Measurements supporting NORM-regulation in Finland

NKS – GammaRay X webinar 20-21.10.2021

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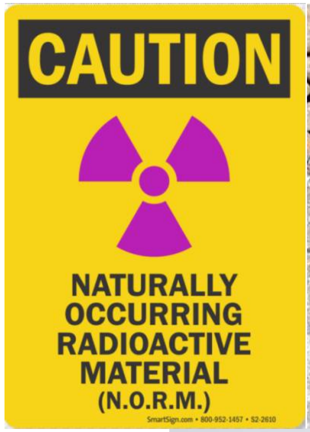
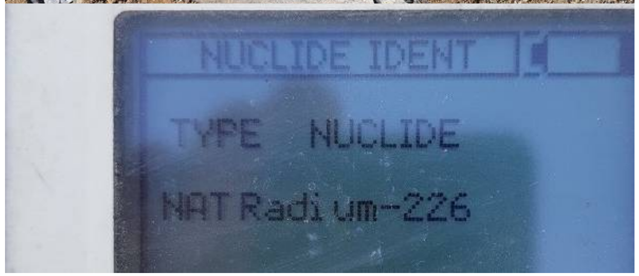
- Discussion on the choice of measured natural radionuclides and the methods used…
- …including some issues of interest relevant for gamma-spectrometry
- Conclusions



Numbers of NORM-measurements at STUK

Numbers of commercial NORM-measurements at the STUK laboratory

- 2020: 131
- 2021: 159 (from January to mid-October)
- At least similar numbers per year were made for research projects
- Some NORM-related characterisation has also been done as field measurements with LaBr-spectrometers
- Some industries have used other laboratories



SÄTEILYTURVAKESKUS
STRÅLSÄKERHETSCENTRALEN
RADIATION AND NUCLEAR SAFETY AUTHORITY

Recent changes in legislation

Revised law and decrees effective from 15.12.2018:

- Radiation Act 859/2018
- Governmental decree on ionisizing radiation 1034/2018
- Ministerial decree on ionisizing radiation 1044/2018

New set of lower-level STUK regulations during 2019, including:

- regulation on Commercial activities causing exposure to natural radiation
- regulation on Exemption and clearance levels
- regulation on Measurement of ionizing radiation

- **Complete revision of the legislation was made for the implementation of the EU-BSS, to match the current constitution, to include international standards, etc.**

NORM-regulation in Finland

Commercial activities causing exposure to natural radiation include:

- Indoor radon at workplaces
- Aviation
- Construction products
- Production of drinking water
- The utilization of soil, rock and other natural materials, and the materials formed in their processing (-> this covers the NORM-related industries from EU-BSS, e.g. mining)

- These commercial activities are classified as existing exposures in Finland (unless exposure is high enough to warrant licensing)
- Exposure assessment is required (unless exempt), and compared to reference levels
- NORM-waste from these activities is legally not radioactive waste, but assessment and approval for recycling and disposal is needed

Building the NORM inventory of Finland – in progress

Industries confirmed to have NORM (not necessarily at every site)	Not enough data yet – incomplete characterisation	Industries confirmed not to have NORM in Finland
▪ Mining&milling ▪ Smelters ▪ Hydrometallurgical plants ▪ TiO2 pigment production ▪ Groundwater treatment ▪ Zirconia ceramics for grinding ▪ Manufacturing of fire-proof mixtures and materials ▪ Recycling of scrap metals +steelworks using scrap ▪ (Old mining waste)	❑ Geothermal energy ❑ Cement production ❑ Primary iron production ❑ Fertilizer production	✓ Oil refining (two oil refineries using imported crude oil, one is being decommissioned) ✓ Coal-burning power plants (Coal is phasing out as a fuel in Finland, but some plants are still operating)

Reference levels for NORM-related industries

- Reference levels for NORM-related industries are given as **effective dose levels**
  - excluding radon, cosmic radiation and other background radiation, which have separate reference levels
- 1 mSv/a for workers
- 0.1 mSv/a for the public

- **NORM-related industries need to characterise their materials**:

➢ To determine activity concentrations for exposure assessments, i.e. to calculate effective doses to workers and public

➢ To determine whether waste is cleared or is in fact NORM-waste, in which case an approval is needed for the recycling or disposal of waste

➢ To determine whether discharge is within the minor discharge limits, which is also an effective dose for aquatic discharge (0.1 mSv/a for the public)

Exemption and clearance

- Exemption from exposure assessment and clearance levels for NOR in solid materials are given as :
- 1 Bq/g for U-238, Th-232, and their decay products
- 10 Bq/g for K-40
- (if discharge is formed, it needs additional consideration of the minor discharge limit)

- No mention of U-235 –series in the exemption levels
- However, Reference levels are set for exposure to natural radiation
- Natural Radiation is defined as ionizing radiation which is originating from space or from naturally occurring radionuclides, when they are not used as radiation sources
- Naturally occurring radionuclides are defined to include K40, U238, U235, Th232 and decay products
- **Therefore the exposure assessment for NORM needs to include the U-235 –chain**

What radionuclide information is needed for exposure assessment?

