IAEA 60 Years

Atoms for Peace and Development

On the analysis of challenging ALMERA Proficiency Test samples

IOLANDA OSVATH

INTERNATIONAL ATOMIC ENERGY AGENCY

ENVIRONMENT LABORATORIES

MONACO

Gammaray 2018, Reykjavik, 25-26 September 2018

Outline

- Introduce ALMERA
- IAEA Proficiency Tests (PT)
- ALMERA 2017 PT
- The experience of a participating lab's gamma spec team with an unusual sample
- What this PT teaches us more than previous ones?

IAEA-NAEL ORGANIZATIONAL STRUCTURE

in Monaco and Seibersdorf

DIRECTOR
David Osborn

Administration
Nima Mashayekhi

Electronic and Engineering Services
Hussein Ramadan

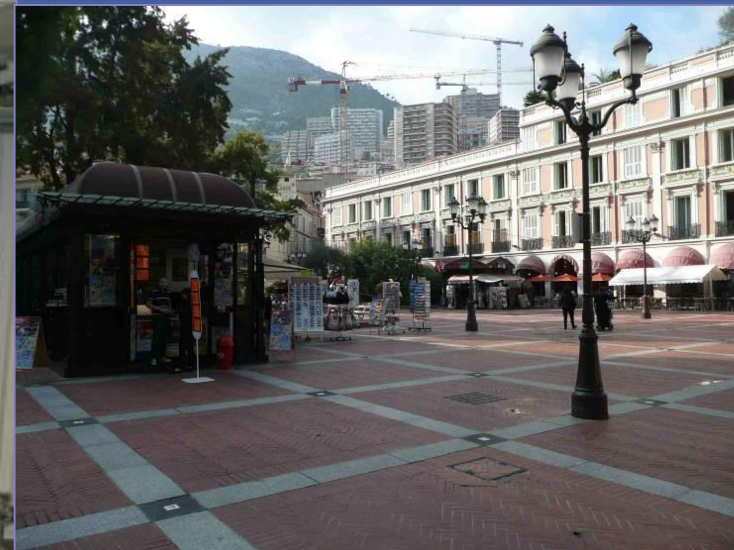
Monaco

- **RADIOMETRICS LABORATORY (RML)** – Iolanda Osvath
- **RADIOECOLOGY LABORATORY (REL)** – Peter Swarzenski
- **MARINE ENVIRONMENTAL STUDIES LABORATORY (MESL)** – Sylvia Sander

Seibersdorf

- **TERRESTRIAL ENVIRONMENT LABORATORY (TEL)** – Manfred Gröning

Underground lab (35 m water-equivalent)



IAEA

ALMERA

Network of Analytical Laboratories for the Measurement of Environmental Radioactivity

- A worldwide network of laboratories capable of providing reliable and timely analysis of environmental samples in the event of accidental or intentional releases of radioactivity to the environment.

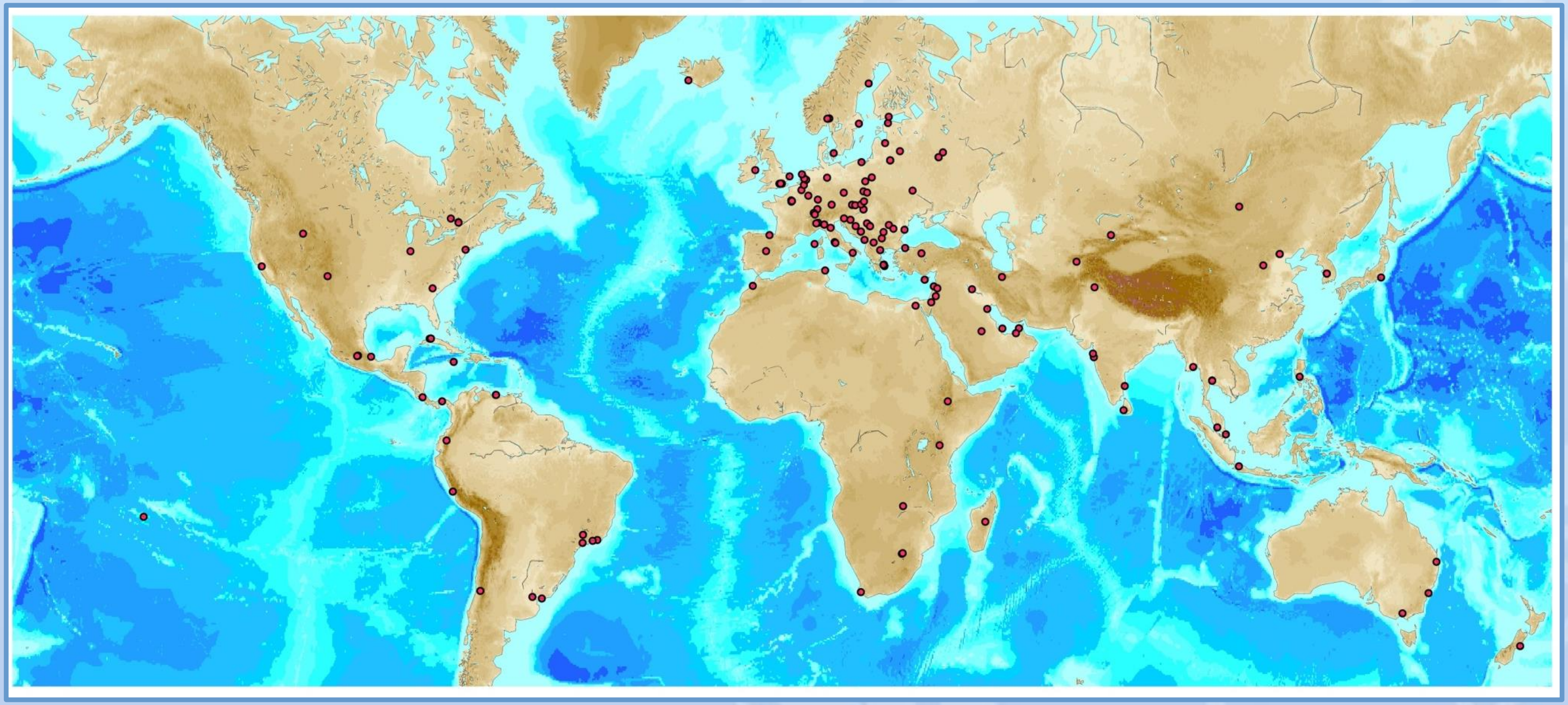
- Coordinated by the IAEA through the Environment Laboratories, Seibersdorf and Monaco

IAEA
International Atomic Energy Agency

IAEA
60 Years
Atoms for Peace and Development

ALMERA

ALMERA member laboratories



177 laboratories in 89 countries (September 2018)

IAEA

60 Years

Atoms for Peace and Development

ALMERA structure

IAEA : Central Coordination

5 Regional Groups

Regional Coordinating Laboratories

- **EUROPE** → *Karlsruhe Institute of Technology*
- **MIDDLE EAST** → *Jordan Atomic Energy Commission*
- **AFRICA** → *South African Nuclear Energy Corporation*
- **ASIA-PACIFIC** → *Korean Institute of Nuclear Safety*
- **NORTH AND LATIN AMERICA** → *Canadian Nuclear Safety Commission*

ALMERA member laboratories in Nordic countries

Denmark

Technical University of Denmark (DTU)

Finland

Radiation and Nuclear Safety Authority (STUK)

Iceland

Icelandic Radiation Safety Authority (IRSA)

Norway

Institute for Energy Technology (IFE)

Norwegian Radiation Protection Authority (NRPA)

Sweden

Swedish Defence Research Agency (FOI)

Swedish Radiation Safety Authority (SSM)

The IAEA assists the ALMERA network of laboratories through:

- Organization of yearly coordination meetings

- Organization of yearly PTs and ILCs as a tool for external quality control, providing participants with documented analytical performance time records

- Development of validated analytical methods for routine and emergency monitoring

- Organization of workshops and training courses (on average 2/year)

- Coordination with other relevant networks and international organisations;

- Production of RMs of interest for ALMERA (with network participation)

