

# IAEA virtual training on measurement techniques for natural and artificial radionuclides and radiochemical methods for their determination in marine environment

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Session 41. **Determination of H-3 in liquid samples (direct measurement and after the electrolytic enrichment)**

Ines KRAJCAR BRONIĆ (Ruđer Bošković Institute, Zagreb, Croatia)

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# Content

About tritium

Methods of determination

GPC

LSC - Direct determination

LSC - Electrolytic enrichment

Measurement in LSC

Vials

Scintillation cocktails

Quenching

Calculation of activity concentration

Control charts

How long should we measure?

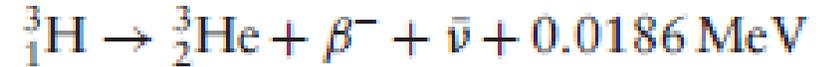
Various tests (vials, scintillation cocktails)

Applications

Environmental  $^3\text{H}$ , precipitation

OBT

# TRITIUM



- Tritium ( ${}^3\text{H}$ )  $T_{1/2} = 12.32 \text{ yr}$  (**4500 ± 8 days**)\*
- Used by national laboratories: **4496.9 ± 9.1 days** \*\*
- of both cosmogenic and anthropogenic origin
- Natural tritium is produced in the atmosphere from the interaction of cosmic radiation with atmospheric nitrogen
- As tritiated water,  $\text{H}^3\text{HO}$ , it enters the natural water cycle

**Note:** tritium activity concentration often expresses  
in Tritium Units (TU)

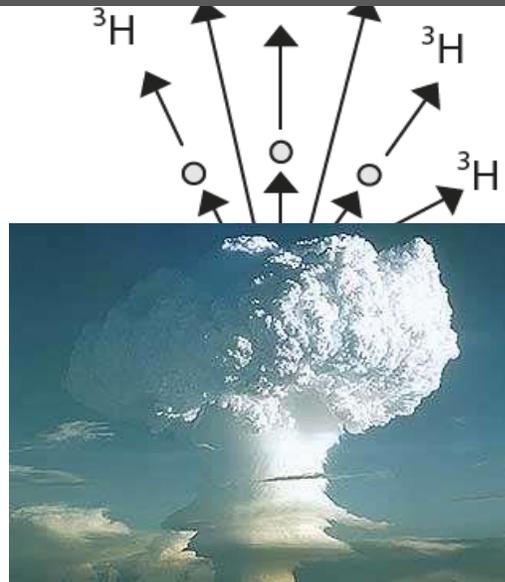
$$\begin{aligned} 1 \text{ TU} &= 0.118 \text{ Bq/L} \\ 1 \text{ atom } {}^3\text{H} &\text{ in } 10^{18} \text{ } {}^1\text{H} \end{aligned}$$

\* Lucas, L. L., Unterweger, M. P., 2000. Comprehensive review and critical evaluation of the half-life of tritium, *J. Res. Natl. Inst. Stand. Technol.*, 105, pp. 541-549

\*\* Christoph Wilhem, pers. Comm.

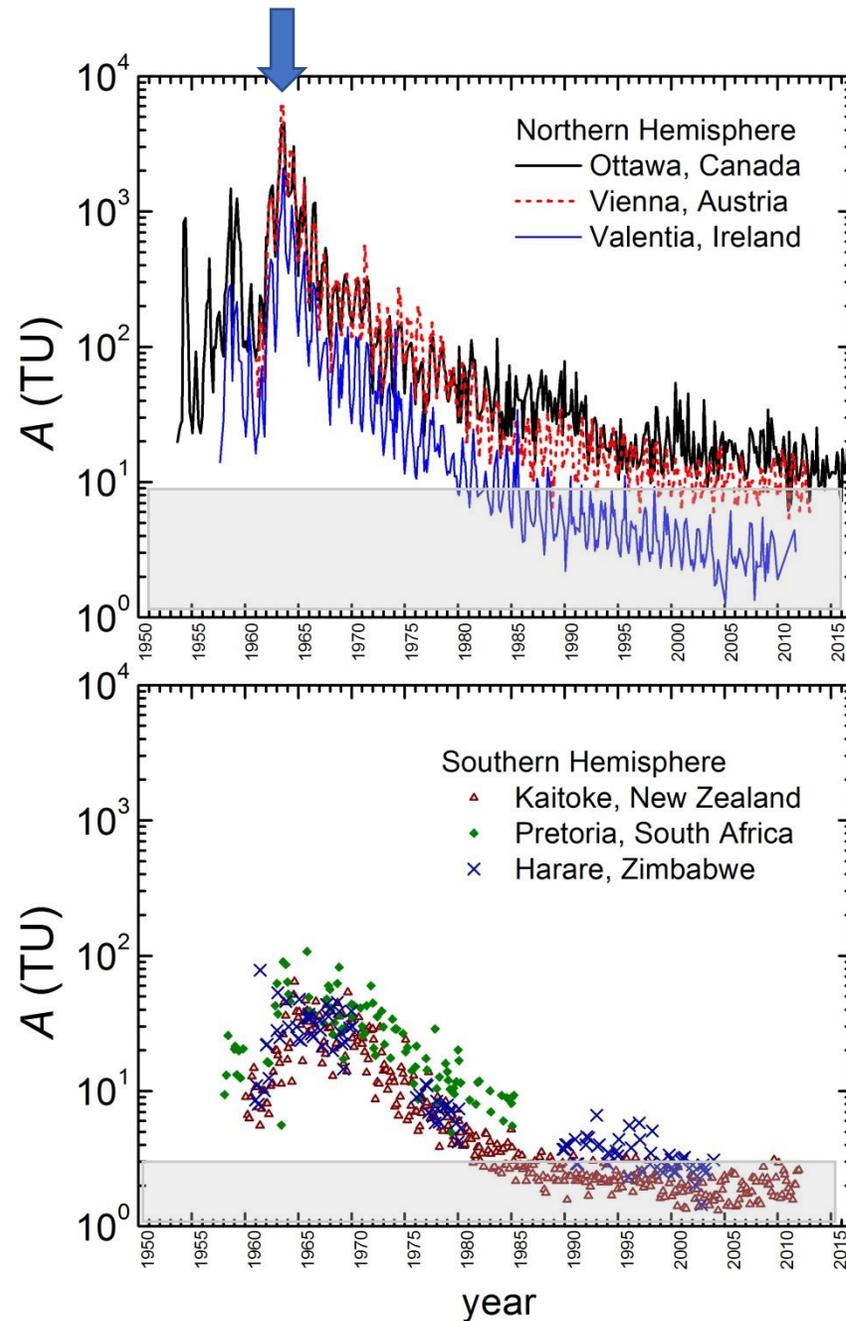
## Anthropogenic origin of $^3\text{H}$

- Nuclear atmospheric tests – **global effect**
- Technogenic - operation of nuclear reactors, and manufacture of nuclear weapons as well as various industrial and medical applications – **local effect**



## BOMB-PEAK

- Massive injections of anthropogenic  $^3\text{H}$  from weapons tests in the 1950s and 1960s caused an almost 1000-fold increase in tritium activity concentration in precipitation - the “bomb peak”.
- After the cessation of atmospheric nuclear weapons tests, a gradual decrease in  $^3\text{H}$  activity concentration in precipitation was observed worldwide
- Currently,  $A$  values approach the natural pre-bomb level.



## Why is tritium measurement needed and important

- its occurrence is mainly in the form of tritiated water (HTO)
- tritium released into the natural water recipients, rivers, lakes and seas, might enter the water wells of drinking water
- Tritium monitoring is important around nuclear power plants in whose vicinity exist water wells that supply the population with drinking water - preventing possibility of internal exposure through ingestion of drinking waters with elevated levels of tritium.
- tritium is carcinogen, mutagen and teratogen
- Besides in water samples, tritium has been monitored in environmental samples organic samples (OBT)
- Tritium monitoring in drinking or surface waters, as well as in groundwater has found application in health and safety considerations as well as in hydrogeological and hydrological studies - Tritium level also provides information on groundwater dynamics and recharge rates, complementing geochemistry and physical hydrogeology investigations
- Possible future fusion reactors – use  $^3\text{H}$  as a fuel for fusion – there will be need for environmental monitoring

## Environmental $^3\text{H}$

- The average natural (cosmogenic) concentration of tritium in environmental waters has been estimated to range from 0.12 to 0.9 Bq/L (up to 10 TU)
- The level of tritium in environment (“background”) currently ranges between 1 and 4 Bq/L

European Commission determined the upper limit for tritium in drinking water to be 100 Bq/L [European Commission, 1998], which is not value based on health effect relative to its consumption but rather on monitoring value that would indicate leakage or release from power plant that needs further check if other radionuclides are present in water.

Activity concentration limit recommended by WHO based on health concerns is 10 000 Bq/L (for a 70 kg man who drinks 2 L of water per day).

# Methods

Difficulties – low energy of beta particles, <18 keV

Low specific activity (1  $^3\text{H}$  in  $10^{18}$   $^1\text{H}$ ) requires sensitive measurement techniques

Common methods for determination of low-level tritium activity concentrations:  
liquid scintillation counting (LSC) and gas proportional counting (GPC)

the GPC technique requires chemical conversion of liquid water to an appropriate counting gas,

$\text{H}_2\text{O}$  in reaction with  $\text{Al}_4\text{C}_3 \rightarrow$   
 $\text{CH}_4$  (methane) gas



## Methods - LSC

In the LSC technique a water sample is directly combined with an appropriate aqueous scintillation cocktail, required pre-treatment is minimal while the counting efficiency and precision are higher than that of GPC

GPC technique provides 2-3 times lower detection limits than LSC direct method

However, if samples are electrolytically enriched, LSC system assures lower detection limits and with better precision is more suitable for most natural water samples including precipitation and groundwater samples.

	V (mL)	Problem	Detection limit
<b>GPC</b>	50	Electronegative impurities, just counts	2.5 TU – 0.3 Bq/L
<b>LSC - direct</b>	< 20	quench	5 TU – 0.6 Bq/L
<b>LSC - EIEn</b>	> 250	Time-consuming	< 0.5 TU – < 0.06 Bq/L

## Direct method

samples do not need any pretreatment procedure – direct mixing of water sample with scintillation cocktail; Purification is recommended if: 1) color is visible, 2) organics are present, 3) sample history or source unknown

establishment of this method involves investigation of the influence of types of vials, different commercially available cocktails and optimal sample : cocktail ratios, parameters of the measurement of tritium activity concentration.

detection efficiency determined based on the measurements of an active samples of known  $c_A$ ,

$$\varepsilon = \frac{s}{V c_A} ,$$

$s$  [ $s^{-1}$ ]  $s$  count rate of the active sample,  $c_A$  [B/L] its activity concentration, and  $V$  [L] its volume.

The activity concentration of any sample,  $c_A$  [Bq/L], determined by:

$$c_A = \frac{r-b}{\varepsilon V} ,$$

$r$  [ $s^{-1}$ ],  $b$  [ $s^{-1}$ ] are count rates of sample, background in ROI

Reference background (tritium-free) water provides a reference point against which all samples will be compared – very important issue in low-level measurement

## Summary about direct method

Direct method is ideal for routine control releases from the nuclear power plants or in case of nuclear accidents, where it is necessary to have rapid, simple, inexpensive and reliable methods for the determination of radionuclides. Thus, tritium releases associated with global fallout, nuclear accidents or nuclear industry, for example nuclear fuel cycle activities (fuel enrichment, fuel fabrication, power generation, and fuel reprocessing) can be easily monitored via inexpensive, rapid and simple direct method.

It is an ideal techniques in environmental monitoring or nuclear emergencies since sample preparation takes few minutes and tritium assessment in sample can be made in few hours of counting.

Optimization of direct method led to conclusions that 8 mL of sample should be mixed with 12 mL of the scintillation cocktail (Ultima Gold LLT showed best performance) in a 20 mL low diffusion polyethylene vial. Measurement time and number of repetitions should be adapted to required measurement uncertainty.

## Electrolytic enrichment method

However, natural background level of tritium activity concentration in precipitation, surface and ground water is becoming very low, and cannot be successfully determined by the direct method

A method of **enrichment of tritium** (or concentration) must be applied

- $^3\text{H}$  concentration prior to counting are physical in character because the mass differences of HTO and  $\text{H}_2\text{O}$  produce greater differences in physical than in chemical properties
- it has long been known that the tritium activity concentration can be increased to an easily measurable level by applying electrolytic enrichment
- An electrolyte must be added to water to make it conductive.
- Due to the difference in masses of  $^1\text{H}$ ,  $^2\text{H}$  and  $^3\text{H}$ , the dissociation energies of these isotopes are different so the dissociation of lighter molecules appears at a lower dissociation energy compared to that of heavier molecules
- during the electrolysis the lighter molecule  $\text{H}_2\text{O}$  dissociates more rapidly compared to the heavier HTO molecule leading to an enrichment of HTO molecule in the remaining water phase. The electrolytic enrichment process therefore not only dissociates water into their respective gases hydrogen and oxygen with the observed depletion in the quantity but also relatively enriches HTO molecules with respect to  $\text{H}_2\text{O}$  molecule in the liquid phase, and the tritium activity concentration in the remaining electrolyte increases

- The reduction of sample quantity by a factor of 10 to 100 or more can be achieved.
- The initial sample mass is usually either 250 mL or 500 mL, but 1 L and 2 L initial volume is also possible
- The larger the initial water volume, the larger the enrichment factor, i.e., the ratio of the final to initial tritium activity concentration of a sample.
- The cells for electrolysis can be connected in a row, so one electrolysis run enables simultaneous enrichment of a series of unknown samples and tritium-free and standard samples under identical conditions, and therefore enables also a quantitative determination of the enrichment factor.