- In principle, to calculate the **committed effective dose** from **inhalation&ingestion**, the following nuclides need to be considered (but all of them not necessarily measured):

Uranium-series	Actinium-series	Thorium-series
U-238, Th-234, Pa234m	U-235	**Th-232**
U-234	Th-231	**Ra-228**
Th-230	Pa-231	Ac-228
Ra-226	Ac-227	**Th-228**
Pb-210, Bi-210	Th-227	Ra-224
Po-210	Ra-223	

- Need to figure out what is the amount of information that is practical to measure and ”good enough” for exposure assessment, considering that:
  – Some subchains are in equilibrium and can be represented by one activity concentration
  – Some nuclides can be calculated from others based on natural isotope ratios

Requirements for NORM-measurements from legislation

Generic requirements for **any radiation measurements used for estimating exposure** according to the radiation legislation:

- Methods need to be fit-for-purpose and verified to be reliable
- Results need to be metrologically traceable to SI-units
- The equipment needs to be properly calibrated
- For construction products it is specified in the lower level regulations that measurements need to be made with high-resolution gamma-spectrometry (HPGe)

- **Contrary to construction products, there are no detailed regulations about NORM-measurements**

➢ This gives options to potentially use results from many different methods
  – Different types of gamma spectrometers, LSC, ICPMS, HR-ICPMS, etc

How to choose analytical methods?
Things to consider in NORM-measurements

Since multiple industrial sectors and many sites are involved, which are typically not equipped for measurements on site, NORM-measurements:

- should be available as a commercial service for anyone
- should not take very long to perform (>6 months is too long?)
- should not be overly expensive
- should be made with fit-for-purpose and reliable methods, that are <u>enough</u> to make exposure assessments and demonstrate safety

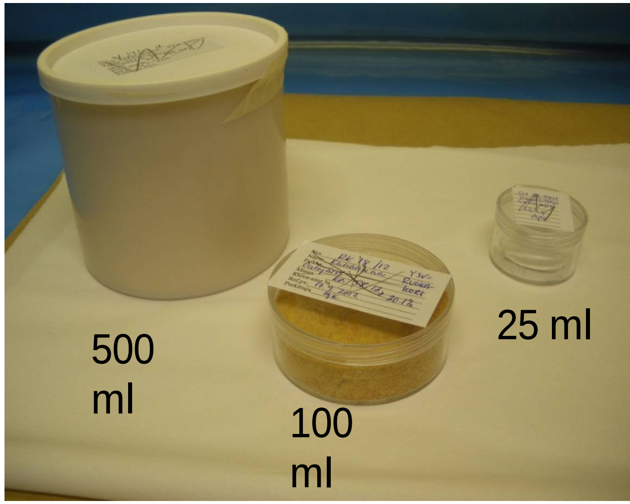
❖ Gamma spectrometry is a good first choice:

➢ there are recognised standards and laboratories with accreditation

➢ method is fairly quick and not too expensive for the customer

➢ Sample preparation is minimal and samples are not destroyed

❖ However it is not enough for NORM-measurements!



Processed materials

- Typically solid NORM are chemically and/or biologically processed
- Typically also water samples or other liquids need to be analyzed