IAEA PTs and ILCs for radionuclides in environmental samples: ~500 labs/year

- Project-dedicated
  - Japan
  - ALMERA
  - Technical Cooperation regional/interregional projects
- World-wide general (mainly terrestrial and atmospheric samples and spiked matrix marine samples)
- World-wide seawater

IAEA

ALMERA and WW PT strategy

- Tradition:
  - As agreed during the 2nd ALMERA coordination meeting (Trieste, 2005)
    - ✓Regular sample set: water, biota, mineral matrix
    - ✓Standard set of isotopes
    - ✓Medium and relatively low activity level
- Trends:
  - ➢Short-lived radionuclides

    Requested by ALMERA members on the 13th Coordination meeting
  - ➢Special samples for gross alpha and gross beta

IAEA

2017-2018 highlights

- ALMERA PT evolved to include new and challenging elements
  - 2017: short-lived fission products, surface contamination samples
  - 2018: short-lived activation products, surface contamination samples
- ConvEx-3 (2017): first time ever a ConvEx exercise includes measurement and reporting during the exercise
- Strategic planning of PT, ILC & RM production with involvement of ALMERA
- Proposal for a systematic approach to resolving the problems shown by PTs (TCS corrections)

IAEA

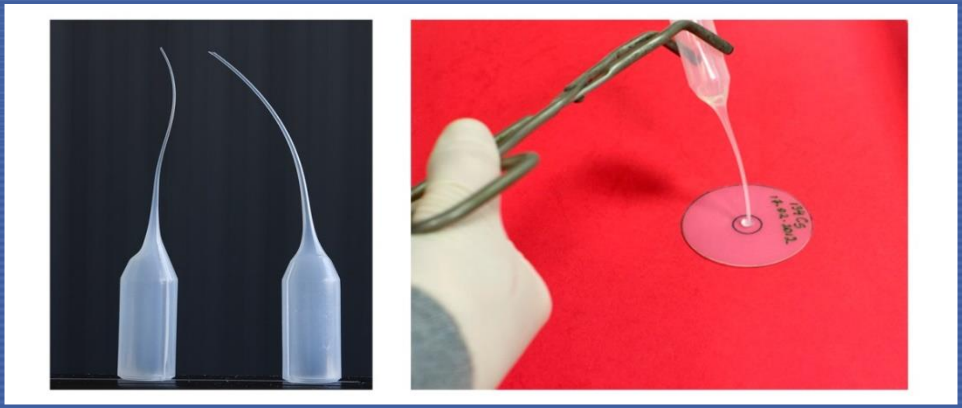
2017 PT Samples

- **Water (1)**
  - Spiked tap water for
    - anthropogenic gamma-emitters (Cs-137, Ba-133)
    - Beta- emitters (H-3, Sr-90)
    - Alpha-emitters (just for the gross alpha determination Cm-244)
- **Water (2) Irradiated natural U sample**
- **Water (3) QC sample**
  - Spiked water, the radionuclides and their massic activity are listed in the cover letter of the PT **(to check the calibration only)**
- **Sample (4) Biological/food sample (spiked milk powder)**
  - Radionuclides: Sr-90, Ba-133, Cs-137
- **Mineral matrix $CaCO_3$ (natural radionuclides)**

IAEA

Sample preparation

- **General principles for spiked samples**
  - Certified isotope solutions with low uncertainty are used
  - Technological material balance (weight tracking during the entire preparation steps)
  - Establishing the traceability chain (up to the certificates)
- **Water**
  - Gravimetric dilution
  - Validation by point source preparation
  - Checking the final dilution by control measurement of volume source



IAEA

Sample characterization (1/2)

- Formulation using the specified values from certificates of the low-uncertainty radioactive standard solutions
  - Sample 01 (Water)
  - Sample 03 (Water)
  - Sample 04 (Milk powder)

- Determination of assigned value by one laboratory using two independent methods and confirmed by another laboratory
  - Sample 02 (several consecutive measurements of point sources and formulation, measurement of control samples)

IAEA

Sample characterization (2/2)

- Determination of assigned value by one laboratory using two independent methods and confirmed by another laboratory
  - Sample 05 (separation of Ra-226 and alpha spectrometry + gamma-ray spectrometry after secular equilibrium)

- Using consensus value from the reported results (interlaboratory comparison)
  - Gross alpha and beta Sample 01, Sample 0/6-7-8
  - Evaluation method: robust statistics (ISO 13528)

Preparation of spiked Sample 02 (200 L)

Steps (1/2)

- Feasbility study
  - Two pre-experiments (irradiation of natural uranium 1mL ampoule NIST standard solution)
  - Study of the behavior of the irradiated sample
  - Determination of the isotope composition (gamma emitters only)
- Optimization
  - Irradiation time (10 min, Φ: $1x10^{13}$)
  - Acceptable cooling time (weekend)
  - Amount of natural uranium

IAEA

Preparation of spiked Sample 02 (200 L)

Steps (2/2)

- Removing partly Np-239 (using TRU resin)
- Preparation of master spike solution
- Activity determination by point source preparation and measurement
- Dilution to final volume (200 L)
- Bottling
- Control measurements
- Assigning target values and uncertainties

IAEA

Gamma emitters in Sample 02 (1/2)

Identified in the master spike solution	Half life	Characterised	Requested as analyte
Nb-95	34.99 days	Nb-95	Nb-95
Zr-95	64.03 days	Zr-95	Zr-95
Mo-99	2.75 days	Mo-99	Mo-99
Tc-99m	6.01 hours	Tc-99m	Tc-99m
Ru-103	39.26 days	Ru-103	Ru-103
Ru-106(Rh-106)	371.5 days		
Te-132	3.23 days	Te-132	Te-132
I-132	2.29 hours	I-132	I-132
I-133	20.87 hours		
I-135	6.57 hours		
Cs-137	30.05 years		