Initial volume	250 mL	500 mL	1000 mL	2 L
Enrichment factor (approximate values)	18	30	75	175

The sample preparation process has three main phases:

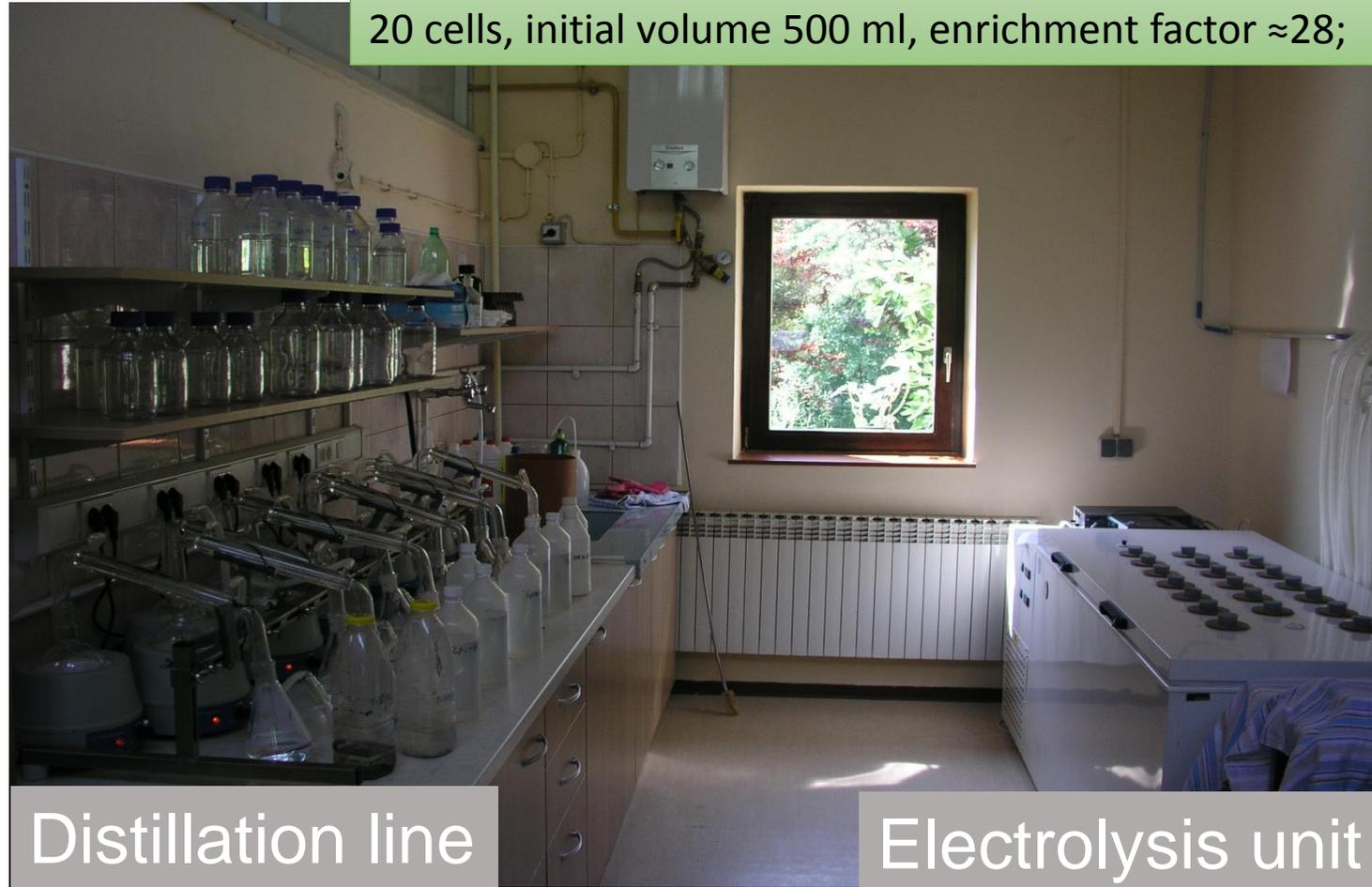
- primary distillation of water,
- electrolysis
- secondary distillation.

The details about the systems (cell design, cell material, etc.) and the technical procedure may vary from systems to system.

As an example of the tritium enrichment system, here we describe in details the system at the Ruđer Bošković Institute (RBI) that was implemented in 2008, following the design of the electrolysis system developed at the IAEA Isotope Laboratory. It was produced by the Faculty of Physics and Applied Computer Sciences, AGH University of Science and Technology, Krakow, Poland.

## RBI – Tritium laboratory - Electrolythic enrichment

20 cells, initial volume 500 ml, enrichment factor  $\approx 28$ ;



Distillation line

Electrolysis unit

Methodology of Tritium Determination in Aqueous Samples by Liquid Scintillation Counting Techniques ,  
I. Stojković, N. Todorović, J. Nikolov, I. Krajcar Bronić, J. Barešić , U. Kozmidis Luburić, In TRITIUM - ADVANCES IN  
RESEARCH AND APPLICATIONS, ISBN: 971-1-53613-507-7 (e-Book), Nova Science Publisher 2018

## Primary distillation

The first step of sample pretreatment is **primary distillation**.

Any impurity in the water that is to be subjected to electrolysis can cause corrosion of the cell anodes and prevent the cathodes from developing efficient hydrogen isotope separation



- Adequacy of purification by distillation can be checked by a water conductivity check.
- The required purity depends on the geometry of the cells, the electrode material and the applied voltage.
- For the system implemented at RBI the required conductivity of distilled samples is  $<50 \mu\text{S}/\text{cm}$ . In case of conductivity  $>50 \mu\text{S}/\text{cm}$ , samples have to be distilled again.

## Electrolysis

The process of electrolytic enrichment of water with tritium requires special equipment placed in an adequate environment.



The main part of the system of electrolytic enrichment consists of 20 cells of 500 mL volume placed in a refrigerator that cools the cells and keeps them at 2–5 °C to prevent the loss of tritiated water molecules by evaporation during the electrolysis.

the electrolysis unit:

left – cooling unit and control of electric power,

right – refrigerator with 20 cell

Anodes are made of stainless steel, and cathodes of mild steel enabling achievement of high tritium enrichment factors, high tritium retention factors and good reproducibility [Morgenstern and Taylor, 2009].

Each cell is filled with 500 mL of previously distilled water sample and 1.50 – 1.55 g of  $\text{Na}_2\text{O}_2$  as electrolyte is added.

Gas produced in each cell passes through a glass bubbler filled with silicone oil for visual checking of the process and then it is led by a ventilation system into the open atmosphere.



Gas bubblers filled with silicone oil, marked by the same number as the cells, enable visual check of the electrolysis going on



# LSC lab – another example



Each enrichment run contains 15 unknown samples, 3 spike waters (water of known tritium activity concentration) used for monitoring the electrolysis performances and 2 tritium-free (“dead water”) samples used for system control.

The position of the three spike waters and 2 dead waters are shifted in the subsequent electrolysis runs and after 20 runs each cell has been subjected to equal numbers of spike and dead waters.

Enrichment procedure lasts for 8 days, i.e., after predefined 1420 Ah it stops automatically.

Each electrolysis run is characterized by the tritium **enrichment factor**  $E$  (symbol  $Z$  is used sometimes in literature) and the **enrichment parameter**  $P$ .

The enrichment factor  $E$  represents a ratio between the final and initial  $^3\text{H}$  activity concentrations,  $\frac{A_f}{A_i}$ .

The tritium enrichment parameter  $P$  indicates the retention of the original tritium content during the electrolytic process

In an ideal case  $P$  would have the value of 1 (100 % retention of tritium). However, in a real case  $P$  value above 0.9 indicates sufficient performance

$$E = \frac{A_f}{A_i} = \left( \frac{m_i}{m_f} \right)^P .$$

$m_i$  and  $m_f$  are the initial and final mass of the sample.

The values of  $E$  and  $P$  for each electrolysis run can be calculated using the initial and final mass of water in cells and individual count rates of **spike water** before and after enrichment

## Spike samples

The mean enrichment factor determined from the three spikes,  $\bar{E}_{\text{spike}}$ , in each run is

$$\bar{E}_{\text{spike}} = \frac{1}{3} \sum_{j=1}^3 \left( \frac{N_{\text{spike},j}}{N_{\text{spike,BE}}} \right)$$

$N_{\text{spike,BE}}$  - net count rate of the spike before enrichment

$N_{\text{spike},j}$  - net count rate of the spike  $j$  ( $j = 1, 2, 3$ ) after enrichment.

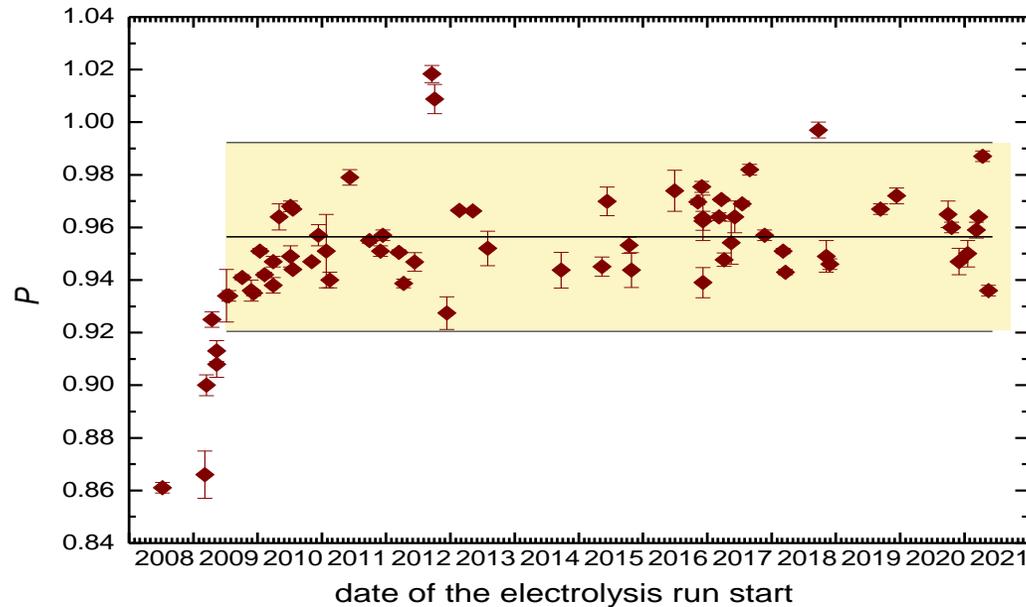
The enrichment parameter  $P$  is obtained as:

$$P = \frac{1}{3} \sum_{j=1}^3 \left( (m_{i,\text{spike}} - m_{f,\text{spike}})_j \times \ln \bar{E}_{\text{spike}} / \left( \ln \left( \frac{m_{i,\text{spike}}}{m_{f,\text{spike}}} \right)_j \times \frac{Q}{2.975} \right) \right)$$

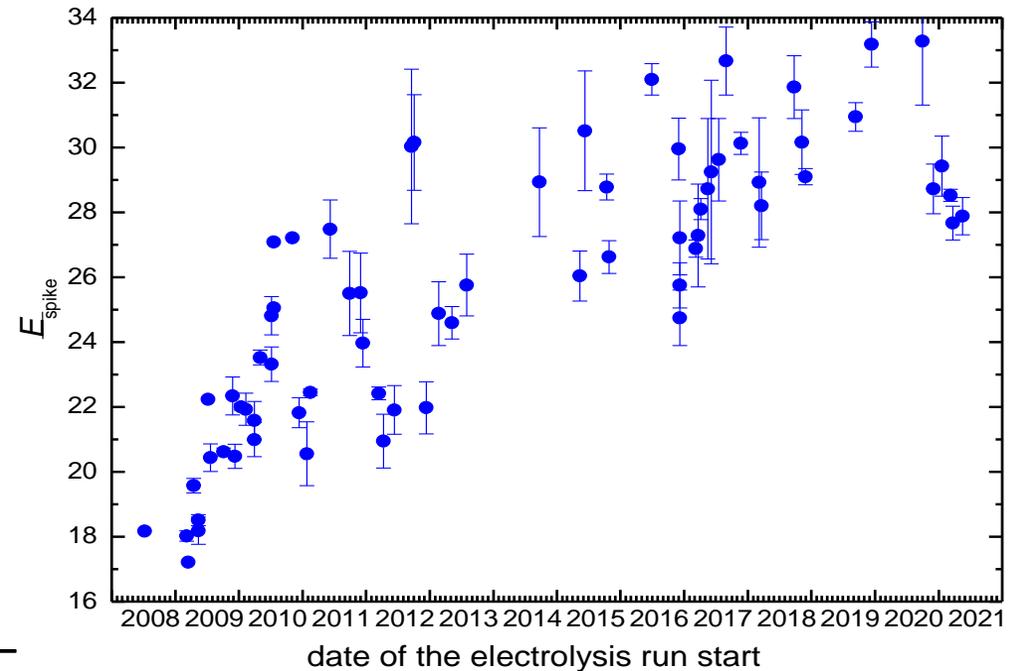
$m_{i,\text{spike}}$  and  $m_{f,\text{spike}}$  are the initial and final masses of the spike  $j$  ( $j = 1, 2, 3$ ),  $Q$  is the number of Ah for the electrolysis run, and 2.975 is the Faraday constant (Ah/g).

Quality control of the electrolysis system includes constant monitoring of  $E$  and  $P$  values.

the enrichment parameter  $P$



mean enrichment factor  $\overline{E}_{\text{spike}}$



The shaded area encompasses  $P$  values in the range 0.920 – 0.992, mean value 0.956, which are characteristic for the RBI system after its consolidation.