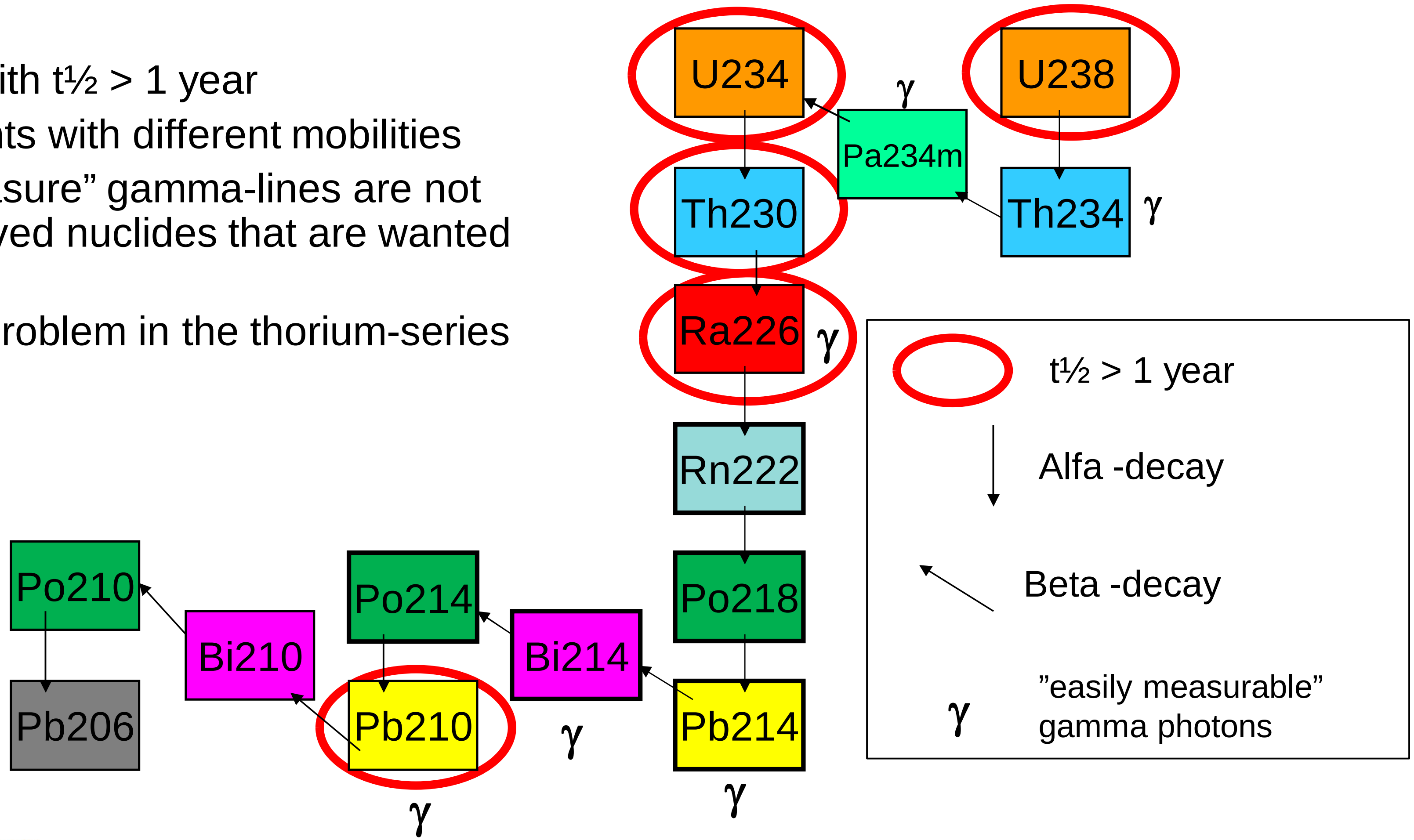
- In processed materials and liquids, it is **not possible to assume decay-series equilibrium**
- This prevents gamma-spectrometric determination of Th232 from Ac228
- Also prevents using Pa-234m for U238, unless the time from processing is known to be long enough for U238-Th234 equilibrium (> 6 months old samples)

- For exposure assessment (or exemption) the concentrations of U-238 and Th-232 are needed
- It would be too slow to determine ingrowth-rates using gamma spectrometry
- ➢ **Other methods are needed: STUK uses ICPMS to determine Th232 and U238 in processed materials**

Uranium series

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

  -> same problem in the thorium-series



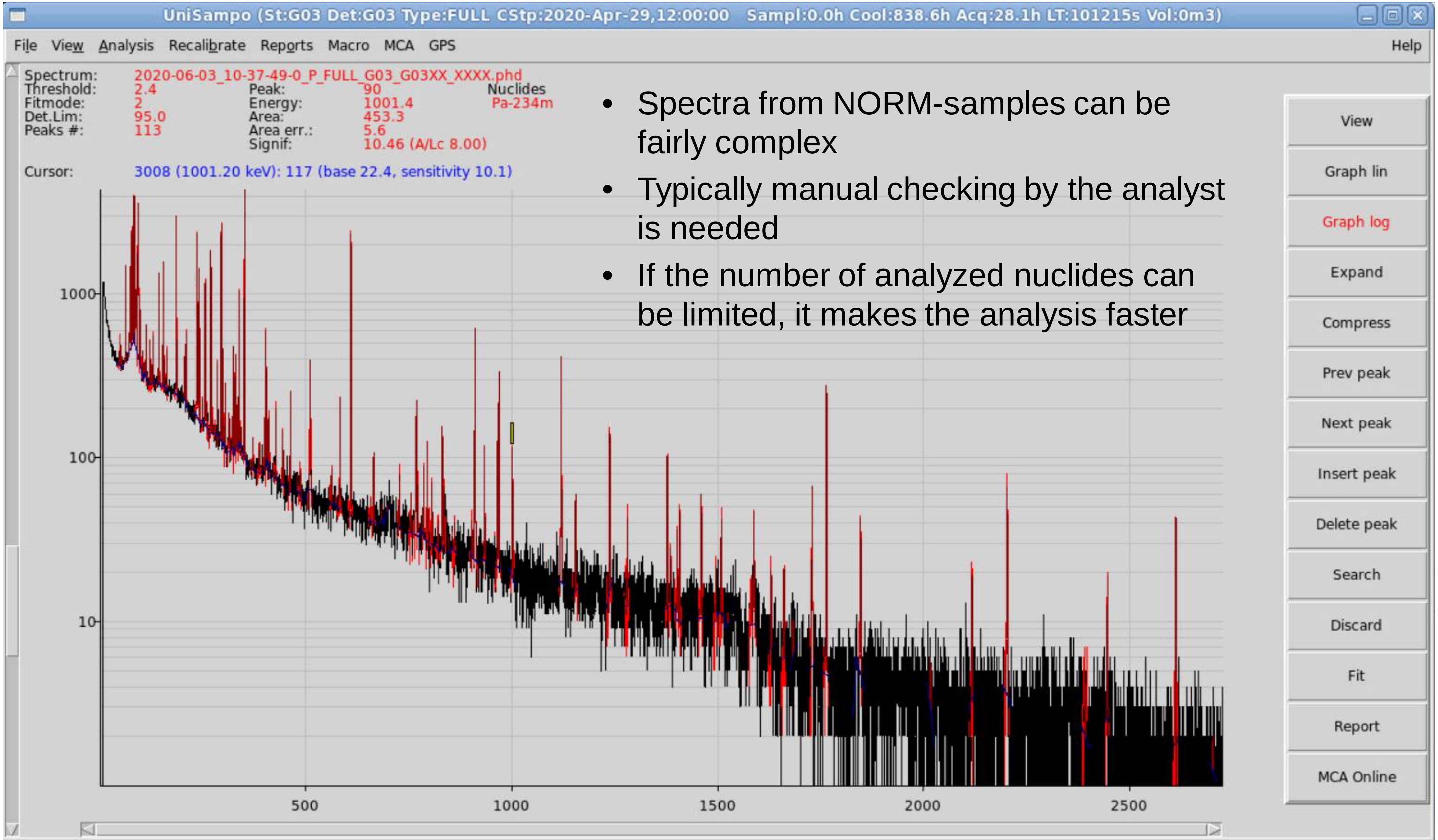
Added complication for gamma spectrometry - sample matrices of NORM