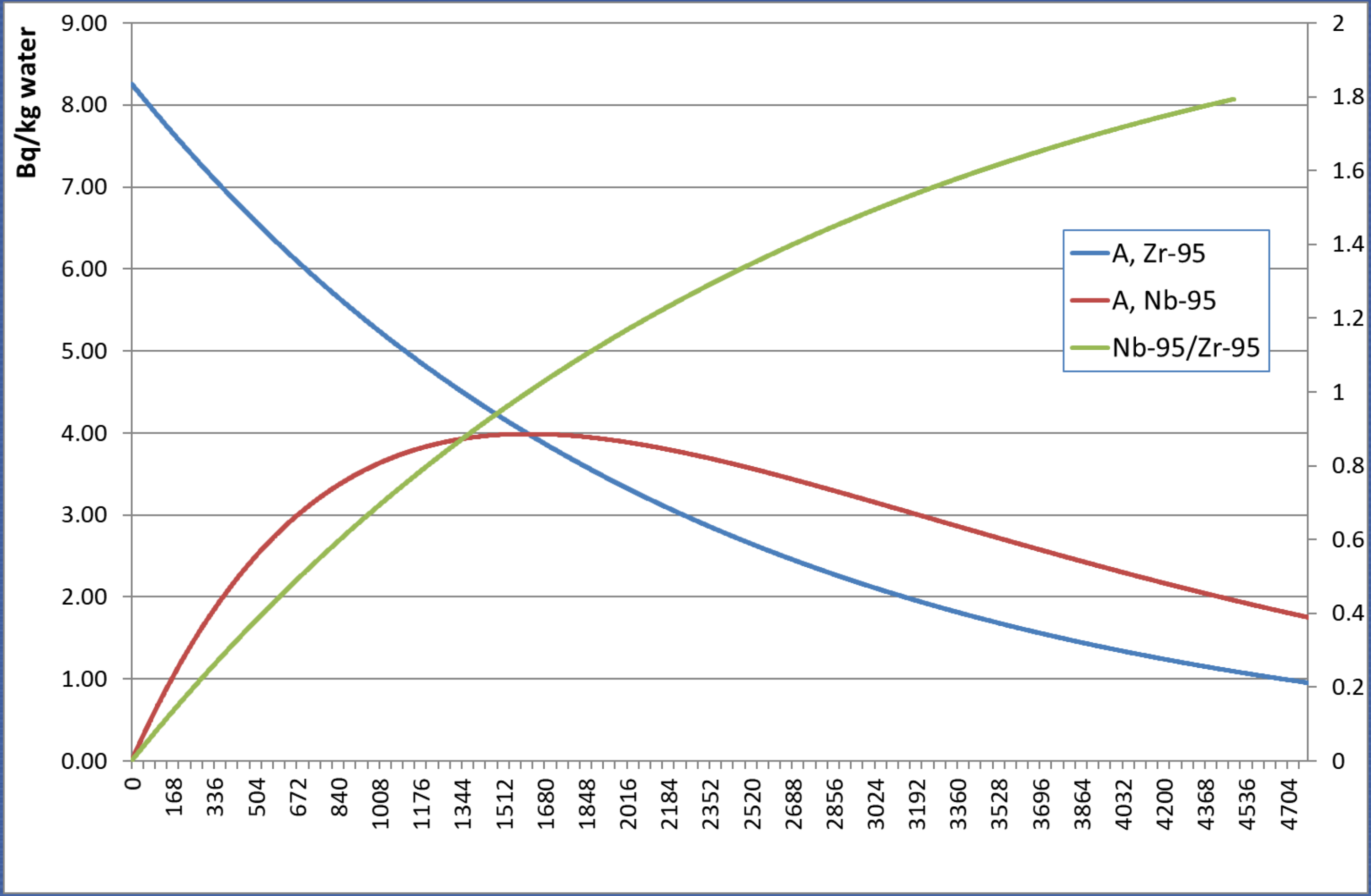
IAEA

Gamma emitters in Sample 02 (2/2)

Identified in the master spike solution	Half life	Characterised	Requested as analyte
Ba-140	12.75 days	Ba-140	Ba-140
La-140	1.68 days	La-140	La-140
Ce-141	32.50 days	Ce-141	Ce-141
Ce-143	33.04 hours	Ce-143	Ce-143
Ce-144	284.89 days	Ce-144	Ce-144
Nd-147	10.99 days	Nd-147	Nd-147
Pm-147	2.62 years		
Sm-153	1.93 days		
Np-239	2.36 days	Np-239	Np-239

Gamma emitters in Sample 02

Zr-95/Nb-95



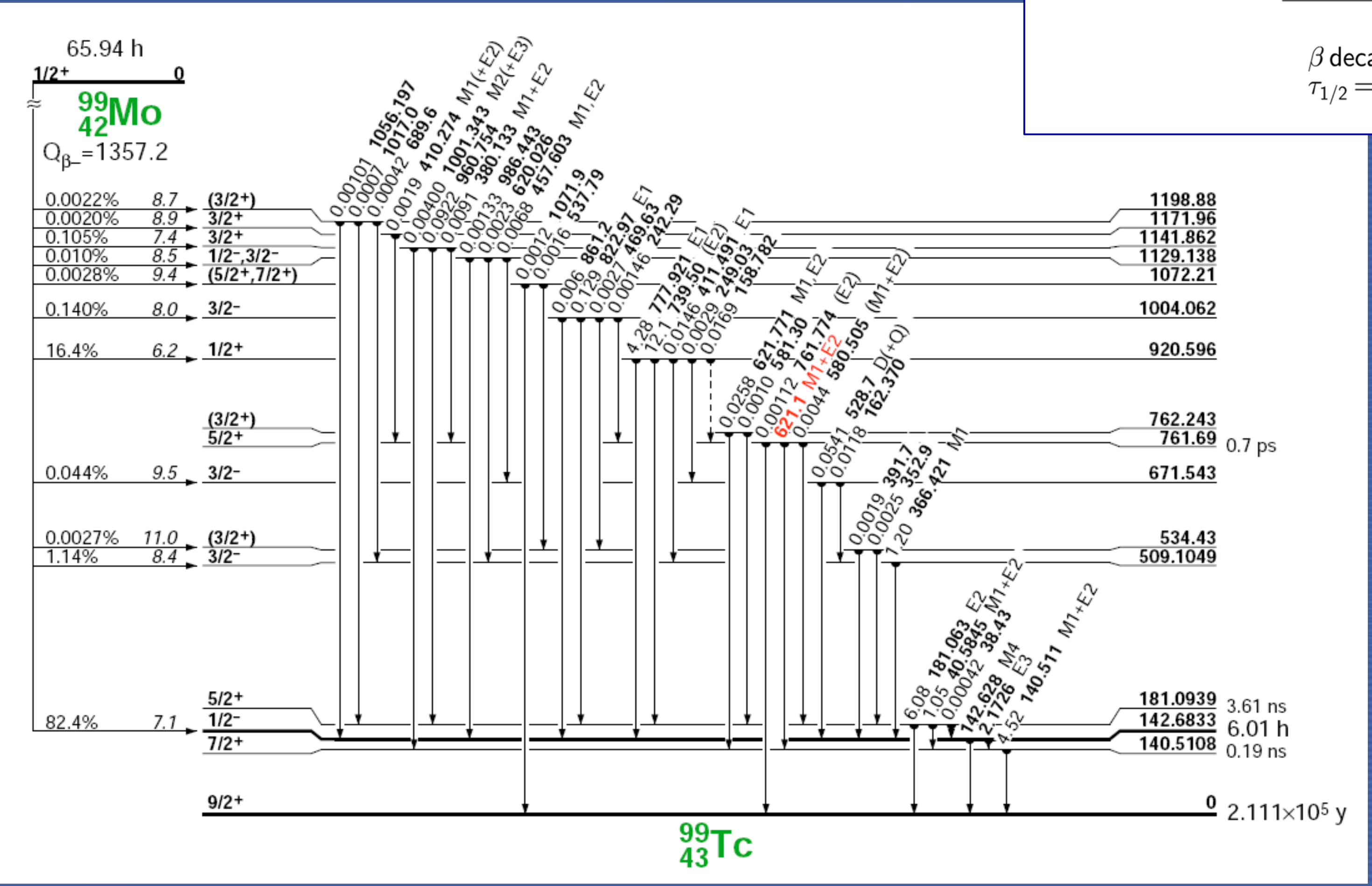
IAEA

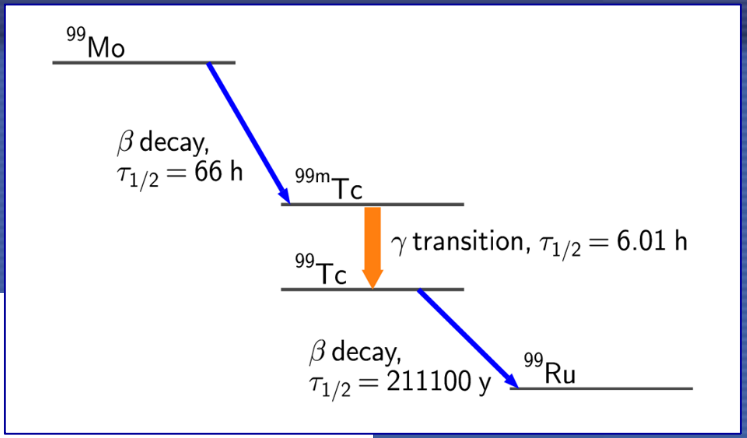
Usually time of production can be dated from successive measurements. Reference date was different from production date, therefore Nb-95>0 at reference date.