Low  $P$  values ( $<0.92$ ) obtained during the consolidation runs are related to the relatively low  $\overline{E}_{\text{spike}}$  values ( $<20$ )

**Mean values**       $P = 0.956 + 0.018$

$\overline{E}_{\text{spike}} = 26.5 + 3.8$

Increase of  $P$  values during first 6 runs is obvious and is explained by consolidation of iron/mild steel electrolytic cells. Namely, the cathode surfaces have to be brought to a state of high catalytic efficiency, and this is usually done simply by running-in the cells over a certain period

## Samples

For each sample in each electrolysis run, the individual tritium enrichment factor has to be determined

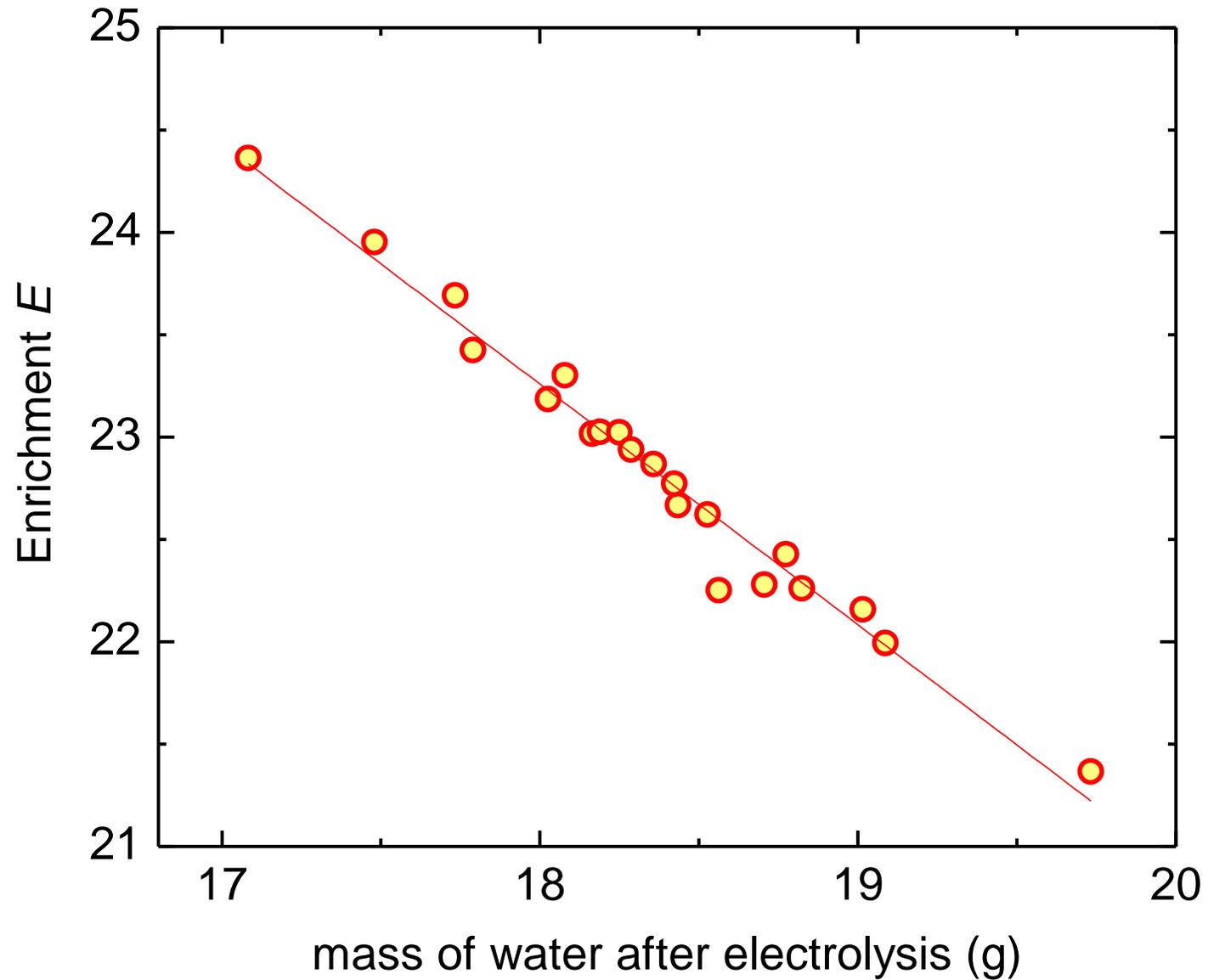
The value of the enrichment factor for each individual sample,  $E_{\text{sample}}$ , can be obtained as:

$$E_{\text{sample}} = \exp\left(\frac{Q}{2.975} \times P \times \frac{\ln(m_{i,\text{sample}}/m_{f,\text{sample}})}{m_{i,\text{sample}} - m_{f,\text{sample}}}\right)$$

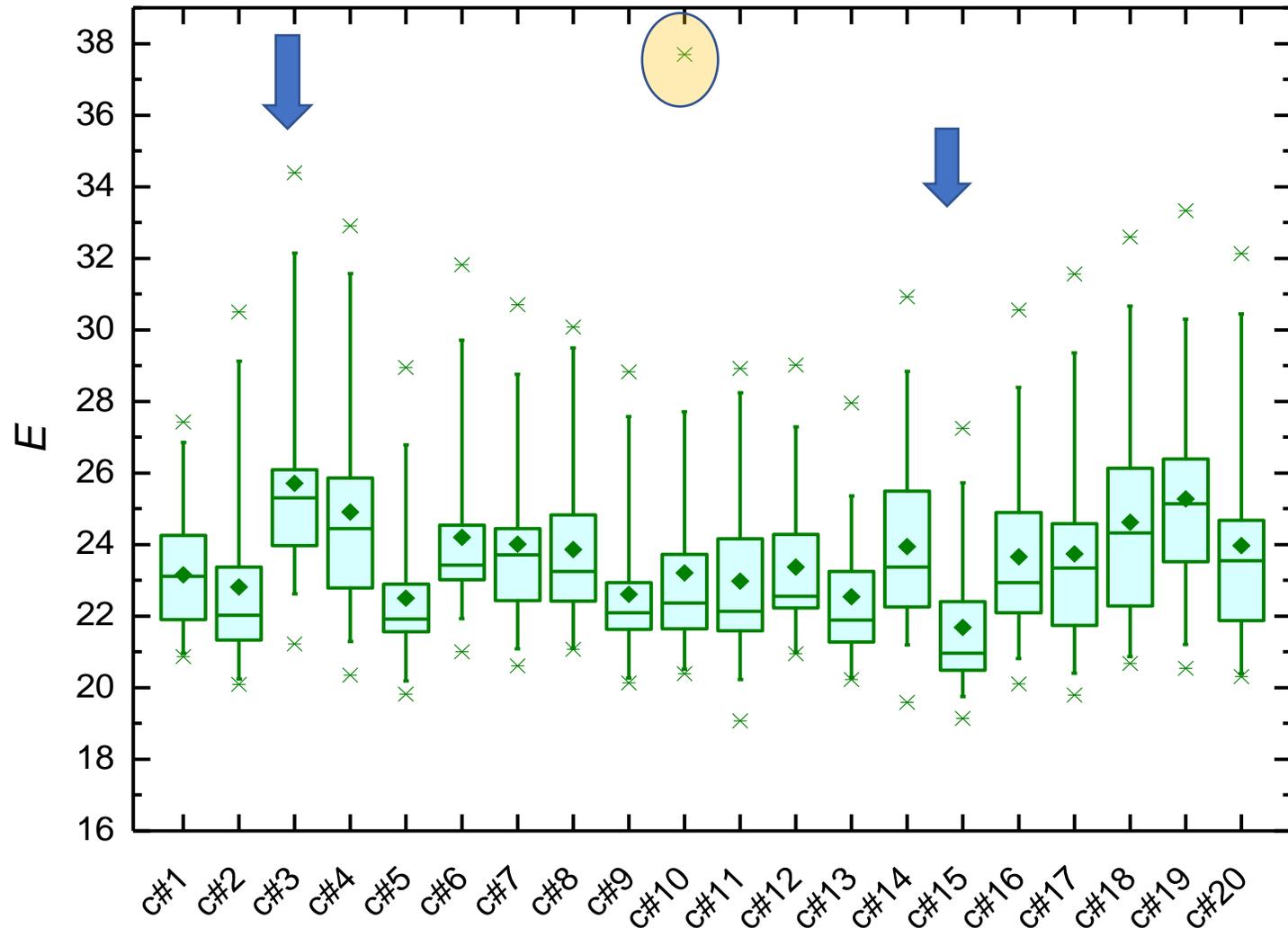
where  $m_{i,\text{sample}}$  and  $m_{f,\text{sample}}$  are the initial and final mass of the sample.

The mass of water is determined gravimetrically by weighing the empty cells, the cells with the sample water before and after the electrolysis.

Relation between enrichment factor and final mass of water after electrolysis  
Initial sample volume 500 mL



In each electrolysis run, the individual tritium enrichment factor has to be determined for each sample, i.e. for each cell  $\rightarrow$  variations in the enrichment factor  $E_{\text{sample}}$  among individual enrichment cells within a single electrolysis, and in the average values among cells



An analysis of the individual  $E$  values in individual cells for electrolysis runs after stabilization of the system.

The highest individual  $E$  value of 37.7 is obtained in cell no. 10 during the electrolysis run 28 in 2012, that was characterized by high values both  $\bar{E}_{\text{spike}}$  and  $P$  values.

The highest mean  $E$  value of  $25.7 \pm 2.9$  was obtained in cell no. 3 and the lowest  $21.7 \pm 2.0$  in cell no. 15.

To check whether the position of a sample in cell no. 3 or no. 15 could influence the final result of tritium activity concentration, we performed electrolysis of the same sample in the same electrolysis run in both cells.

The obtained final result was the same in both cases, showing that the enrichment factors for both cell were determined correctly and that the position of a sample in the particular cell does not affect the final tritium activity concentration.

cell. no	$E_{\text{sample}}$	$c_{A_{\text{sample}}}$ [B/L]
3	28.7	<b>0.83 ± 0.16</b>
15	22.6	<b>0.84 ± 0.20</b>

After electrolysis enriched samples are very basic and sometimes coloured due to spending of cathode material and they have to be distilled again.

A quantity of 6-8 g of  $\text{PbCl}_2$  is added into each sample prior to **secondary distillation**.

Once the distilled enriched water is obtained, the measurement process in liquid scintillation counter can start.

## Summary about electrolytic enrichment

Tritium determination by electrolytic enrichment requires expensive equipment, multi-stage procedure and long time (approximately 8 days) for sample preparation. However, this method has high precision and low detection limit, which varies between 0.03-0.05 Bq/L for total counting time 300-500 min, which makes it applicable in broad spectrum of research.

Measurements of tritium activity concentration are regularly used in hydrogeological, hydrological and oceanic processes study in the environment, groundwater movement and dating research since natural low levels of tritium can be quantified.

## Comments on electrolytic enrichment

The electrolytic enrichment of water with tritium is by no mean a **complex procedure**, although the basic principles seem to be very simple.

The **analytical challenges** are growing as the environmental tritium activities in precipitation and groundwater are decreasing. Laboratories are involved in **constant improvement** of the process to reach better performances of the system, higher operational safety standards and better protection against tritium cross-contamination during sample preparation.

Since during the electrolysis a large amount of highly explosive hydrogen/oxygen gas mixture is produced, several **security and safety features** have to be implemented in each tritium laboratory, such as automatic stopping the electrolysis after a predefined number of Ampere-hours, temperature control of the refrigerated system and automatic stopping in case of either too high or too low temperature, stopping in case of the failure of the cooling system, control of gas flow by glass bubblers filled with silicone oil, efficient ventilation system.

Finally, **good quality assurance and quality control measures**, including monitoring of  $E$  and  $P$  values, as well as monitoring of individual performance of each cell, special care to avoid any contamination or memory effect of the cells, and participation in various international intercomparison studies, can result in a reproducible, accurate and precise results of tritium activity concentration down to very low detection limits.

## Preparation of the source

Chapter 7.2 of ISO 9698 – Water quality - Tritium – test method using liquid scintillation counting.

- Known quantities of the test sample and the scintillation cocktails introduced into the counting vial
- Close the vial and thoroughly shake the mixture to homogenize it
- Indicate sample/vial identification on the top of the vial cap
- Storage until the measurement – depends on various parameters, as soon as possible, but allow for relaxation of the photo- and chemi-luminescence

## *Plastic Vials*

Volume 20 mL

To allow mixing of 8 – 12 mL of water sample with 12 – 8 mL of a scintillation cocktail

PE vials (Low-diffusion Polyethylene Vials – 20 ml Anti-Static)



Maxi Vial



Super Polyethylene Vial glass vial thread



Super Polyethylene Vial quick closure



Low Diffusion Vial

## Cocktails

The selection of the optimal performing LS cocktail should be based on well balanced compromise between cocktail performance, laboratory requirements, additional considerations about handling/storage characteristics, cocktail expense, and waste treatment implications

As a consequence, no specific cocktail can be identified as fit for all purposes;

Quenching is the most important factor responsible for a reduction in counting efficiency for a given sample/cocktail mixture

- The response of a cocktail to one quench agent relative to that of another is not consistent from cocktail to cocktail.
- For example, better resistance to quench presence was confirmed for Ultima Gold LLT compared to OptiPhase HiSafe 3.
- Ultima Gold LLT in general, is a cocktail most adequate for low level measurements, with minimal background and provides better alpha/beta separation significant for environmental samples.

Measurement parameters as performance indicators of the direct LSC method of tritium activity determination (8:12 sample : cocktail volume ratio).

Vial type	Scintillation cocktail	B [s <sup>-1</sup> ]	SQP(E)	Detection efficiency [%]	FOM	MDA [Bq/l] (t = 600 min)
PE vials: Low-Diffusion Polyethylene Vials - 20ml Anti-Static	Ultima Gold uLLT	0.022	783.0	32.45 (7)	4.79	1.43
	<b>Ultima Gold LLT</b>	<b>0.023</b>	<b>793.2</b>	<b>36.45 (15)</b>	<b>5.78</b>	<b>1.30</b>
	OptiPhase HiSafe 2	0.024	800.3	35.1 (5)	5.13	1.38
	OptiPhase HiSafe 3	0.024	774.3	31.82 (12)	4.22	1.53
Glass vials: High Performance Glass Vial - 20ml	Ultima Gold uLLT	0.153	787.5	31.72 (10)	0.66	3.81
	Ultima Gold LLT	0.190	792.8	31.27 (10)	0.51	4.30
	OptiPhase HiSafe 2	0.201	792.4	36.4 (6)	0.66	3.80
	OptiPhase HiSafe 3	0.200	772.5	30.8 (6)	0.47	4.48

# Measurement method

Activity concentration of  $^3\text{H}$  was measured by liquid scintillation counting in LSC Quantulus 1220



standard laboratory procedure  
(sample:cocktail ratio 8:12 in HDPE vials,  
tritium window 25-253 channel)

$^3\text{H}$  – direct measurement  
 $^3\text{H}$  – with el. enrichment  
8 mL + 12 mL UG LLT

At RBI we use

- low-diffusion polyethylene 20 ml vials
- Sample to cocktail ratio: 8 mL of sample and 12 mL of scintillation cocktail
- Currently – scintillation cocktail Ultima Gold LLT.