Sample matrices are industrial materials with highly variable **chemical compositions and densities**:

- Rocks and minerals
  - silicates, oxides, sulphides, hydroxides, etc
- Leaching residues
- Precipitates
- Sludges
- ”Ash” (fly ash, bottom ash, bottom slag)
- Slags and dust from smelters
- Various liquids

➢ **The analyst does not necessarily know the chemical composition (only density)**

- Spectra from NORM-samples can be fairly complex
- Typically manual checking by the analyst is needed
- If the number of analyzed nuclides can be limited, it makes the analysis faster



Current routine NORM-measurements at STUK laboratory

<u>Solid samples</u>:

- **U-238 and Th-232 with ICPMS** (except for unprocessed rocks e.g. ores and waste rock, where these can be measured from daughters using gamma-spectrometry)
- **Ra-226, Ra-228, Pb-210, Th-228, Pa-234m, K-40, (Cs-137) by gamma-spectrometry** using vacuum-packed geometries with three weeks of waiting for radon-daughters

<u>Water samples</u>:

- U-238 and Th-232 with ICPMS
- Total-alfa and Ra-226 with LSC
- Ra-228, Pb-210, Th-228, Pa-234m, K-40 using gamma-spectometry in the Marinelli-geometry

Some choices made for NORM-measurements

- Why Pa-234m instead of Th-234?
- Why no U-235?
- Why no Po-210?
- Why no Th-230?

Why use low yield Pa234m?
- Issues with Th-234

- The yield for Th234 (63 keV) is higher than for Pa234m (1001 keV), so better statistics and lower MDC's should be achieved
- There should be no interfering nuclides or overlapping X-rays at 63 keV