Gamma emitters in Sample 02

Mo99/Tc-99m

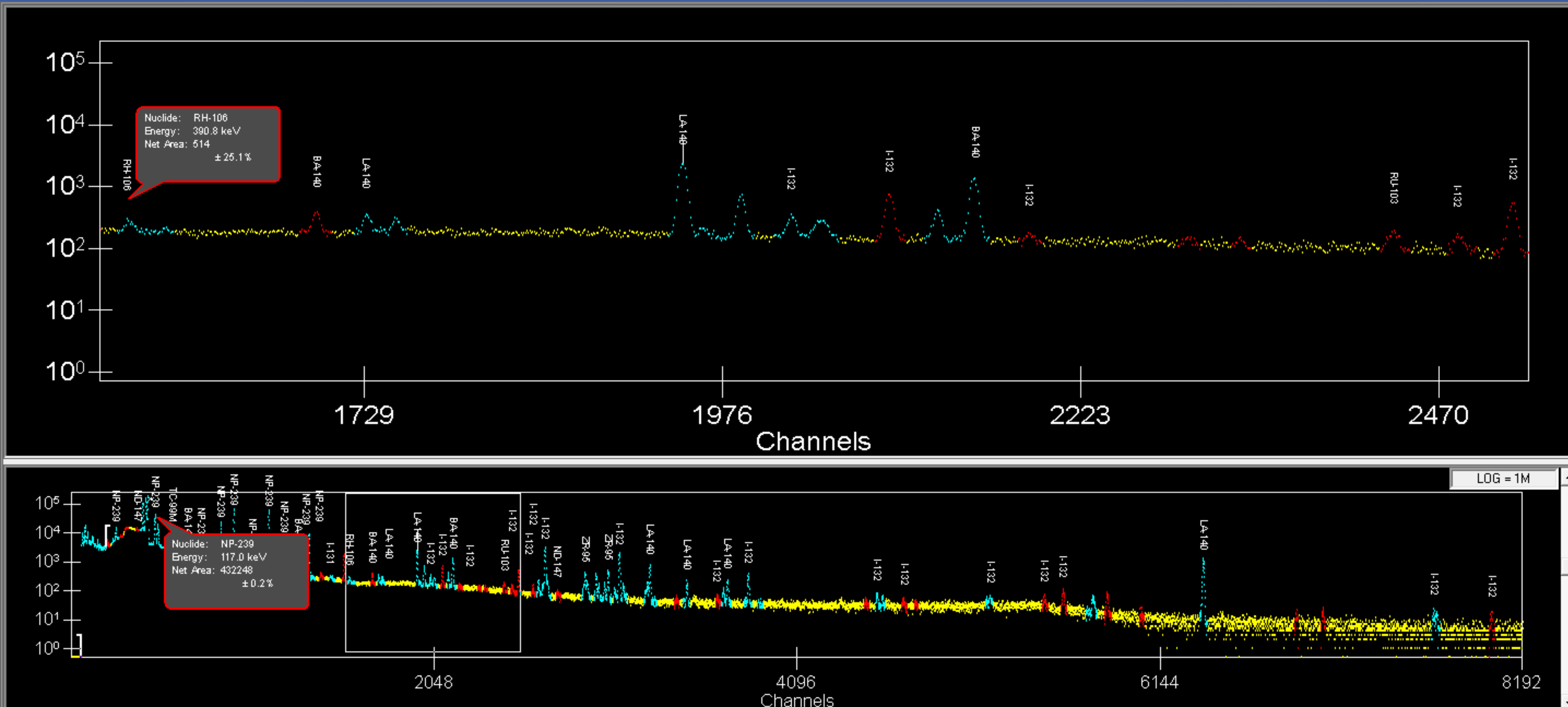
Different decay data and convention used for reporting.





Gamma emitters in Sample 02

Ba-140/La-140



On 17 May 2017 the ratio of La-140/Ba-140 was >1.
Most probably the sample contained unsupported La-140, therefore decay correction using Bateman eq/transient equilibrium was not possible.

PT evaluation method

MARB

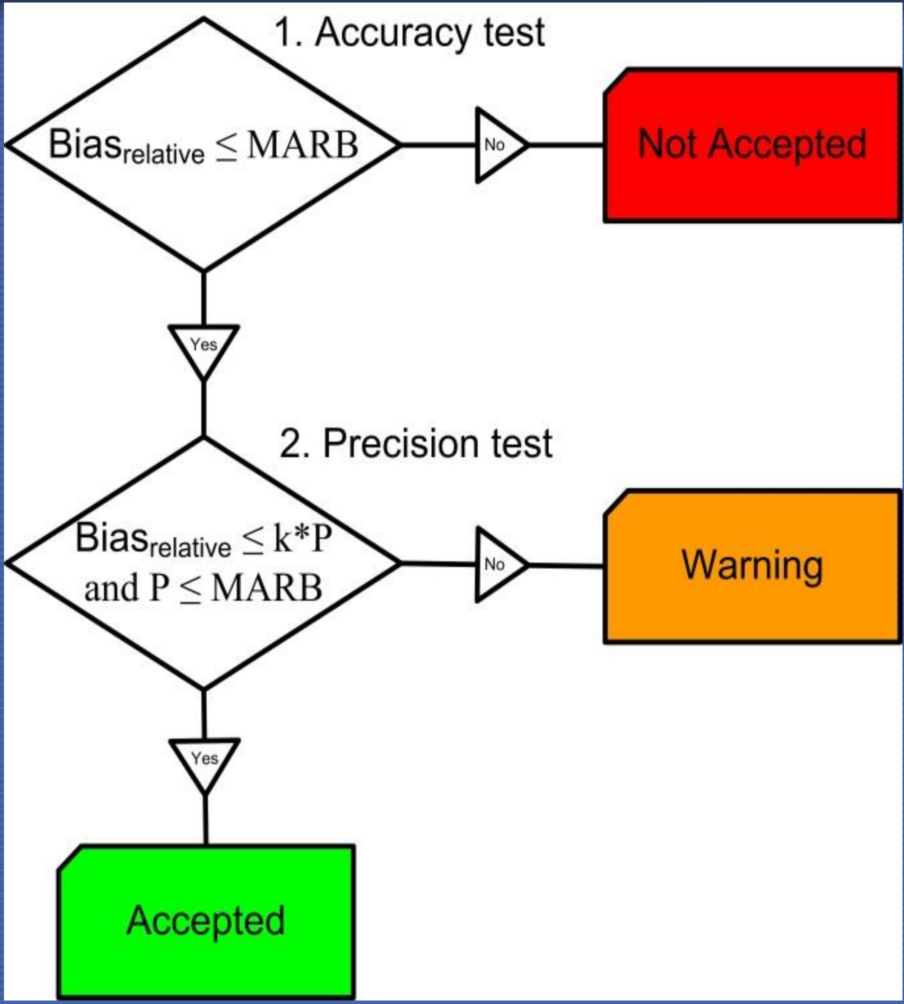
Maximum Acceptable Relative Bias specified in %

$$P = \sqrt{\left(\frac{u_{target}}{A_{target}}\right)^2 + \left(\frac{u_{reported}}{A_{reported}}\right)^2} \times 100$$