Each **ElEn measurement run** consists of 20 enriched samples (3 of them are spike waters, 2 are tritium-free waters and 15 unknown samples) and 4 non-enriched samples: 2 tritium-free samples, a spike and a referent sample of known activity for calibration.

Samples are usually measured in 8 cycles of 50 minutes, resulting in an average of 400 min measurement of each sample.

By optimization of the measuring conditions in Quantulus 1220, the interval between 25th and 253th channel was determined as the best region of interest. This region comprises 92 % of the tritium spectrum and 82 % of the background spectrum, resulting in an efficiency of 23.6 %.

Each **measurement run for the direct method** consists of a tritium-free sample, a referent sample of known activity for calibration and up to 22 unknown samples.

Samples are usually measured in 6 cycles of 50 minutes, resulting in an average of 300 min measurement of each sample.

## Quenching

the lower the energy of the decay, the greater is the effect of quench on the counting efficiency for beta-emitting radionuclides → it means that tritium spectrum is most greatly affected by quench presence since it emits beta particles with lowest energy,  $E_{\max} = 18.6 \text{ keV}$ .

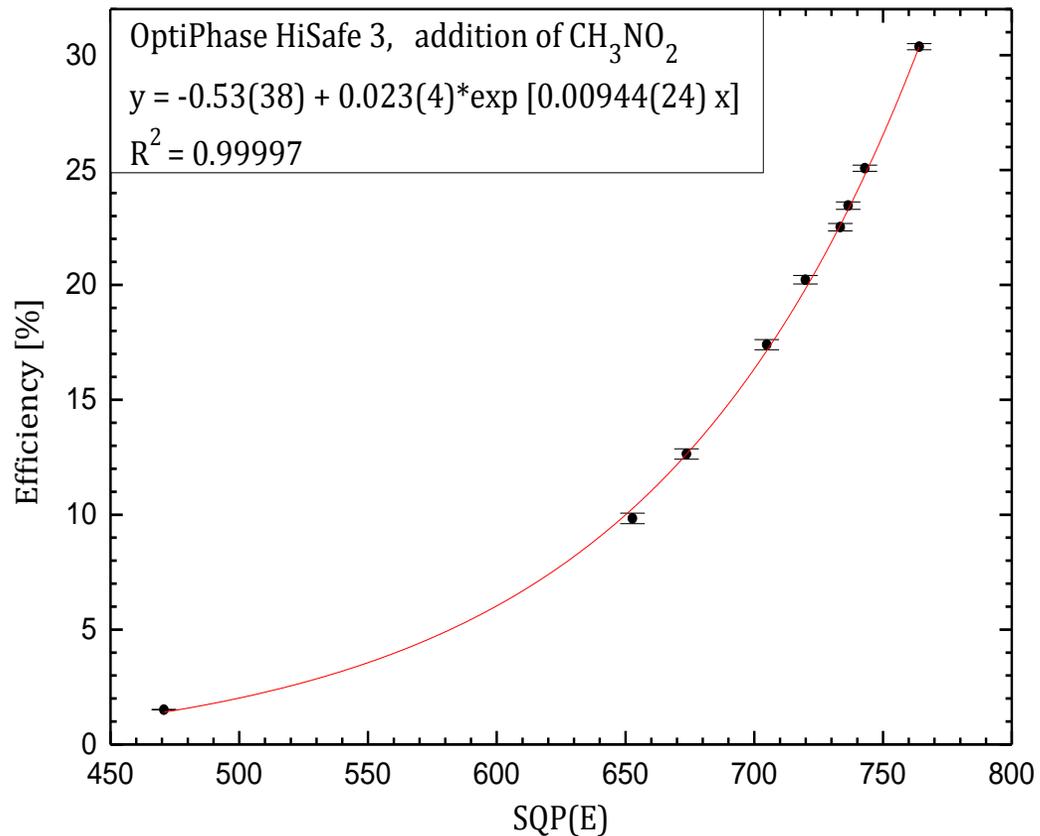
Quench influences tritium spectra in two ways: the endpoint or maximum intensity of the pulse height spectrum is being reduced - shifted towards lower channels in multichannel analyzers i.e. towards lower energies, whilst area under spectrum is being diminished which means decreased total number of counts that are recorded. These effects significantly reduce efficiency detection.

Quench set of sealed standards in vials can be purchased for the radionuclide and scintillation cocktail of interest, or made in laboratory according to the following demands: ISO 9698 recommendations for calibration.

The sample, the blank sample as well as the calibration source should be put in the same type of vial in the same geometry, keeping the same ratio between sample and scintillation cocktail, the detection equipment should maintain the same temperature while the value of quench parameter should be included in the calibration curve. This means that the quench curves are specific to the LS counter and to the sample composition. Selection of appropriate chemical quenching agent should be done so that the properties of aqueous sample and sample-cocktail mixture are preserved or not significantly influenced

Quench set of vials represents identical vials with the same amount of known radionuclide activity but with varying levels of quench (i.e. with gradually increased amounts of quenching agent). From the count rates of each tritium standard and SQP(E) value measured by the LSC, a curve of counting efficiency vs. SQP(E) is plotted.

When a sample of unknown activity is analyzed in the LSC, the instrument will determine the SQP(E) value of the sample, and extract the counting efficiency from the obtained calibration curve. One example of quench curve established for the use of OptiPhase HiSafe 3 cocktail, obtained with the addition of nitromethane as a quenching agent



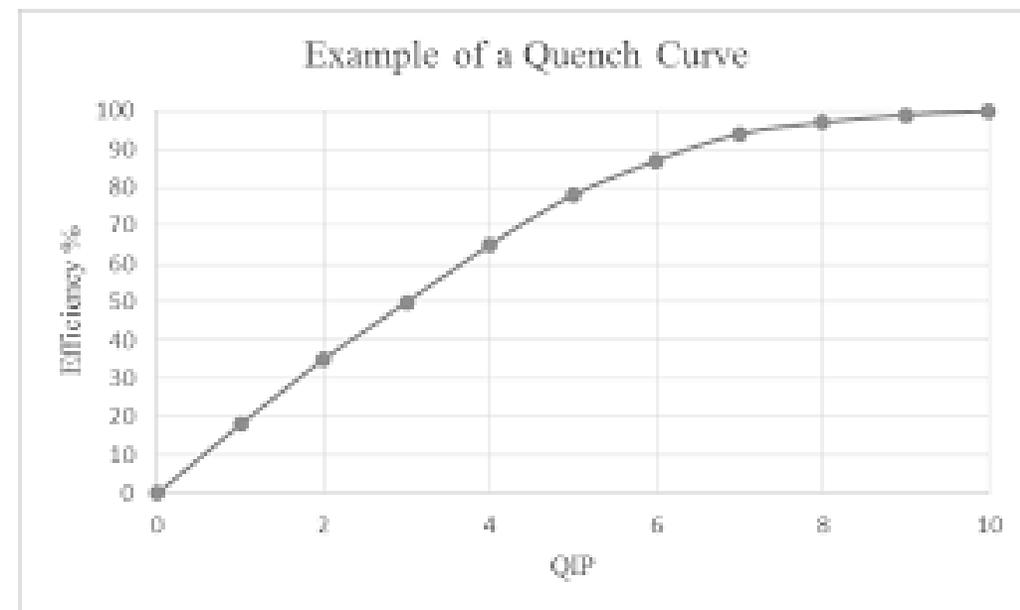
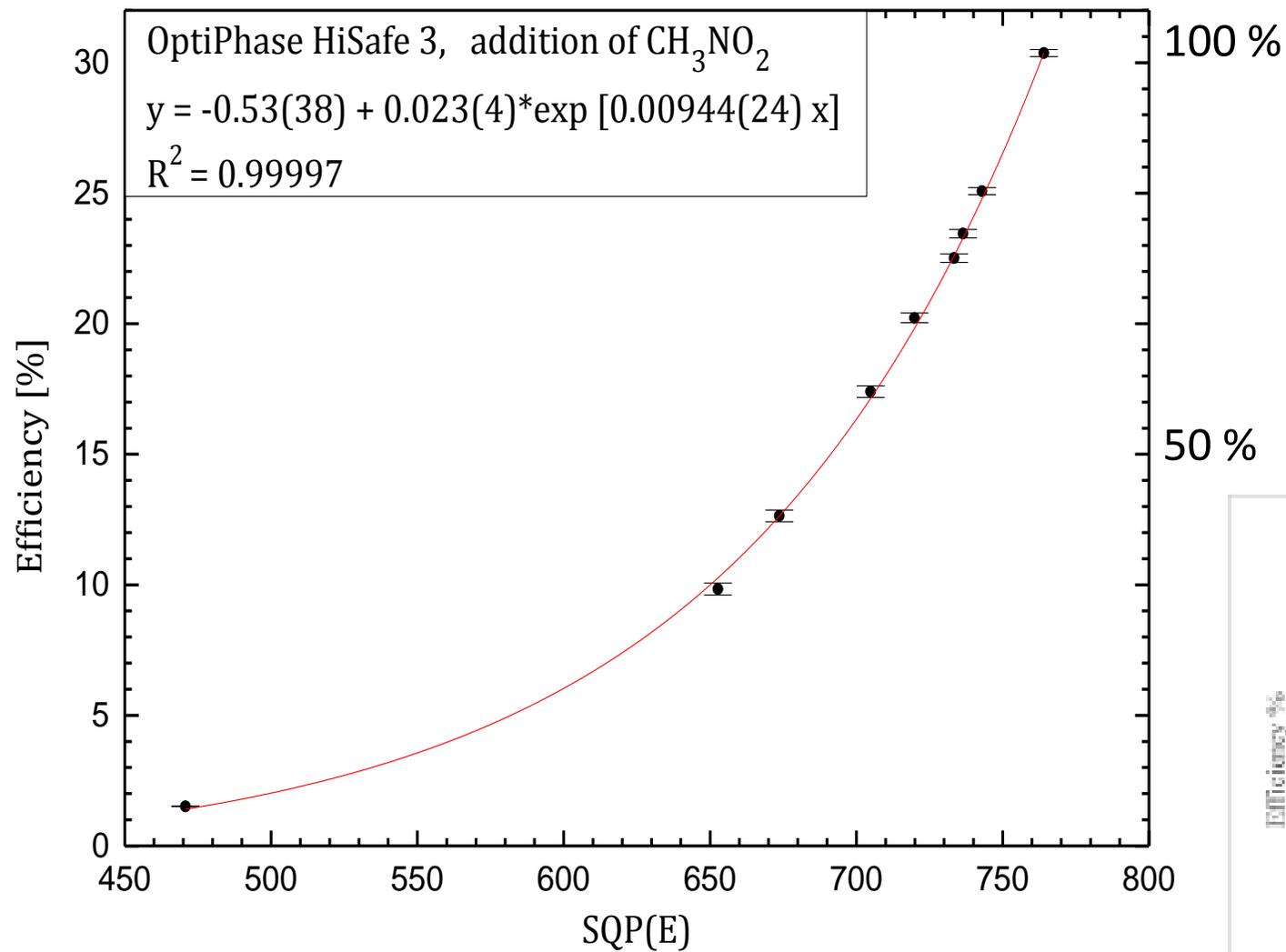
selection of quenching agent should be made after comprehensive study of sample matrix that is going to be analyzed so that expected mechanisms of quench in real samples are as similar to the ones in quench set of vials as possible.

Once the quench curve is obtained, it is possible to store it in LS counter so that it can be automatically applied it in further routine measurements.

Example of quench correction curve for direct LSC method of tritium activity determination (8:12 sample : cocktail volume ratio in 20 ml PE vials).

# Absolute efficiency

# Relative efficiency



# Calculation of tritium activity concentration

Chapter 7.2 of ISO 9698 – Water quality - Tritium – test method using liquid scintillation counting.

$$c_A = \frac{r_g - r_0}{V \varepsilon f_q} = (r_g - r_0) \frac{1}{f_q} w$$

{ x D }

$$c_A = \frac{r_g - r_0}{V \left(\frac{r_s - r_0}{A_S V}\right) f_q} = \frac{(r_g - r_0)}{(r_s - r_0) f_q} A_S = \frac{(r_g - r_0)}{f_q} CF$$

$D$  decay correction factor, to determine  $c_A$  on the reference date (the date of measurement).

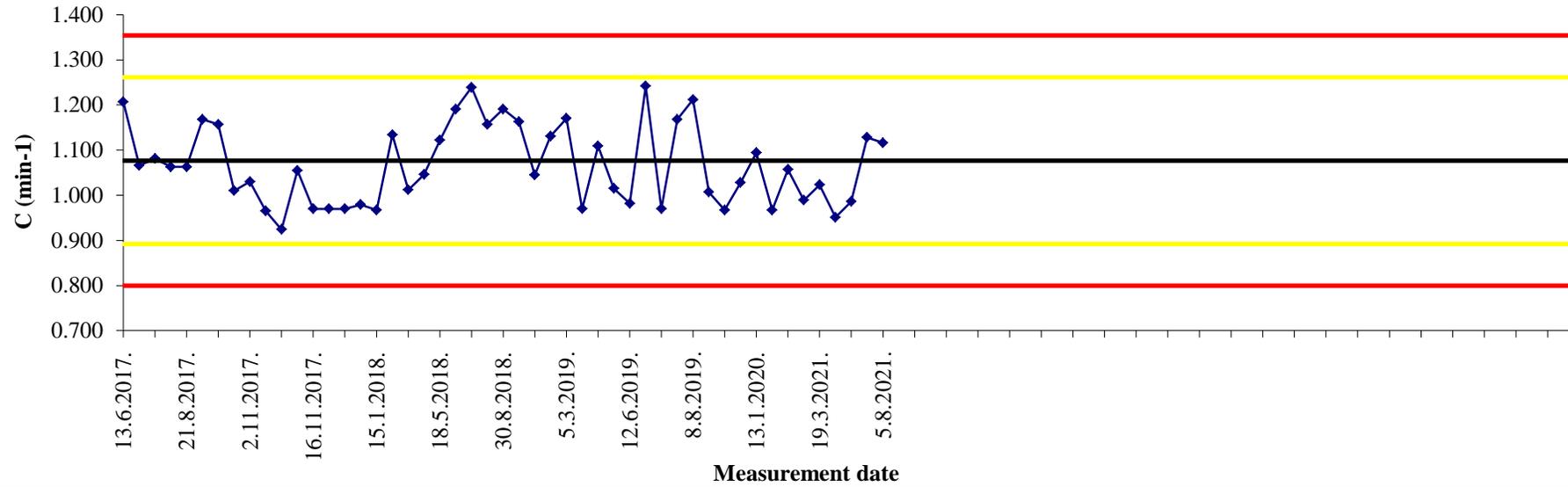
$$c_A = \frac{(r_g - r_0) A_S}{(r_s - r_0) f_q E_{\text{sample}}} D$$

If the standard and a sample are prepared in the same way, and are both measured under identical conditions, the measurement efficiency is the same for all samples.