➢ However there seems to be issues with Th234 and Pa234m results not matching

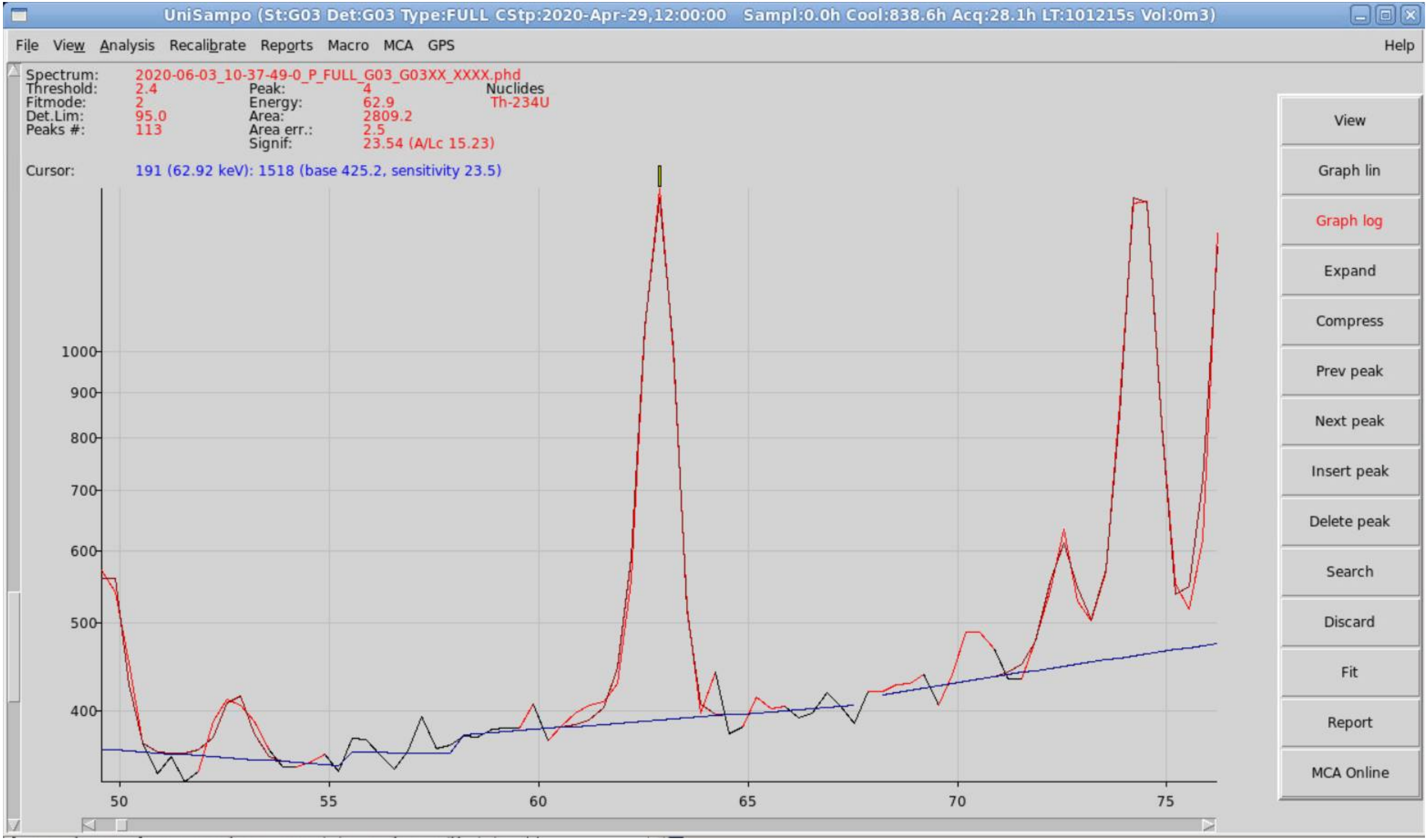
- Due to the short half-life of Pa234m, this cannot be a disequilibrium effect;

➢ Th234 and Pa234m are in equilibrium within minutes

- When the discrepancy is seen, Pa234m is typically in agreement with the uranium isotopes (U235 from gamma or U238 from ICPMS), and Th234 is not