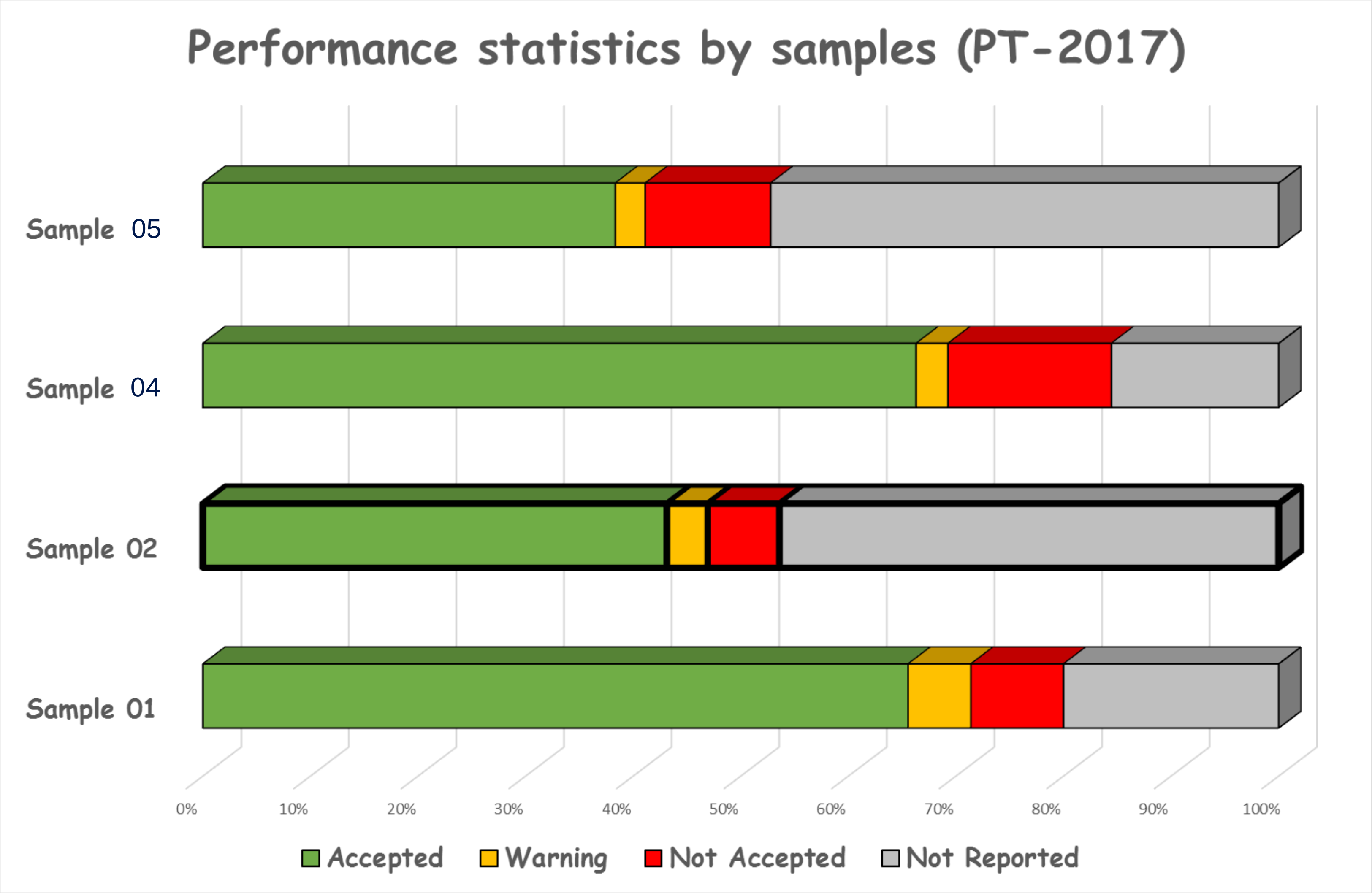
$$Bias_{relative} \leq k * P$$

k = 2.56

"Warning" has a new interpretation!



60 Years
Atoms for Peace and Development

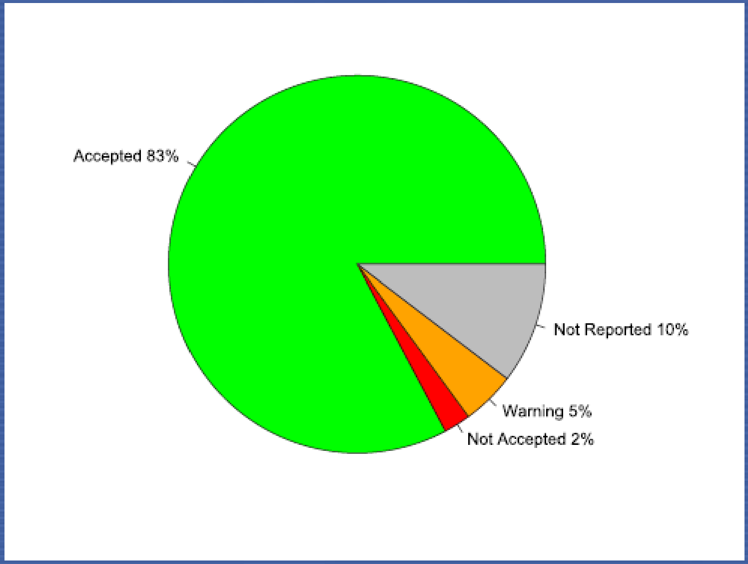


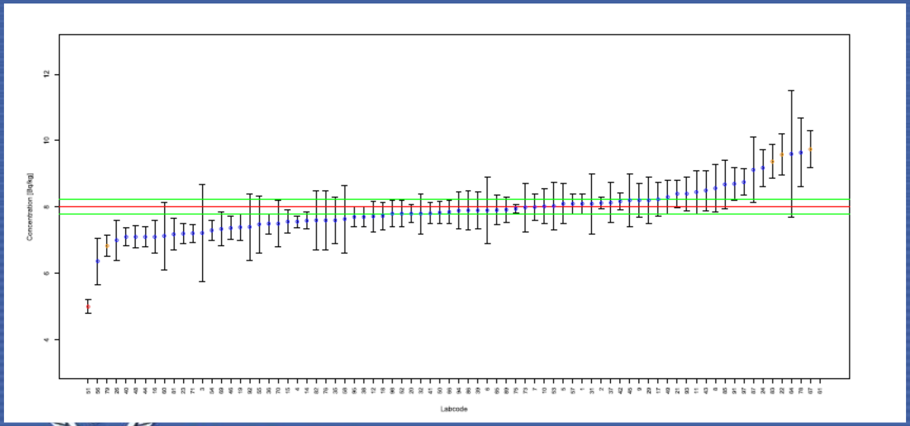
Results (radionuclide-specific)

