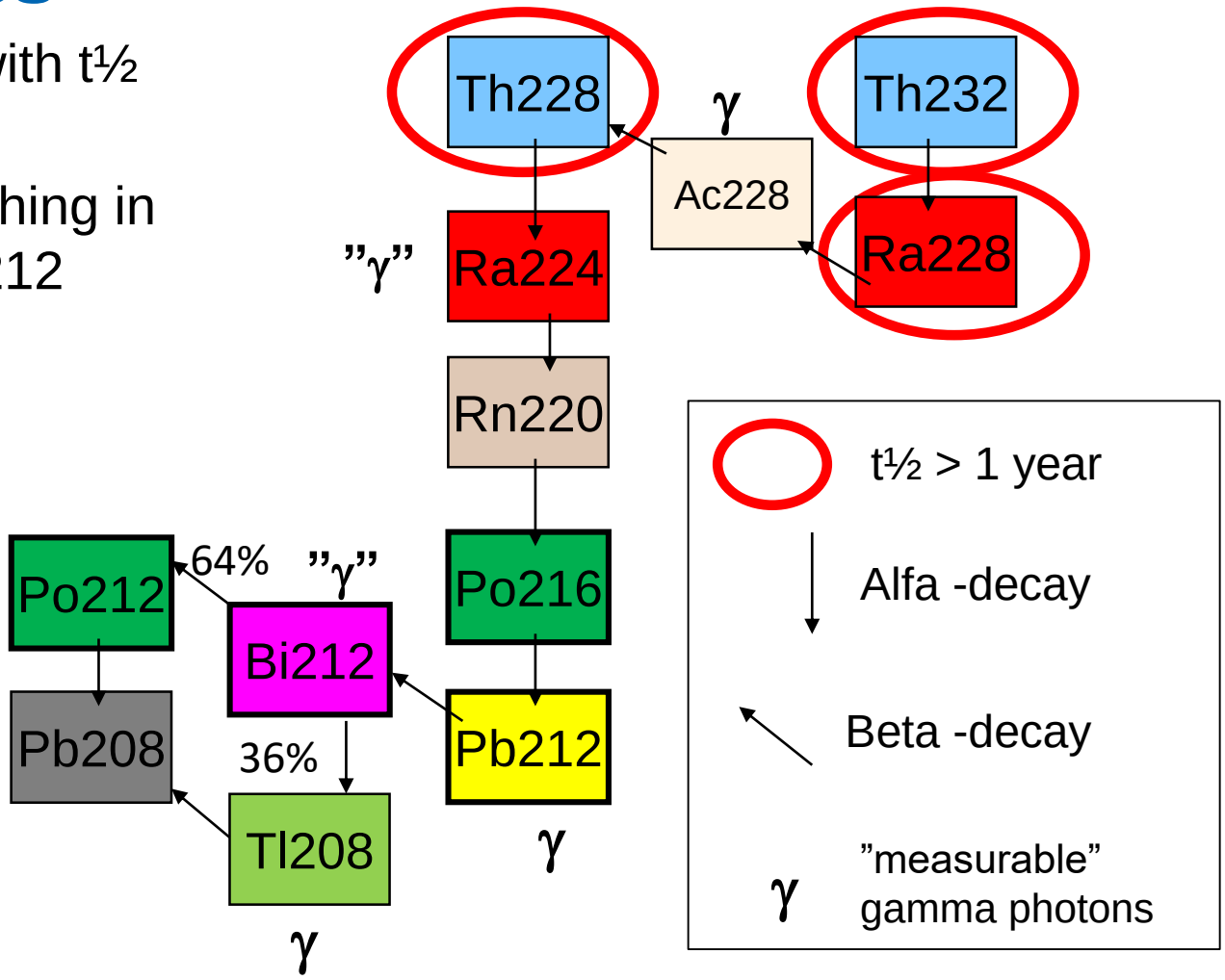
If waiting time is significant, e.g. > 1 year, the ingrowth during waiting time must be subtracted step-by-step before making a decay correction.

And Th-232 must be measured using other methods than gamma spectrometry (e.g. ICPMS)

Optional: Insert measurement time as the reference time, no decay corrections needed

Thorium-series

- Three nuclides with t½ > 1 year
- Significant branching in the decay of Bi-212



Actinide-series

- U-238/U-235 activity ratio in natural samples 21,44
- Three nuclides with t½ > 1 year