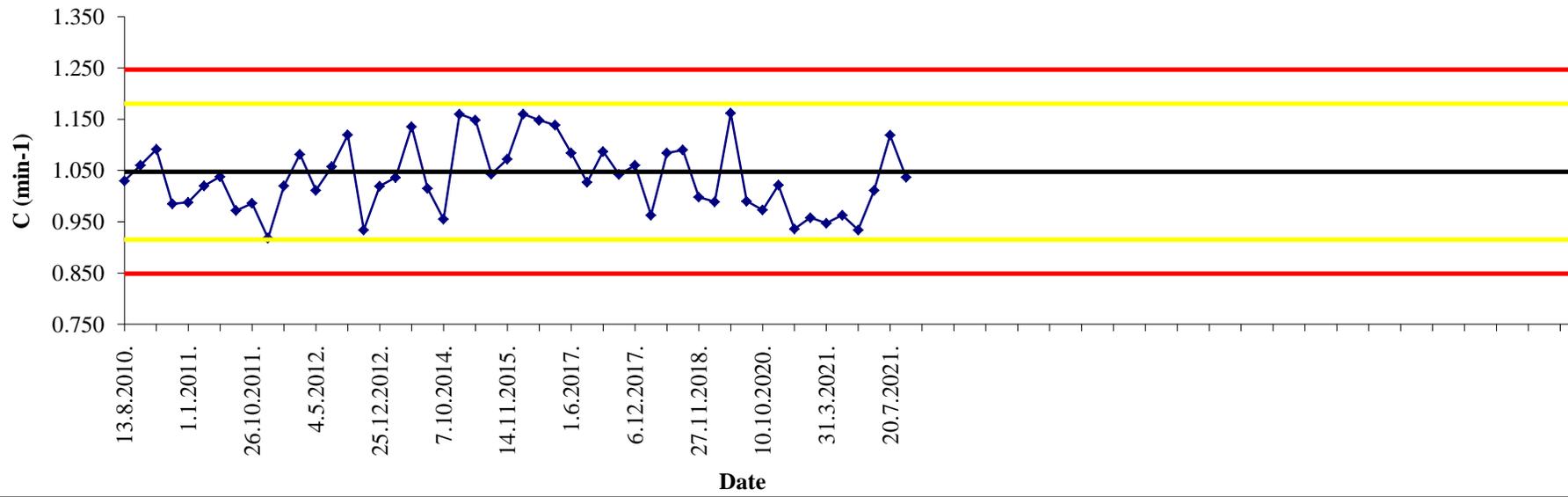
$E_{\text{sample}}$  is the enrichment factor for the sample,

Enrichment run No:				67	Q [Ah]	LSC measurement:				TRIT13-2021	No.cycles:	Standard (ref.date):				07.07.08.	11552	Diff.[years]:					
Start date:				19.05.21.	1420	Start date:				08.06.21.	8	Standard (meas.date):				08.06.21.	5584	12.920					
Q/2.975 =				477.31		Uncorr.				Konc.akt.		sqp											
ElEn ćelija no.	redos lijed	LSC pozi- cija	Oznaka uzorka T-	Opis/naziv uzorka	m prazna ćelija [g]	m puna ćelija prije [g]	m puna ćelija poslije [g]	Datum uzorkovanja	srednja vr. CPM	error	P nadopuna	CPM net	poč.masa vode (Wi) [g]	konačna masa v (Wf) [g]	uzorak E-factor	konc.akt. [TU]	T-	ElEn ćelija no	Na dan uz. [TU]	mj.nes. [TU]			
7									25-253 ch														
19	1	1	5394	G-HGI-VIS,PIZ, 13.1.20	2524.98	3024.68	2537.79	13.01.21.	1.808	0.072	1.000	0.798	499.18	11.96	30.58	1.96	5394	19	2.00	0.40	775.34		
20	2	2	5395	G-HGI-VIS,K-1, 13.1.20	2520.84	3020.63	2535.12	13.01.21.	1.789	0.067	1.000	0.779	499.27	13.43	27.76	2.11	5395	20	2.16	0.43	781.02		
1	3	3	5284	P-Grič, 10-2020	2527.82	3027.46	2543.93	15.10.20.	2.546	0.08	1.000	1.536	499.12	15.26	25.00	4.61	5284	1	4.79	0.73	780.99		
2	4	4	5285	P-Grič, 11-2020.	2522.48	3022.00	2538.31	15.11.20.	2.381	0.078	1.139	1.701	499.00	14.98	25.40	5.03	5285	2	5.19	0.74	780.48		
3	5	5	5290	Oborina, Glavna mete	2537.30	3037.00	2551.53	15.11.20.	2.979	0.087	1.000	1.969	499.18	13.38	27.86	5.31	5290	3	5.48	0.73	782.36		
4	6	6	5291	Oborina, Glavna mete	2519.50	3018.76	2534.03	15.12.20.	2.445	0.079	1.000	1.435	498.74	13.68	27.41	3.93	5291	4	4.04	0.60	775.37		
5	7	7	5292	P-Varaždin, 12/2020	2524.66	3024.66	2539.96	15.12.20.	2.624	0.081	1.039	1.715	499.48	14.45	26.10	4.94	5292	5	5.07	0.72	784.25		
6	8	8	5293	P-Legrad, 12/2020	2526.76	3026.45	2541.88	15.12.20.	2.617	0.081	1.037	1.703	499.17	14.27	26.41	4.84	5293	6	4.98	0.70	782.85		
7	9	9	5294	P-Bilogora, 12/2020	2523.24	3022.62	2538.10	15.12.20.	2.834	0.085	1.024	1.890	498.86	14.01	26.86	5.29	5294	7	5.43	0.74	781.48		
8	10	10	5295	P-110 KO, 1/2021	2521.14	3020.78	2535.17	15.01.21.	1.501	0.062	4.845	6.262	499.12	13.18	28.22	16.68	5295	8	17.05	1.70	780.44		
9	11	11	5318	P-Grič, 12/2020	2521.27	3021.20	2536.96	15.12.20.	2.427	0.078	1.000	1.417	499.41	14.84	25.55	4.17	5318	9	4.28	0.66	779.48		
10	12	12	5389	Solun, E-KA20, 30.3.20	2520.95	3020.42	2535.86	30.03.21.	2.533	0.08	1.000	1.523	498.95	14.06	26.77	4.27	5389	10	4.32	0.64	781.13		
11	13	13	5390	Solun, PHTH Sim/PA, 3	2524.34	3024.08	2539.84	30.03.21.	2.482	0.085	1.000	1.472	499.22	14.65	25.84	4.28	5390	11	4.33	0.68	781.96		
12	14	14	5392	P-IRB, 4/2021	2515.42	3014.79	2529.84	15.04.21.	5.421	0.117	1.000	4.411	498.85	13.57	27.58	12.02	5392	12	12.12	1.37	782.70		
13	15	15	5393	G-HGI-VIS, BO-2, 13.1.	2519.44	3018.43	2533.43	13.01.21.	1.977	0.071	1.000	0.967	498.47	13.14	28.38	2.56	5393	13	2.62	0.46	783.62		
14	16	16	5044	DW-Lipik B8	2517.95	3018.42	2532.63	07.02.18.	1.048	0.051	1.000	0.038	499.95	13.83	Spike		27.00	0.10	5044	14	0.13	0.34	777.04
15	17	17	5044	DW-Lipik B8	2557.17	3056.74	2573.14	07.02.18.	1.177	0.055	1.000	0.167	499.05	15.12	E-fact.	P-fact.	25.20	0.50	5044	15	0.60	0.40	777.56
16	18	18	5288	SPIKE	2530.66	3030.15	2545.03	20.01.21.	125.206	0.563	1.000	124.196	498.97	13.52	27.65	337.56	5288	16	344.87	34.56	778.56		
17	19	19	5288	SPIKE	2521.89	3021.56	2536.55	20.01.21.	120.202	0.552	1.000	119.192	499.15	13.81	27.14	329.99	5288	17	337.13	34.42	783.80		
18	20	20	5288	SPIKE	2519.08	3018.50	2532.78	20.01.21.	129.053	0.572	1.000	128.043	498.90	12.85	28.85	333.55	5288	18	340.77	32.74	784.21		
	21	21	5288	B.E. spike				20.01.21.	5.451	0.117	1.000	4.441					5288				783.97		
	22	22		S.F. standard					75.323	0.437	St.net:	74.313	499.102	13.900	27.882	0.936	27.08	← Averages			780.01		
	23	23		B.E. dead water					1.030	0.036	Dead:	1.011	0.305	0.833	0.999	0.003	1.38	← St.dev.			778.96		
	24	24		B.E. dead water					0.991	0.037			0.068	0.186	0.577	0.002	0.31	← St.dev.mean			780.37		
Cal.factor:												75.145	TU/CPM										
Comment:				svi sa Ultima Gold LLT (UG), protokol: el-en 67, svi SQPO od 775 do 784																			