IAEA

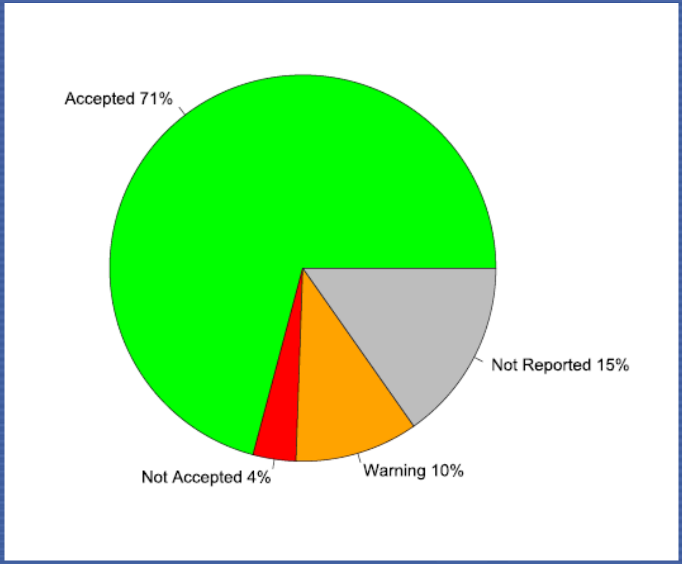
Zr-95 in Sample 02

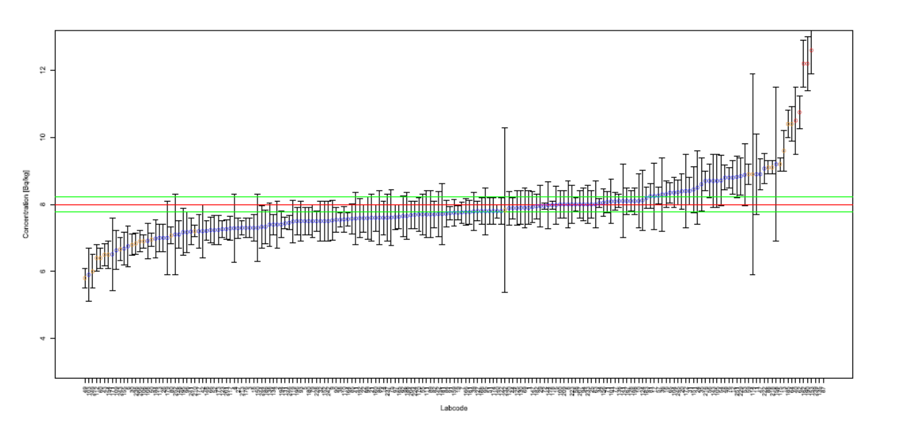
ALMERA





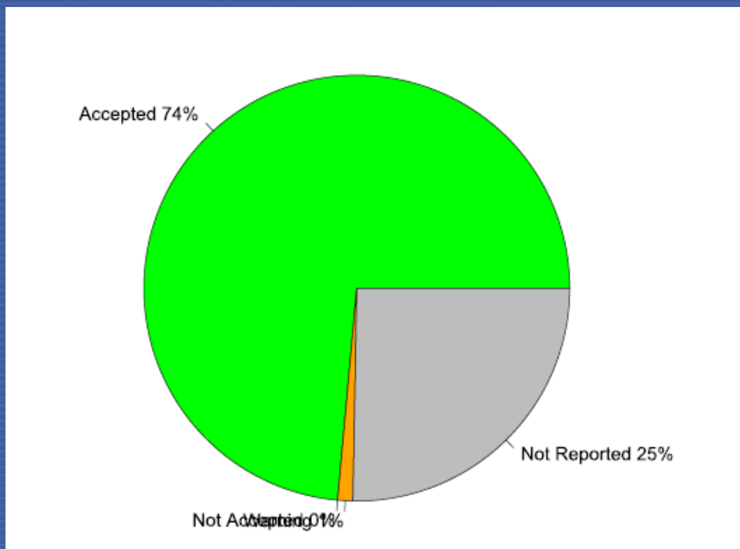
WW

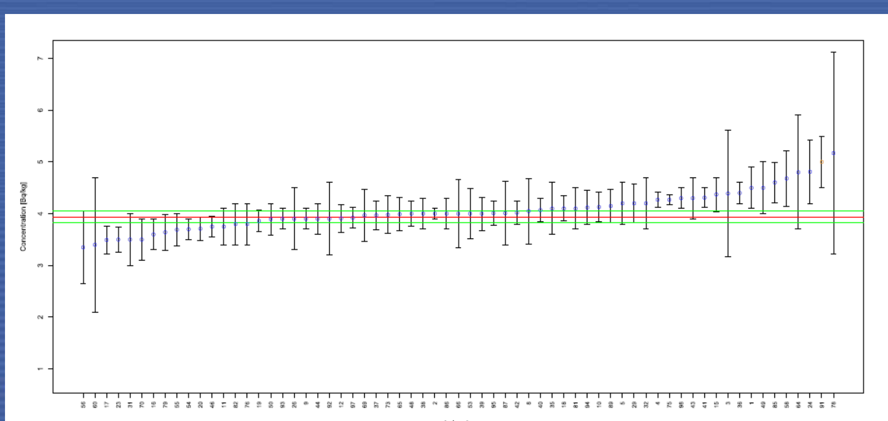




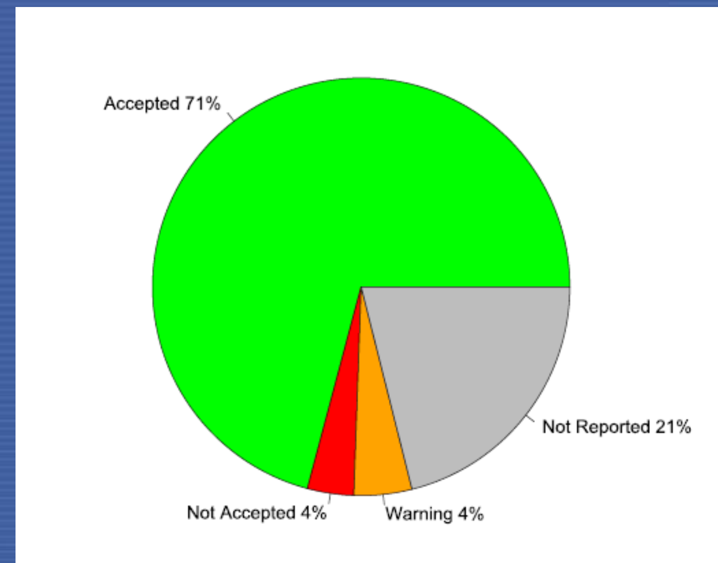
Ru-103 in Sample 02

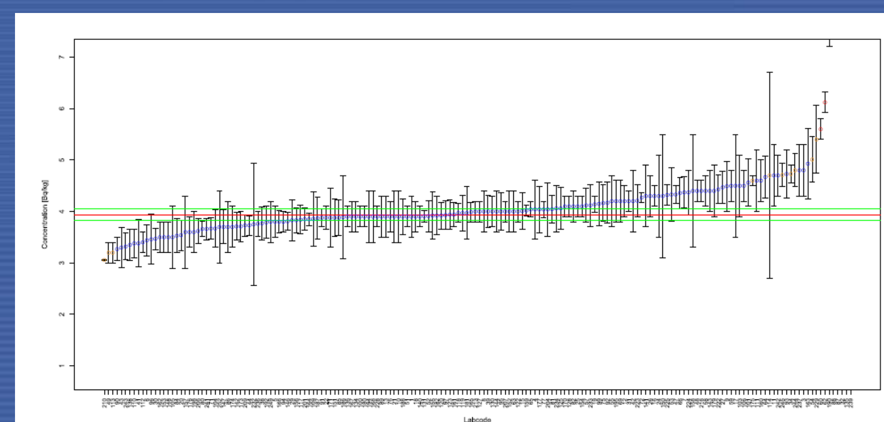
ALMERA





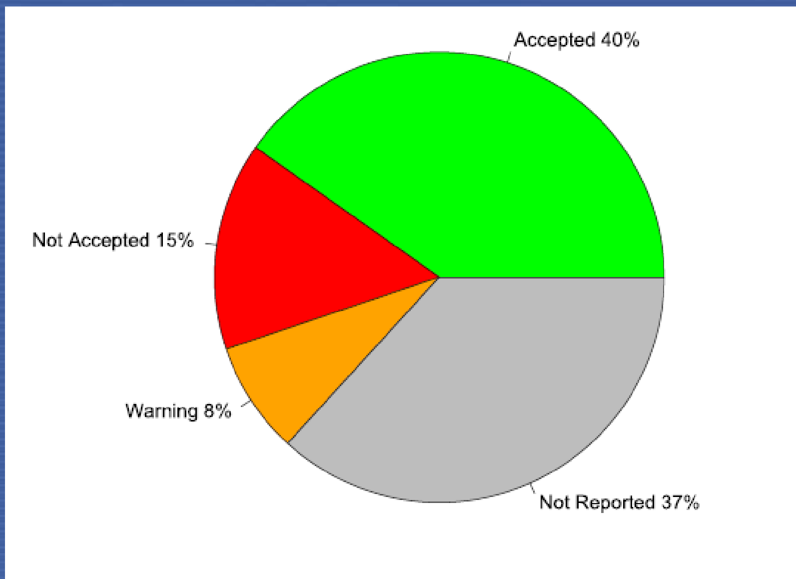
WW



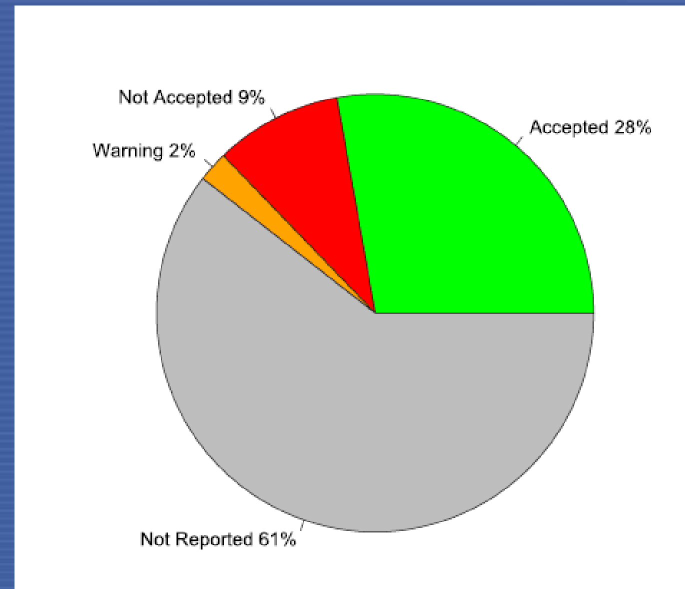


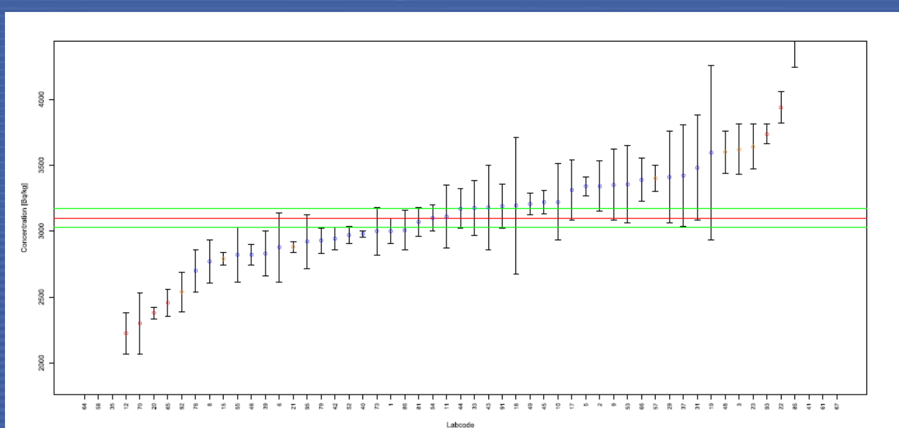
Np-239 in Sample 02

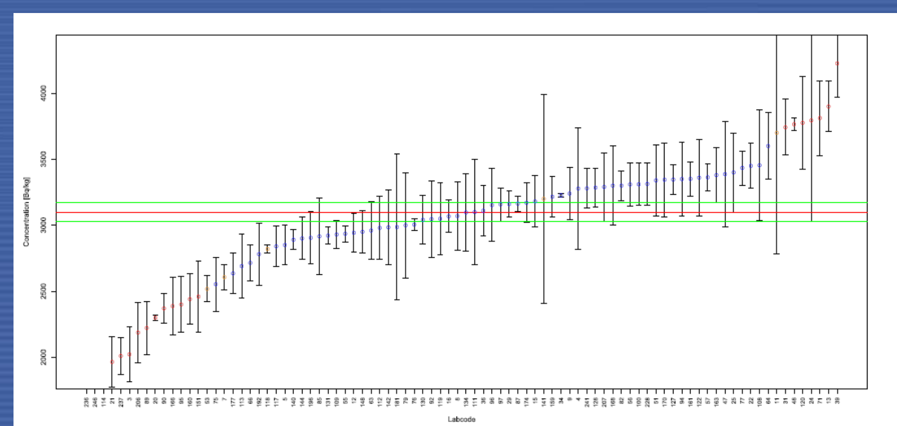
ALMERA



WW







IAEA-TEL-2017-04 ALMERA proficiency test on determination of anthropogenic and natural radionuclides in water, milk powder, Ca-carbonate and simulated filter samples

Sample code	Matrices	Approx. mass in grams	Requested analytes
01	Spiked water	500	Anthropogenic gamma emitters, ^{3}H and ^{90}Sr
02	Spiked water	500	Short lived anthropogenic gamma emitters
03	Spiked water	500	Quality control sample with known massic activity of gamma emitters
04	Milk powder	180	Gamma emitters and Sr-90
05	Ca-carbonate	100	Natural radionuclides
06	Simulated filter		For gross beta measurement
07	Simulated filter		For gross beta measurement
08	Simulated filer		Mixed alpha and beta

The identification of gamma-ray emitter radionuclides is one of the tasks of this proficiency test so they are not specified in advance.