➢ Therefore Pa234m is used for NORM-measurements instead of Th234

- Matrix compositional effect? Problems in the density correction?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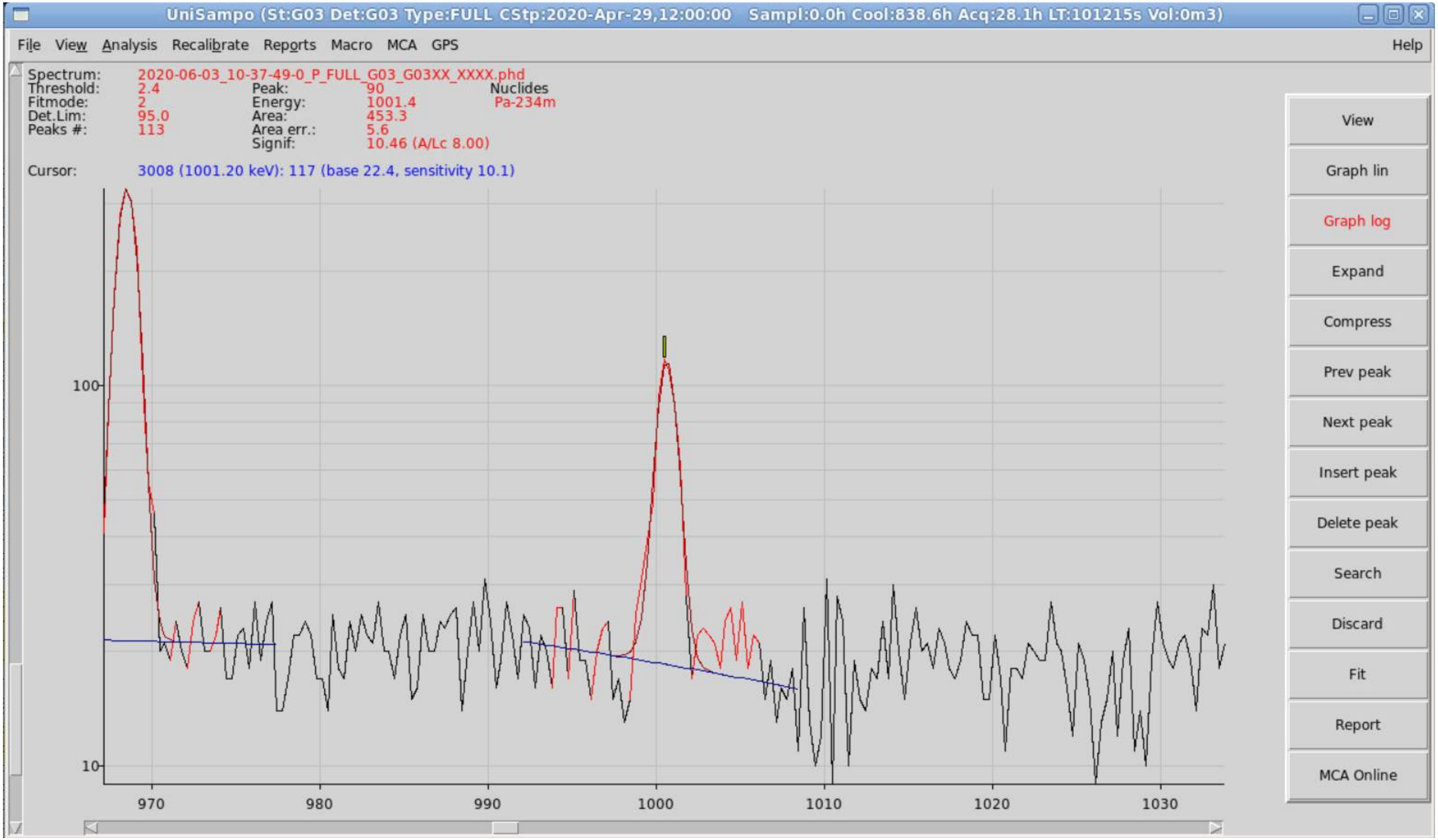
File View Analysis Recalibrate Reports Macro MCA GPS Help
Spectrum: 2020-06-03_10-37-49-0_P_FULL_G03_G03XX_XXXX.phd
Threshold: 2.4
Fitmode: 2
Det.Lim: 95.0
Peaks #: 113
Peak: 4
Energy: 62.9
Area: 2809.2
Area err.: 2.5
Signif: 23.54 (A/Lc 15.23)
Nuclides
Th-234U
Cursor: 191 (62.92 keV): 1518 (base 425.2, sensitivity 23.5)
1000
900
800
700
600
500
400
50
55
60
65
70
75
View
Graph lin
Graph log
Expand
Compress
Prev peak
Next peak
Insert peak
Delete peak
Search
Discard
Fit
Report
MCA Online



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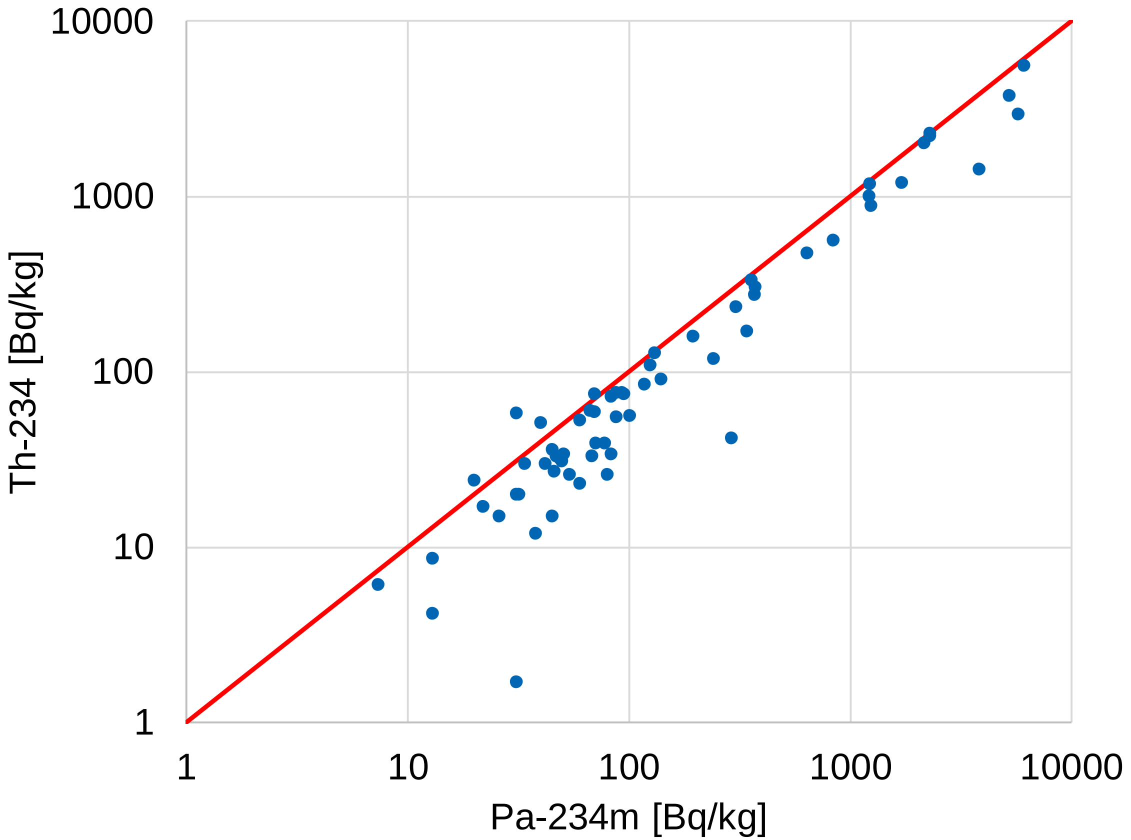
File View Analysis Recalibrate Reports Macro MCA GPS Help
Spectrum: 2020-06-03_10-37-49-0_P_FULL_G03_G03XX_XXXX.phd
Threshold: 2.4
Fitmode: 2
Det.Lim: 95.0
Peaks #: 113
Peak: 90
Energy: 1001.4
Area: 453.3
Area err.: 5.6
Signif: 10.46 (A/Lc 8.00)
Nuclides
Pa-234m
Cursor: 3008 (1001.20 keV): 117 (base 22.4, sensitivity 10.1)
100
10
970
980
990
1000
1010
1020
1030
View
Graph lin
Graph log
Expand
Compress
Prev peak
Next peak
Insert peak
Delete peak
Search
Discard
Fit
Report
MCA Online