**Control chart – background count rate - direct**

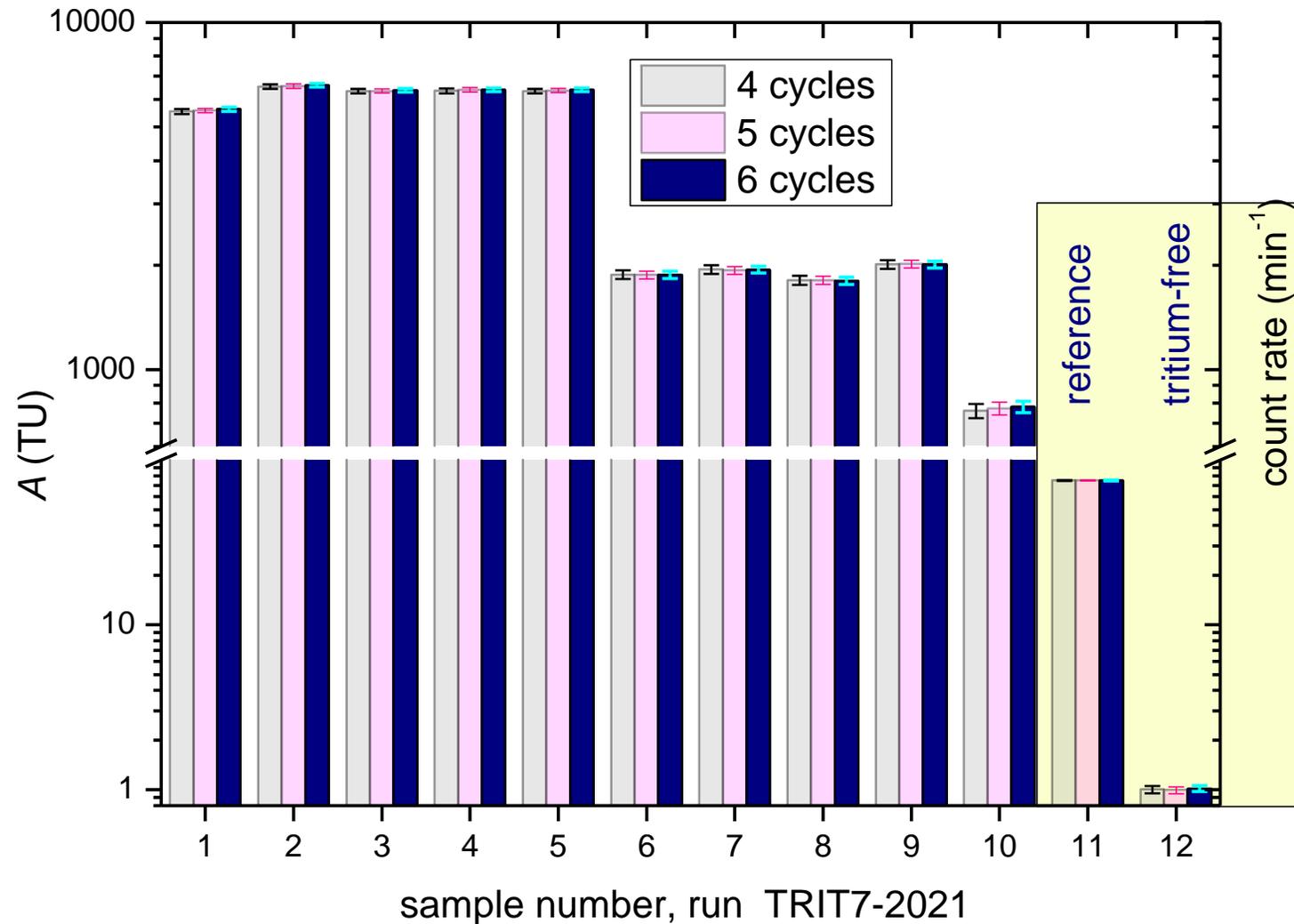


**Control chart – background count rate - E1En**



# How long should we measure?

High-activity samples, direct method, 8 mL sample : 12 mL UGLLT, cycle 50 min

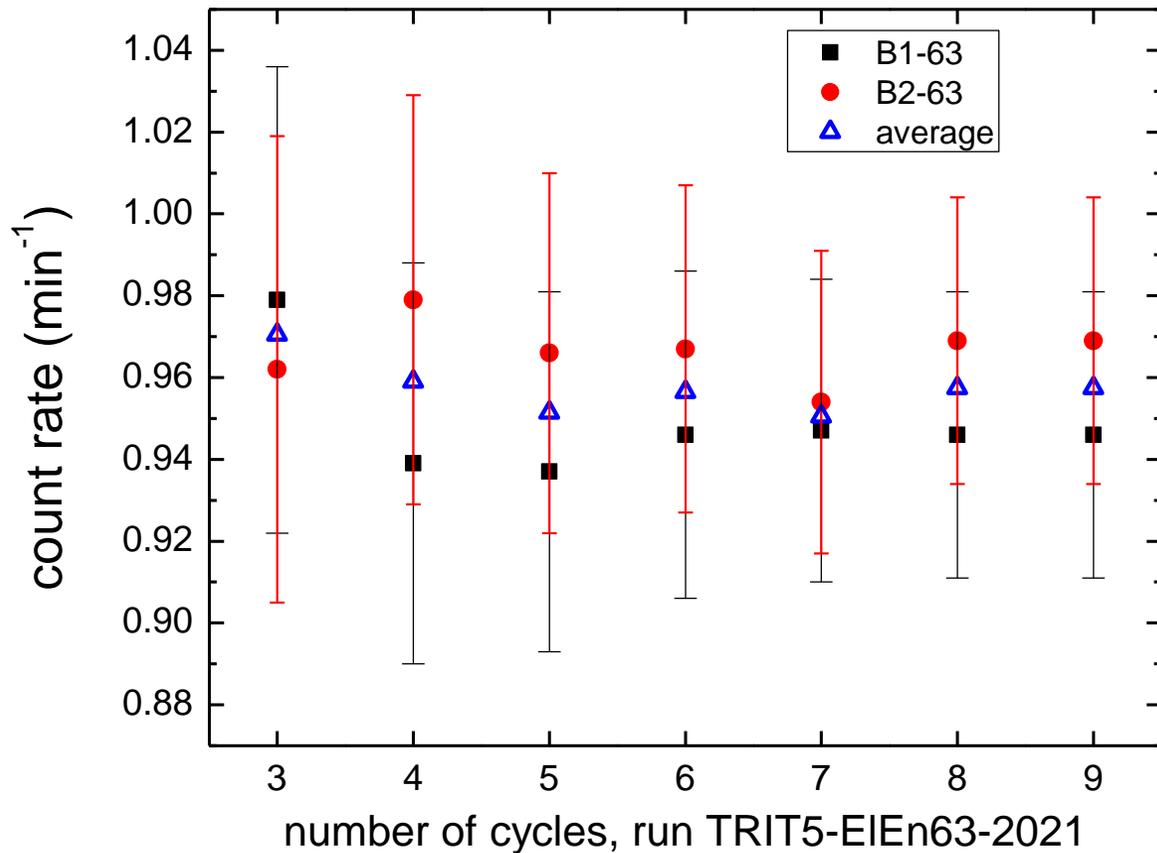


Conclusion:  
6 cycles x 50 min

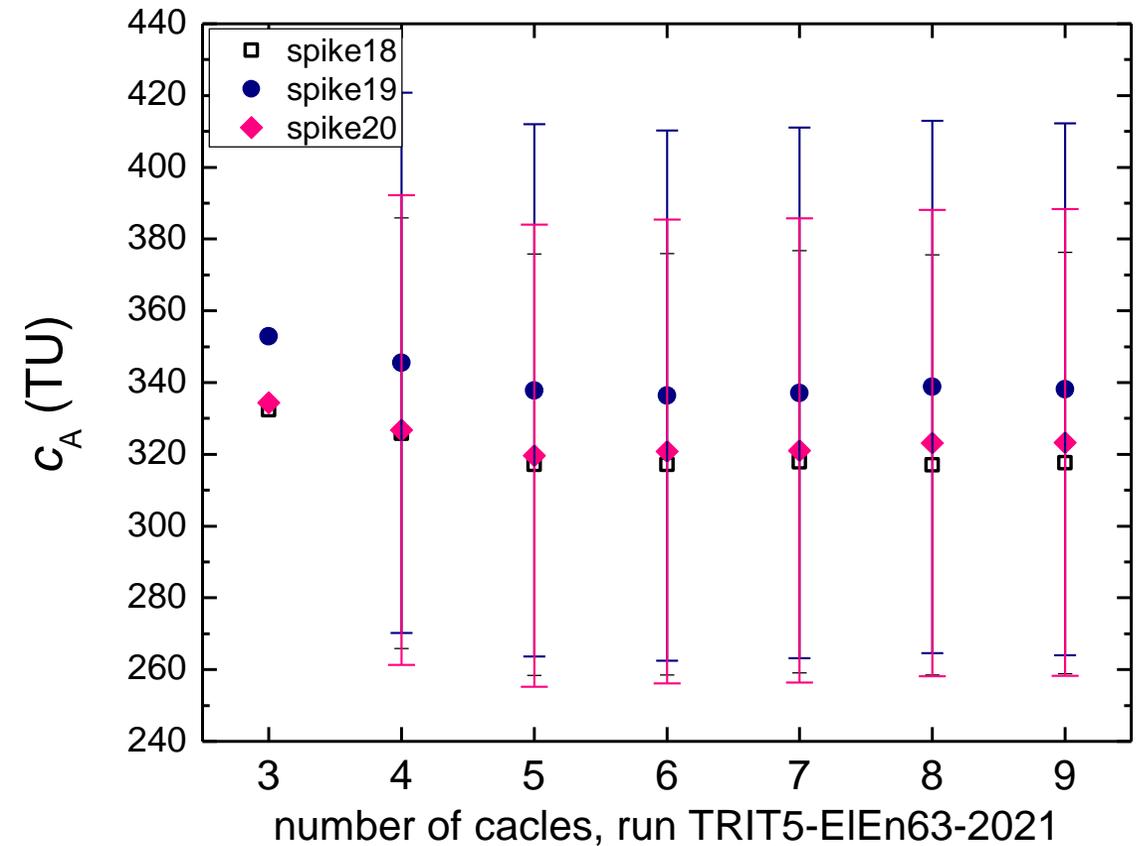
# How long should we measure?

Low-activity samples, after EIEn, 8 mL sample : 12 mL UGLLT, cycle 50 min

### Background (tritium-free)

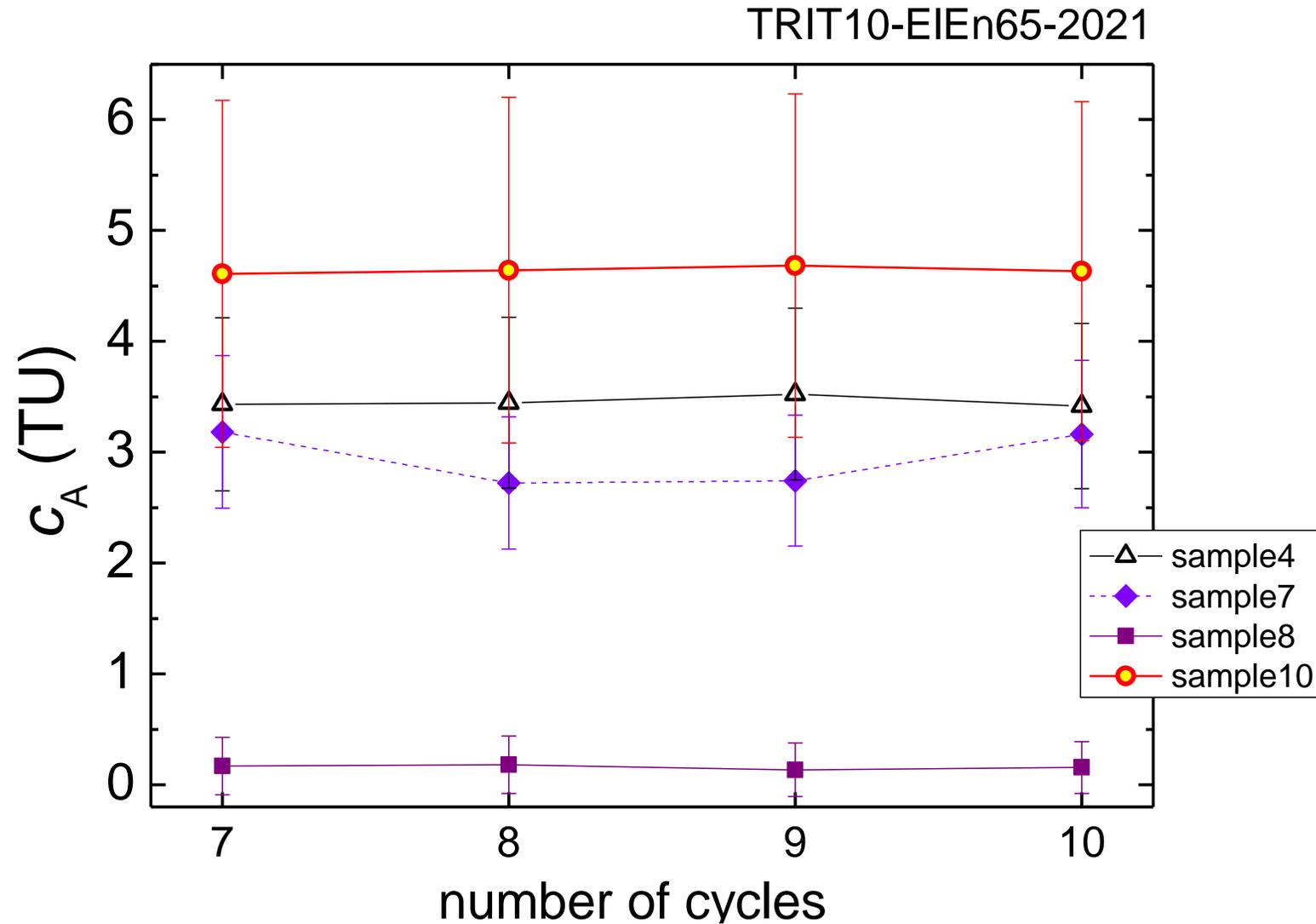


### Spike samples



## How long should we measure?

Low-activity samples, after EIEn, 8 mL sample : 12 mL UGLLT, cycle 50 min



Conclusion:  
8 cycles x 50 min

## Tests

- ❑ Determination of low-level tritium ( $^3\text{H}$ ) activity concentration in environmental water samples by liquid scintillation counting requires use of a scintillation cocktail mixed with a sample in an appropriate vial.
- ❑ From the point of the measurement quality, it is required that the new scintillation cocktails have at least the same performance characteristics as the currently best cocktails used.
- ❑ Comparison of different vials and scintillation cocktails for determination of  $^3\text{H}$  activity concentration in LSC Quantulus 1220 - under the same conditions, with the same water samples and standards

## Parameters compared

- background count rate       $B$  [ $\text{min}^{-1}$ ]
- counting efficiency       $E$  [%]
- Calibration factor  $w$        $CF$  [ $(\text{Bq/L})/\text{min}^{-1}$ ]
- quenching parameter       $SQP(E)$  [channel]
- detection limit       $c_A^\#$  [Bq/L]
- Figure of Merit       $FOM = (S-B)^2 / B$

## Vials

- Two series of **PerkinElmer** (Low diffusion PE vial, cat. no. 6000477)
- Two series of **Zinsser Analytic** (ZA) (Polyvials 20 ml, natural, HDPE, ZINSSER POLYVIALS® cat.no 3071401), new batch used in tests 2 and 3
- anti-static PV1AS-HDPE - **Meridian** Biotechnologies

Scintillation cocktail UGLLT, sample to cocktail ratio **8 mL:12 mL**

# Vials

## Parameter comparison – different vials, UGLLT

Vial type	Ratio	<i>SQP</i>	<i>B</i> (min <sup>-1</sup> )	<i>CF</i>	<i>FOM</i>	<i>DL</i> (Bq/L)	<i>E</i> (%)
PerkinElmer (in use)	8:12	776	1.112 ± 0.047	8.88	7768	1.20	23.48
PerkinElmer – new batch	8:12	780	1.221 ± 0.064	8.55	7614	1.21	24.36
Zinsser – sample vials	8:12	779	1.231 ± 0.053	9.12	6662	1.29	22.88
<b>Zinsser – new batch</b>	<b>8:12</b>	<b>787</b>	<b>1.207 ± 0.070</b>	<b>8.26</b>	<b>8250</b>	<b>1.16</b>	<b>25.21</b>
Wallac teflon- copper 7 mL	3:3	711	0.41 ± 0.03	35.4	1334	2.93	5.9

PerkinElmer LOW DIFFUSION PE VIAL, replacement for 1200-422

ZINSSER POLYVIALS® V 20 ml, HDPE

## Scintillation cocktails



- **Ultima Gold LLT (UGLLT)** - Perkin Elmer - biodegradable scintillation cocktail, „Safer“ cocktail, contains DIPN (*Diisopropyl naphthalene isomers*) as solvent in concentration 40-60 %. DIPN are also harmful for environment
- **Gold Star LT2 (GS)** - Meridian Biotechnologies - contains NPE (*Substances of Very High Concern*), requires special disposal procedures, poisonous for aquatic biota
- **ProSafe LT+ (PS)** - Meridian Biotechnologies – biodegradable, no NPE, considered as safe material, does not require special disposal conditions

In addition – earlier comparison **UGLLT** vs. **OptiPhase HiSafe 3** (PerkinElmer) - safer LSC cocktail, with the solvent di-isopropylnaphthalene (DIN) to achieve improved safety without decreasing performance – no observed difference in performances

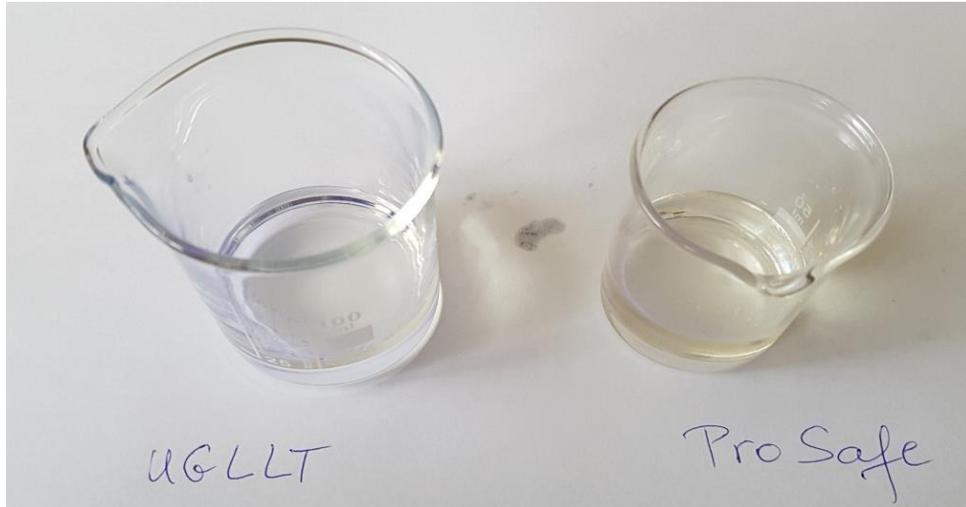
## Test description

- **Test 1:** scint. cocktails **UGLLT** and ProSafe LT+ in aluminum container (**PS-AI**) .
- **Test 2:** scint. cocktails **UGLLT**, ProSafe LT+ in glass container (**PS-glass/1**) and Gold Star LT2 (**GS/1**), repeated test with PS-AI.
- **Test 3:** scint. cocktails **UGLLT**, new batches of ProSafe LT+ (**PS-glass/2**) and Gold Star LT2 (**GS/2**) (possible small changes in cocktail composition).