The reference date of the Sample 01, Sample 04 and Sample 05 for decay correction is 01 January 2017.

The reference date of the Sample 02 is 15th May 2017.

IAEA

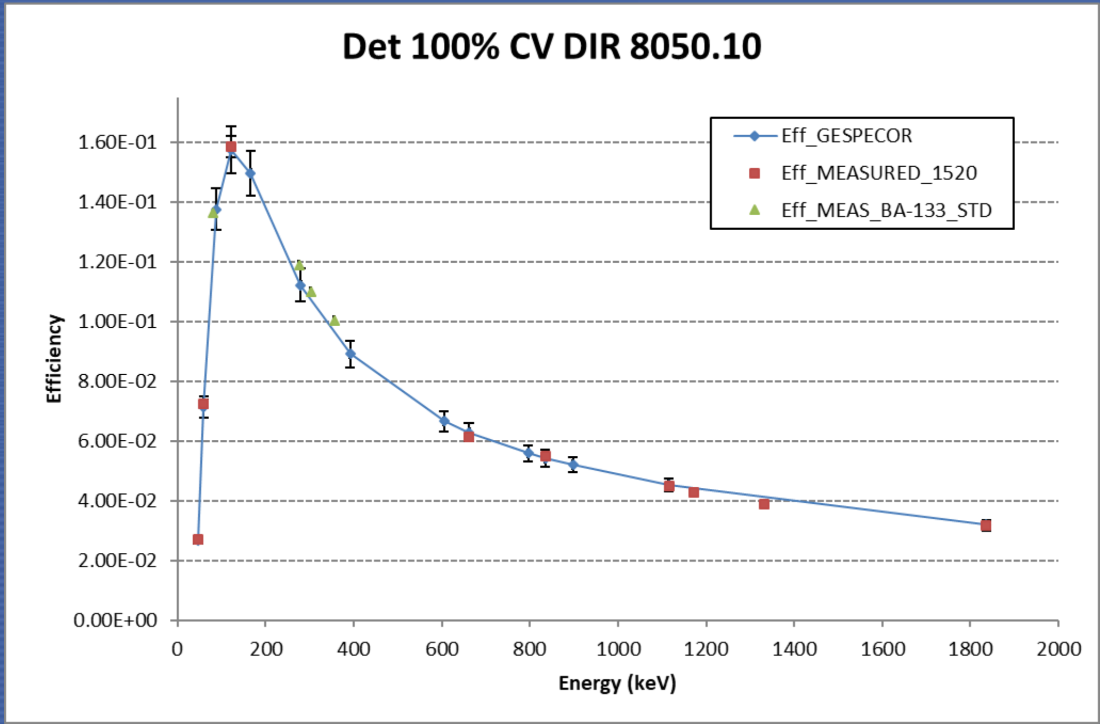
The **Sample 02** was spiked with a mixture of fresh fission products. It is strongly recommended to obtain three spectra of the sample at different points in time:

- The first spectrum should be collected immediately after receiving the sample, with a minimum spectrum collection time of 10000 s. Results obtained from this measurement shall be used for rapid reporting.
- The second spectrum should be collected after 15 days from the reference date, with 20000-80000 s collection time (depending on the relative efficiency of the detector).
- The third spectrum should be obtained after 30 days from the reference date with minimum 80000 s collection time.

IAEA

Analyses of Sample 02 at IAEA Monaco

- Detector GC10023-ULB, p-type, shielding: ultra-low level Pb + cosmic veto, used direct mode (not anti-coincidence)
- Geometry 8050/10: dia 80mm, h 10mm - polyethylene container.
- Efficiency and TCS corrections calculated using GESPECOR



IAEA

ANALYSES OF SAMPLE 02 AT IAEA MONACO

Sample 02 reference date: 15.05.2017

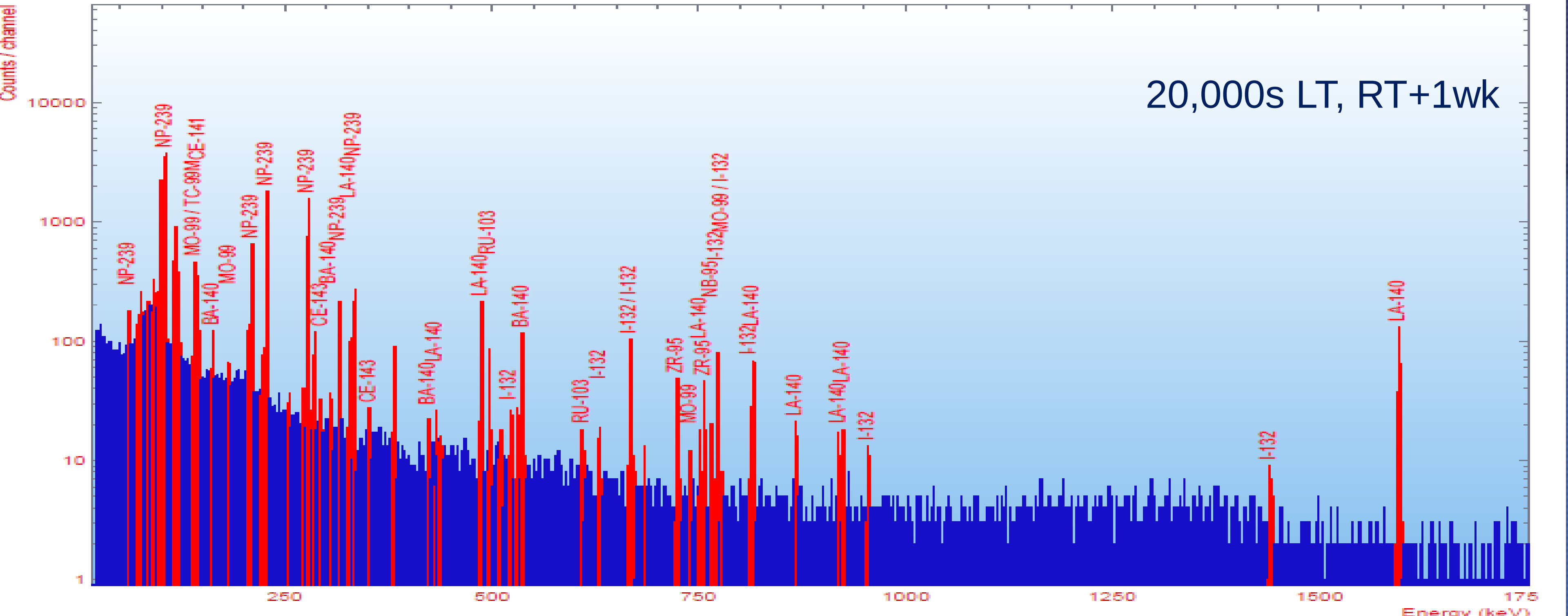
3 measurements:

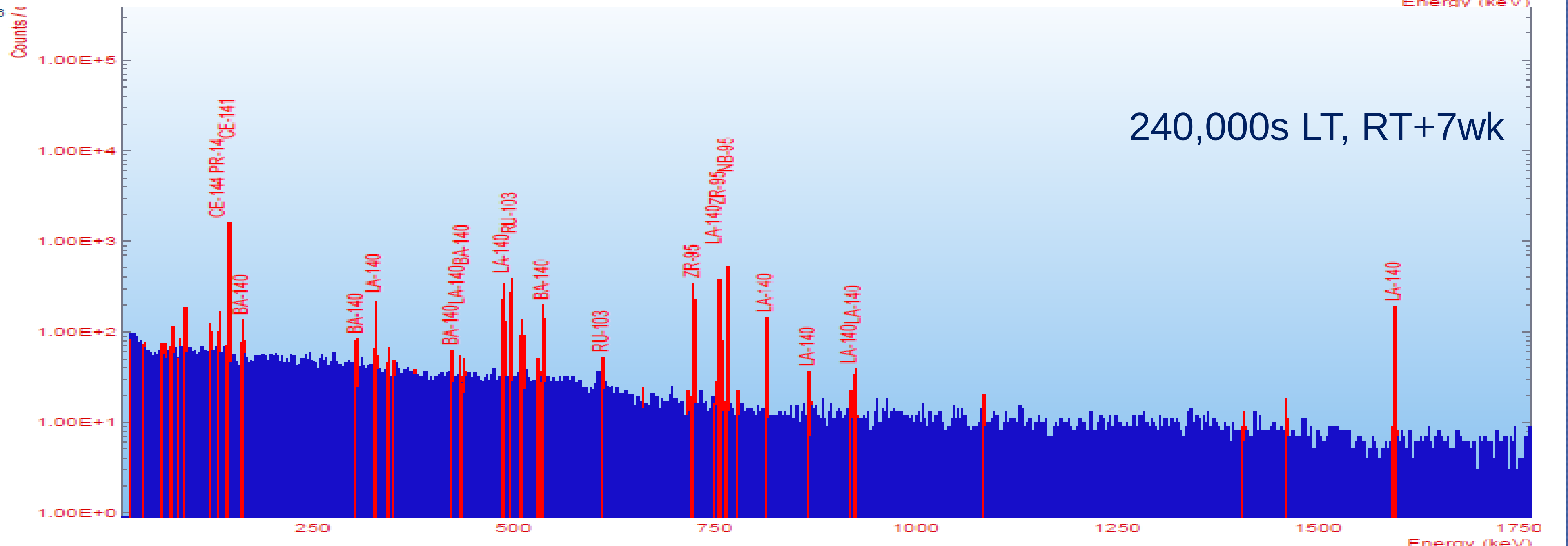
- 22.05.2017 (+1week) ~ 20 000 s LT

- 08.06.2017 (+3.5 weeks) ~160 000 s LT

- 30.06.2017 (+7weeks) ~240 000 s LT

IAEA


20,000s LT, RT+1wk
Counts / channel
Energy (keV)


240,000s LT, RT+7wk
Energy (keV)

Lab 95 evaluation report

Table of Target Values and Evaluation Parameters (MARB) for Sample 2

Sample Code	Analyte	Target Value	Uncertainty	MARB
2	Zr-95	8	0.22	30 %
2	Tc-99m	53.8	2.2	30 %
2	Mo-99	55.9	1.9	25 %
2	Ru-103	3.94	0.12	40 %
2	I-132	54.1	2.2	25 %
2	Ba-140	37.1	1.1	30 %
2	Ce-141	15.7	0.4	30 %
2	Ce-143	48	4	25 %
2	Ce-144	1.85	0.24	60 %
2	Nd-147	15	0.5	30 %
2	Np-239	3100	70	20 %

Evaluation Result Table for Sample 2

Sample Code	Analyte	Target Value	Target Unc.	MARB	Rep. Value	Rep. Unc	Rel. Bias	Robust SD	Z-Score	U-Test	Accuracy	P	Precision	Final Score
2	Ba-140	37.1	1.1	30 %	36.9	2.1	-0.54 %	3.5	-0.06	-0.08	A	6.42	A	A
2	Ce-141	15.7	0.4	30 %	15.8	0.8	0.64 %	0.9	0.11	0.11	A	5.67	A	A
2	Mo-99	55.9	1.9	25 %	56	4	0.18 %	10.1	0.01	0.02	A	7.91	A	A
2	Nd-147	15	0.5	30 %	17.1	1.4	14.00 %	1.2	1.75	1.41	A	8.84	A	A
2	Np-239	3100	70	20 %	2921	204	-5.77 %	363	-0.49	-0.83	A	7.34	A	A
2	Ru-103	3.94	0.12	40 %	4.01	0.24	1.78 %	0.3	0.23	0.26	A	6.72	A	A
2	Zr-95	8	0.22	30 %	7.7	0.3	-3.75 %	0.6	-0.50	-0.81	A	4.77	A	A

Sample 02 / PT 2017 Irradiated natural uranium: What did we learn?

- Challenges for IAEA:
  - Sample preparation & shipment
  - Real-time characterization

- Challenges for the participants:
  - Isotope identification
  - Decay correction

Similar for IAEA-TEL-2018 Sample 02: Dilution of primary coolant water (half-life of many decay products <1 week)

In emergency samples ARE “unusual”. Better be exposed beforehand and go no-risk through the thinking required to solve such “puzzles”. The software can’t do it for us!

IAEA

PT sample and RM production

Developing large surface RM production

- Gross alpha beta samples as of 2017
- Samples for surface contamination measurement
- Large surface mosaic sample for in situ gamma-ray spectrometry (validation and training purposes)
- Aerosol samples (including fission products)
- CRMs of interest for NKS?

The first experiment with mozaic sample!!!

1.4 MBq Eu-152 / 451 individual sources (3080 Bq each)

IAEA 60 Years
Atoms for Peace and Development

Ru-106 in atmospheric aerosol analytical challenges

SnowWhite in Monaco!

Measurements done in underground lab

Coincidence correction ~20%

$A_{Ru\text{-}106}$

25.09-02.10.2017	1.8 ± 0.3	µBq/m^3
02-09.10.2017	86 ± 5	µBq/m^3
09-12.10.2017	4.7 ± 1.1	µBq/m^3
12-16.10.2017	< 1	µBq/m^3

Acknowledgements:

Sandor Tarjan, Alexander Mauring, Bojan Seslak, Alex Trinkl (TEL)

Arvic Harms, Marian Fujak, Paul McGinnity, Mai Pham (RML)

IAEA

CONTACTS

ALMERA coordinator: Iolanda Osvath

ALMERA scientific coordinator: Aurelien Pitois

ALMERA PT organiser, RM specialist: Sandor Tarjan

almera@iaea.org

IAEA

Thank you!