Discrepancy of Th-234 and Pa-234m

- ~60 results from 2019-2021 pulled from the STUK database
- Includes many matrices: ash, construction products, sediments, sludges, etc.
- Most points plot below the 1:1 line (Th234 ”too low”)
- **Median Th234/Pa234m = 0.71**
- Clearly there is an issue, but the full extent of is not even visible, because most samples do not have results for both nuclides
- Problem is not limited to one or a couple of detectors – more general



Issues with Th-234

- Fe-precipitates from groundwater treatment facilities also show measured **median Th234/Pa234m of 0.78** (N=30)
- **The same samples have median U238/Pa234m of 1.01 (which shows again why Pa234m is preferred)**

- In waste-incineration bottom ash, the difference between measured Th234 and Pa234m can be up to a factor of 2

- Tests are currently being made at STUK using mass-scans by ICPMS to take into account the chemical composition of the samples using EFFTRAN (in progress)

- QUESTION: Has anyone else found they have a discrepancy between Th234 and Pa234m, and any ideas why that is?

Why no U-235?

- Due to Th-232, ICPMS is already used. Therefore it makes sense to also analyze U238 at the same time
- Natural uranium has a constant U238/U235 activity ratio of 21,45 even if the material is processed in NORM-related industries
- Natural isotope ratio and activity concentration of U238 is enough to estimate the dose from U235-series in the screening assessments for most cases
- For uranium leaching residues the activity ratio can be applied to U235-daughters using Ra226 as the reference