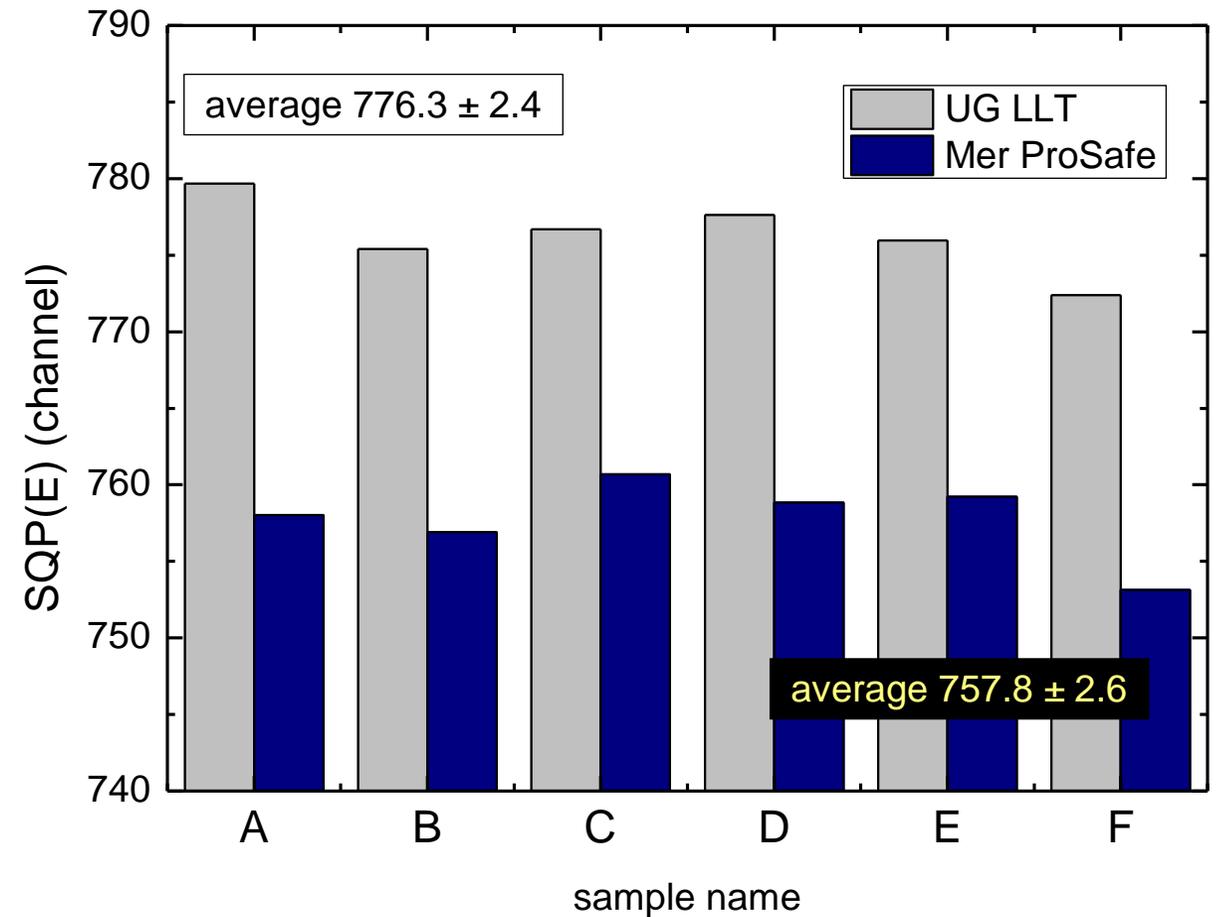
## Measurement conditions

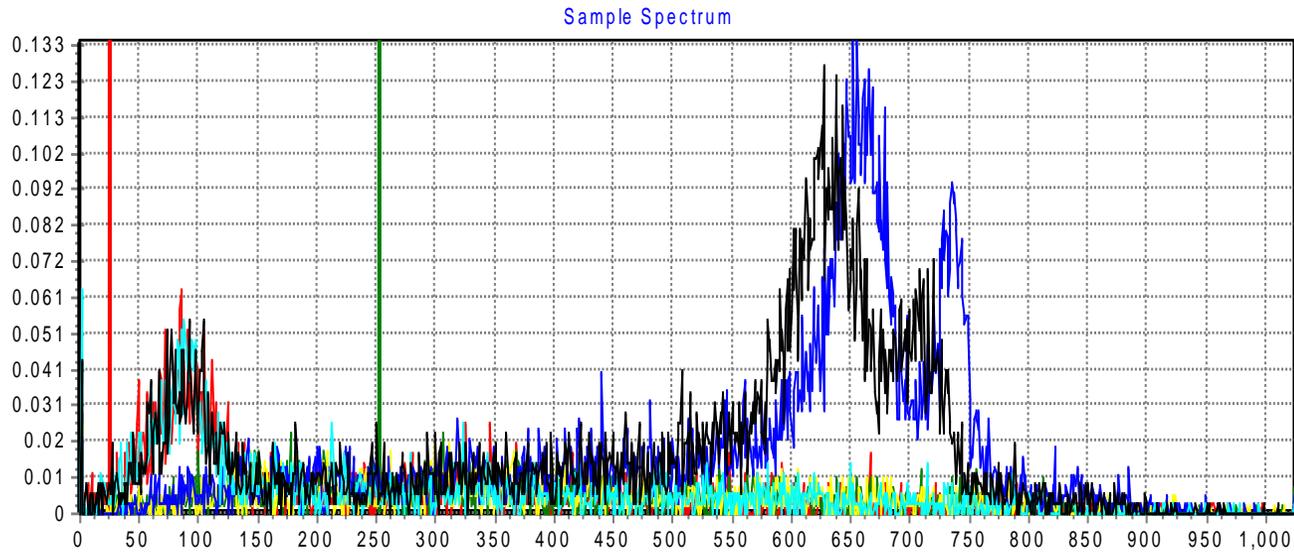
- PE vials (HDPE) ZINSSER POLYVIALS® 20 mL
- 4 or 6 samples (0 Bq/L to 600 Bq/L)
- sample to cocktail ratio **8 mL:12 mL**
- LSC Quantulus 1220
- Direct measurement of  $^3\text{H}$  activity concentration
- Measurement duration 300 min (6 cycles x 50 min)
- Optimized tritium window, 25 – 253 channels

## Step 1: UG LLT and Prosafe LT+ in Al container

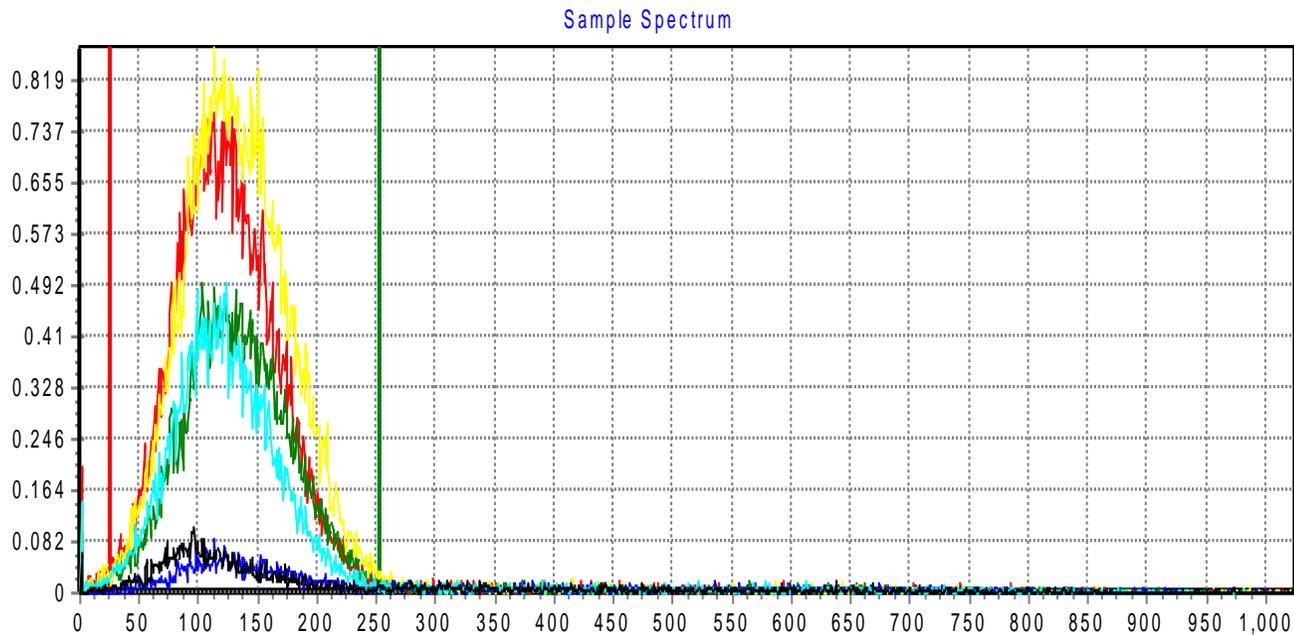


Samples prepared 17 May, 2018  
Measurement start 18 May, 2018  
7 x 50 min per sample





- ...TRIT10\S12.sum 12
- ...8\TRIT10\S1.sum 12
- ...8\TRIT10\S2.sum 12
- ...8\TRIT10\S3.sum 12
- ...TRIT10\S11.sum 12
- ...TRIT10\S13.sum 12



- ...TRIT10\S12.sum 12
- ...8\TRIT10\S1.sum 12
- ...8\TRIT10\S2.sum 12
- ...8\TRIT10\S3.sum 12
- ...TRIT10\S11.sum 12
- ...TRIT10\S13.sum 12

	UGLLT	Mer ProSafe LT+ Al container
<b>B</b>	<b>1.164 ± 0.054</b>	<b>3.340 ± 0.098</b>
<b>CF</b>	<b>9</b>	<b>11</b>
<b>SQP(E)</b>	<b>776.3 ± 2.4</b>	<b>757.8 ± 2.6</b>
<b>DL</b>	<b>1.63</b>	<b>2.73</b>
<b>FOM</b>	<b>6504</b>	<b>1195</b>