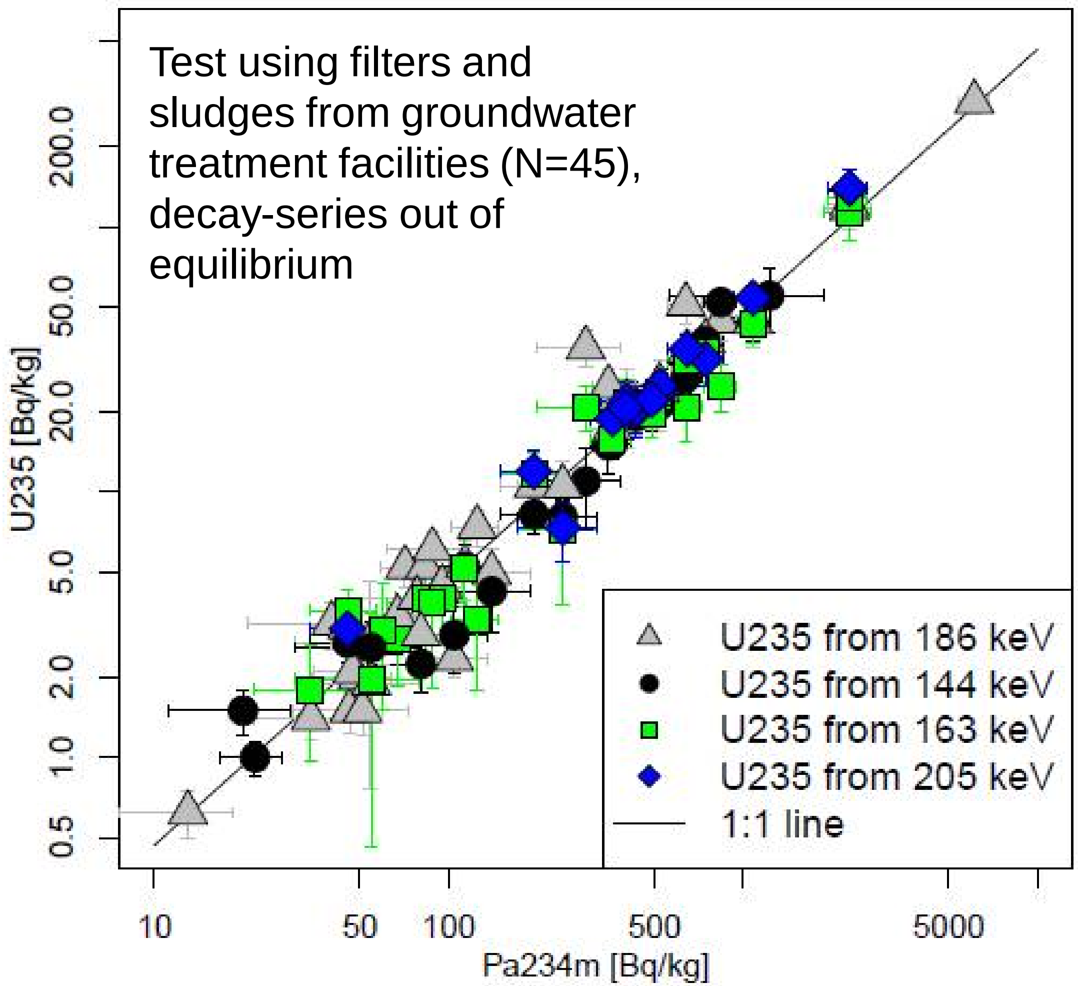
- Measurement of U235 is of course possible with gamma-spectrometry, but there are some complications for processed materials

➢ Therefore U235 is not routinely included in the NORM-measurements at the moment (…but perhaps it should be included?)

- Measuring U235 from processed materials with UniSampo-Shaman requires additional manual calculation steps if 163 keV or 205 keV peaks are not detected, since decay-series equilibrium cannot be assumed and ”standard” overlap corrections cannot be used

For cases of non-equilibrium:

- Use of 186 keV peak requires calculation and subtraction of Ra226-share (using Bi214 and Pb214)
- Use of 144 keV peak requires calculation and subtraction of Ra223-share (typically correction from Th230 or Bi212 is much smaller)
- Shaman is quite well suited for measuring Ra223: peaks overlap with Ac228, but the shares of Ra223 and Ac228 can be calculated by USS well because both nuclides have multiple peaks in the spectra



Why no Po-210?

- The radiochemical analysis of Po210 is slow and expensive (not ideal for screening exposure assessments)
- The half-life is so short (138 d) that in the disposal of waste Po210 is fairly quickly in equilibrium with Pb210

➢ Pb-210 is measured already and can be used to estimate longer-term Po210

- For aquatic discharge the total-alfa and U238, Ra226, Th232, Th228 are measured, and U234 can be esimated from U238 (approximately equal)

➢ Maximum Po210 can be estimated from difference of total-alfa and measured alfa-nuclides, and this can be used in screening exposure assessment

➢ Therefore Po210 is not routinely analyzed in NORM-measurements, but can be included if judged necessary by the regulator

Why no Th-230?

- There is little evidence so far for the selective mobility of thorium in Finnish NORM-related industries - typically uranium and/or radium are more mobile
- Unlike lead and polonium, thorium is not easily volatilized at high temperature
- For screening exposure assessments it is currently assumed that Th230 is equal to the higher of U238 or Ra226
- For uranium leaching residues Ra226 is a good estimate for Th230
- For uranium or radium containing precipitates using the higher of U238 or Ra226 gives an overestimate of Th230, if thorium was not mobile
  - This is ok, makes exposure assessment more conservative
- In cases where both uranium and radium are leached, the Th230 in residue would be underestimated, but these cases have not been found (yet) to be relevant in Finland

➢ Therefore Th230 is not routinely included in the NORM measurements at the moment

Conclusions

Good quality NORM-measurements are important, because the results are used:

- ➢ To estimate the exposure of workers and public in NORM-related industries
- ➢ To determine whether discharge to the environment is significant
- ➢ To make regulatory decisions about the recycling and disposal of NORM-waste

❖ Gamma-spectrometry is very useful for NORM-measurements, but not quite enough by itself

- There is still room for improving the gamma-spectrometry of NOR and research in this area would be welcome (both for laboratory and field gamma-spectrometry)
- Investigation about the Th234 and Pa234m discrepancy is on-going
- Hopefully the future routine use of efftran with UniSampo-Shaman will improve the situation in terms of taking into account the sample chemical composition
- Perhaps U235 needs to come back to routine NORM-measurements – if this is ok in terms of accreditation