## Step 2:

Prosafe LT+ in glass container

GoldStar LT<sup>2</sup>

UGLLT test 2

ProSafe LT+-AI test 2

Samples prepared 5 July 2018

Measurement start 6 July 2018

2nd: 30 August 2018

6 x 50 min per sample

For comparison

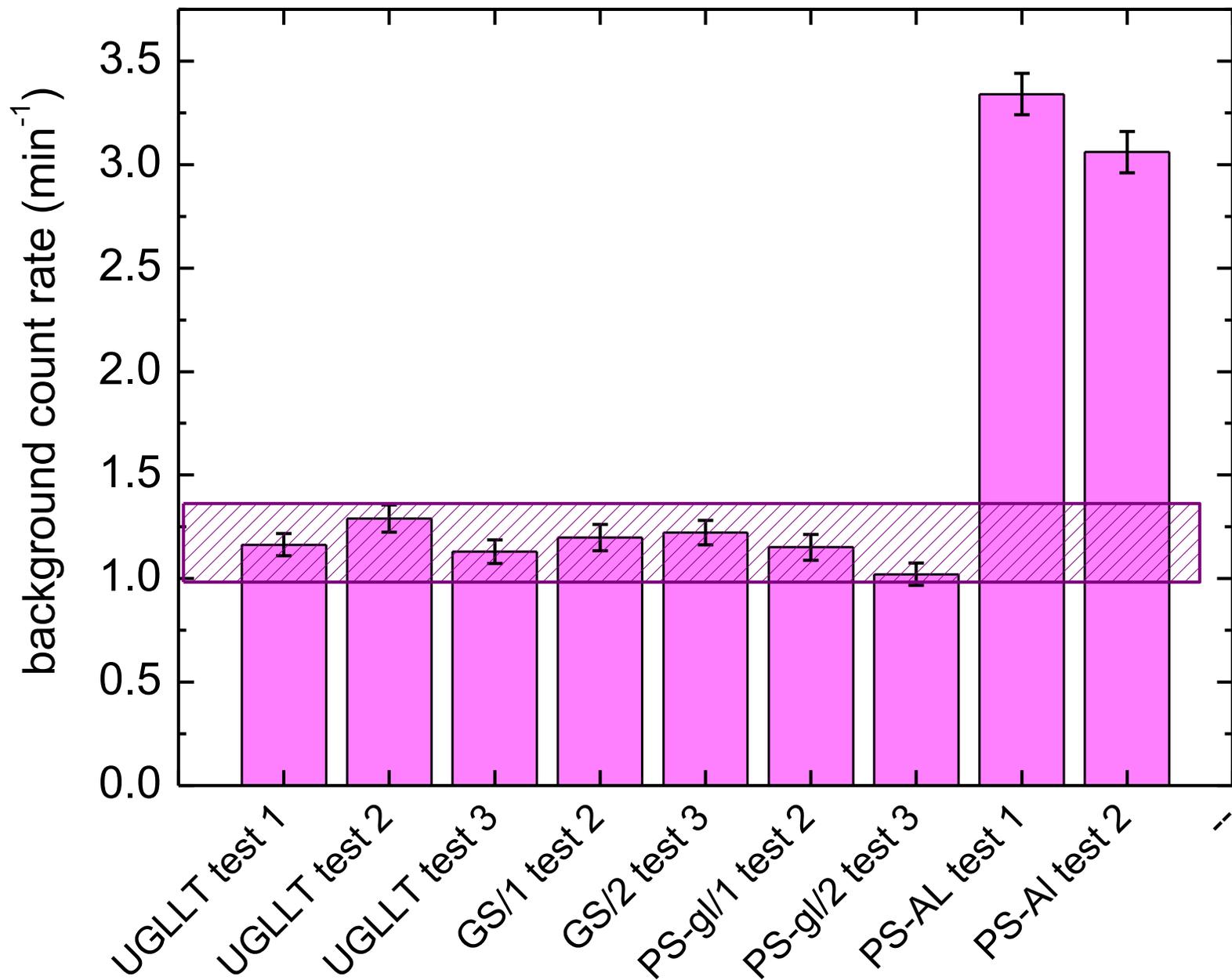
UGLLT test 1

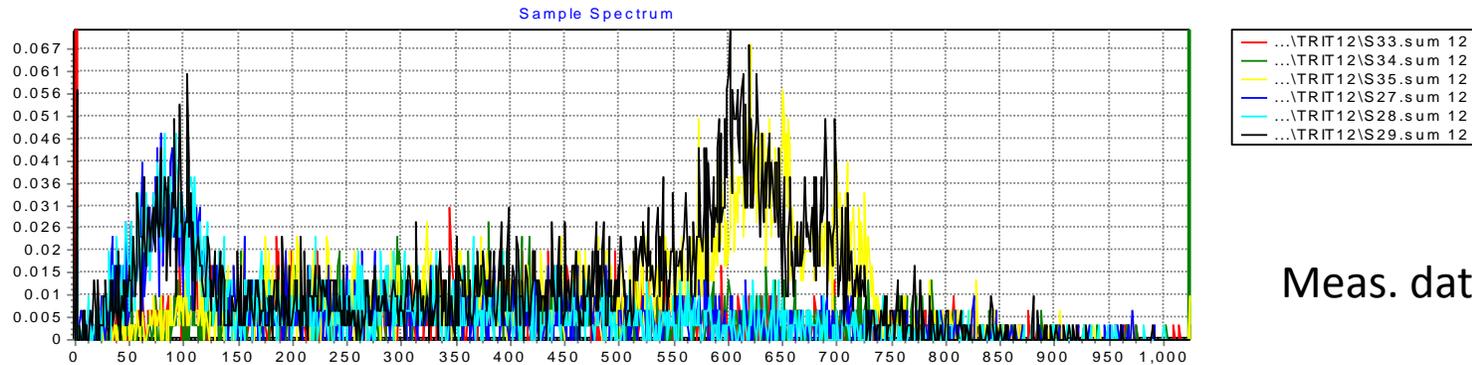
ProSafe LT+ - AI test 1

## Parameter comparison – different cocktails, Zinsser vials.

<b>Scint. cocktail</b>	<b><i>B</i></b> (min <sup>-1</sup> )	<b><i>CF (w)</i></b> (Bq/L)/min <sup>-1</sup>	<b><i>SQP(E)</i></b> (channel)	<b><i>DL</i></b> (Bq/L)	<b><i>FOM</i></b> (min <sup>-1</sup> )	<b><i>E</i></b> (%)
<b>UGLLT test 1</b>	1.164 ± 0.054	9.0	776.3	1.63	6504	23.2
<b>UGLLT test 2</b>	1.239 ± 0.065	8.8	776.3	1.64	6303	23.7
<b>UGLLT test 3</b>	1.131 ± 0.057	8.8	776.1	1.56	6432	23.6
<b>GS/1 test 2</b>	1.198 ± 0.064	9.1	777.1	1.66	6122	23.0
<b>GS/2 test 3</b>	1.223 ± 0.059	11.8	745.8	2.16	3355	17.7
<b>PS-glass/1 test 2</b>	1.151 ± 0.062	10.9	756.3	1.95	4428	19.1
<b>PS-glass/2 test 3</b>	1.021 ± 0.054	11.3	751.3	1.90	4368	18.5
<b>PS-Al test 1</b>	3.34 ± 0.10	11.0	757.8	2.73	1523	19.0
<b>PS-Al test 2</b>	3.06 ± 0.10	12.8	<b>740.4</b>	3.72	1195	16.2

# Background count rate



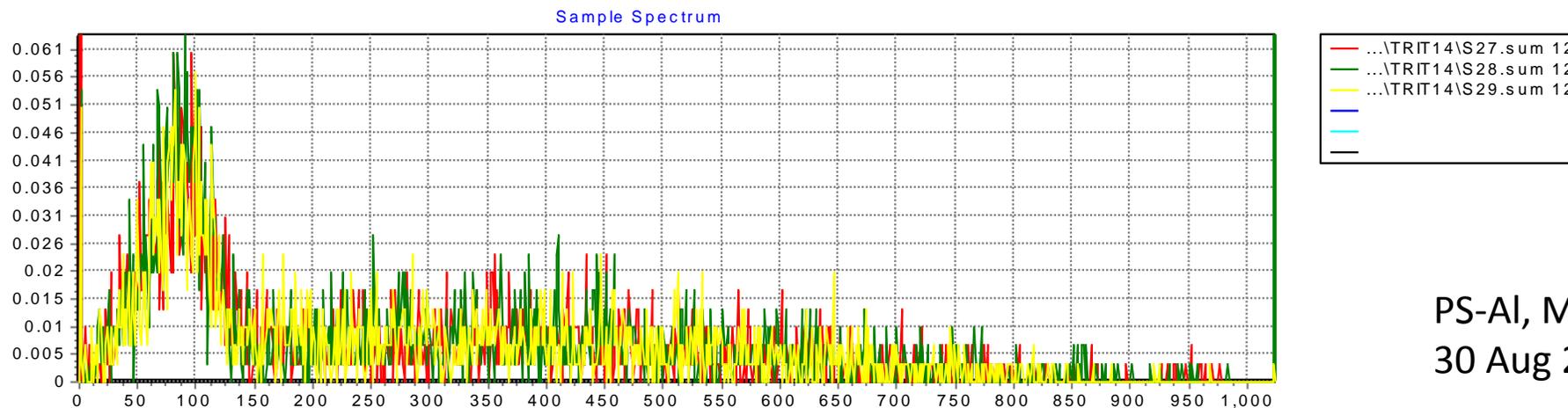


Meas. date 6 July, 2018

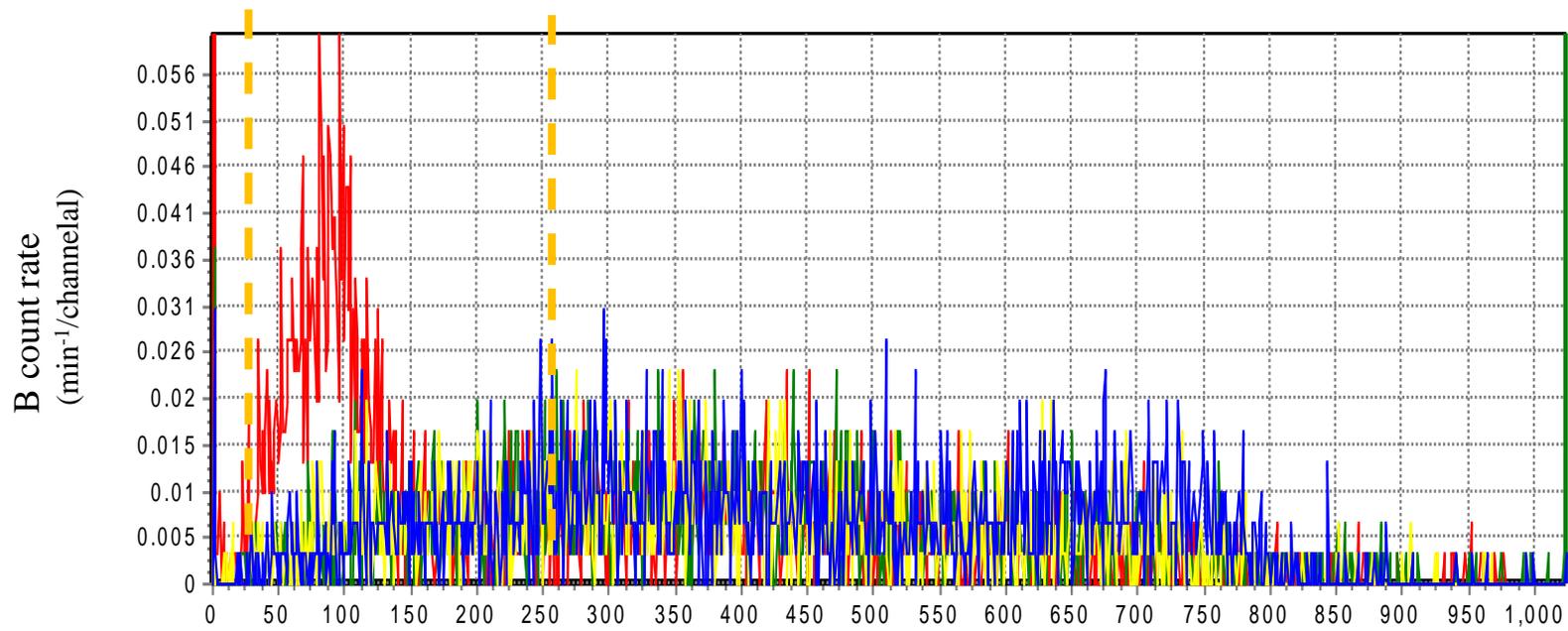
Tritium spectra of samples A, B and C prepared with the Meridian ProSafe LT+ from Al (S27, S28, S29) and glass (S33, S34, S35) containers.

PS-Al cocktail causes a peak in the channel region 0 – 150 for all 3 samples, while the peak is not visible with the PS-glass cocktail.

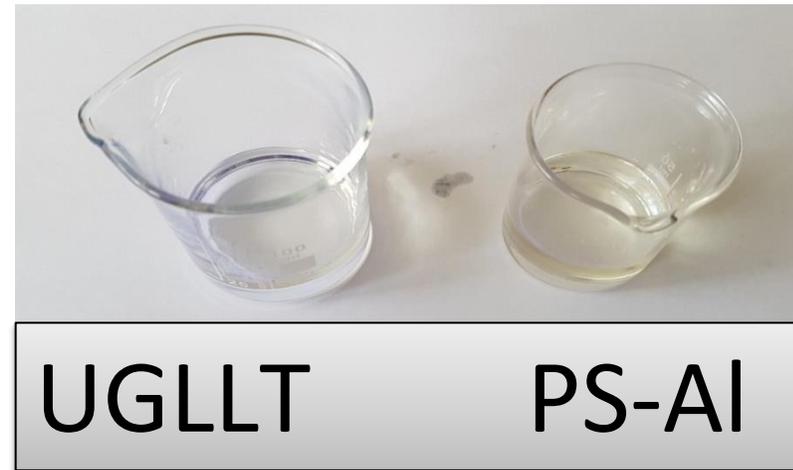
The feature in the channel range 550 – 750 is due to the presence of radon in water sample C.



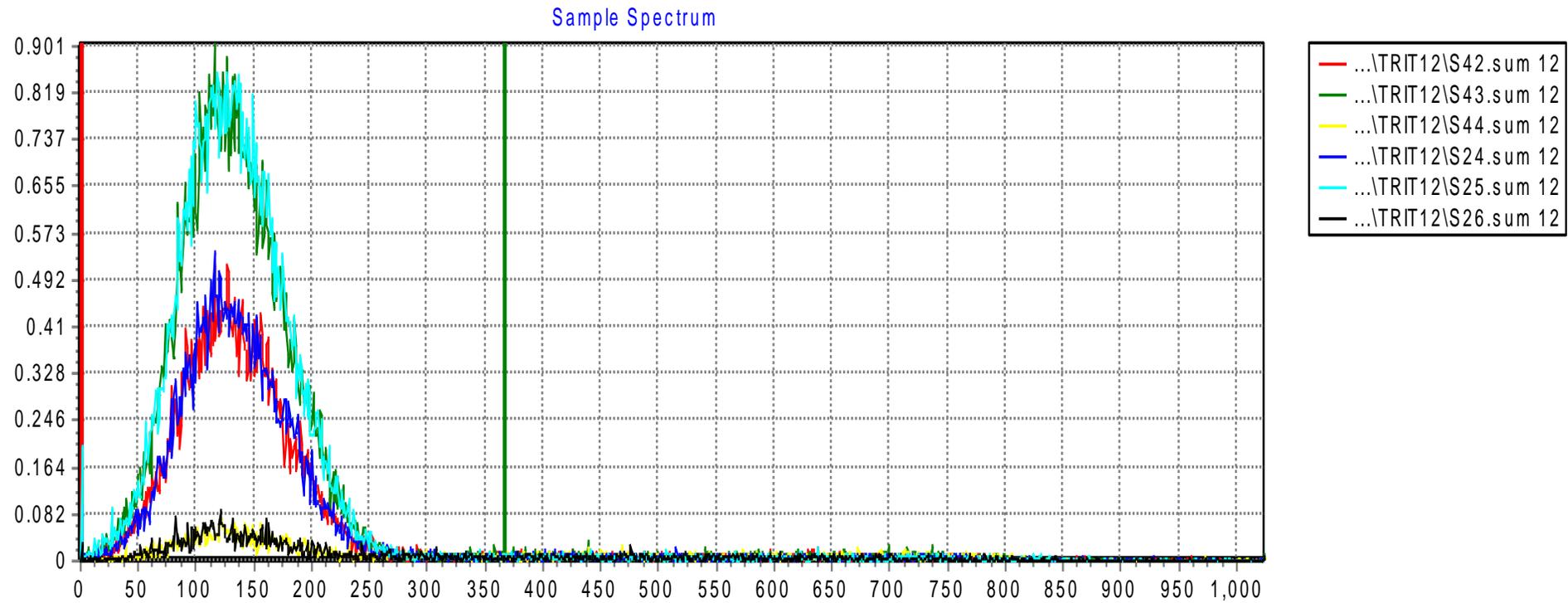
PS-Al, Meas.  
30 Aug 2018



Background spectra – prepared by UGLLT, GS/1, PS-glass/1 and **PS-Al (red)**.  
 8 mL:12 mL, optimized window 25-253 ch.

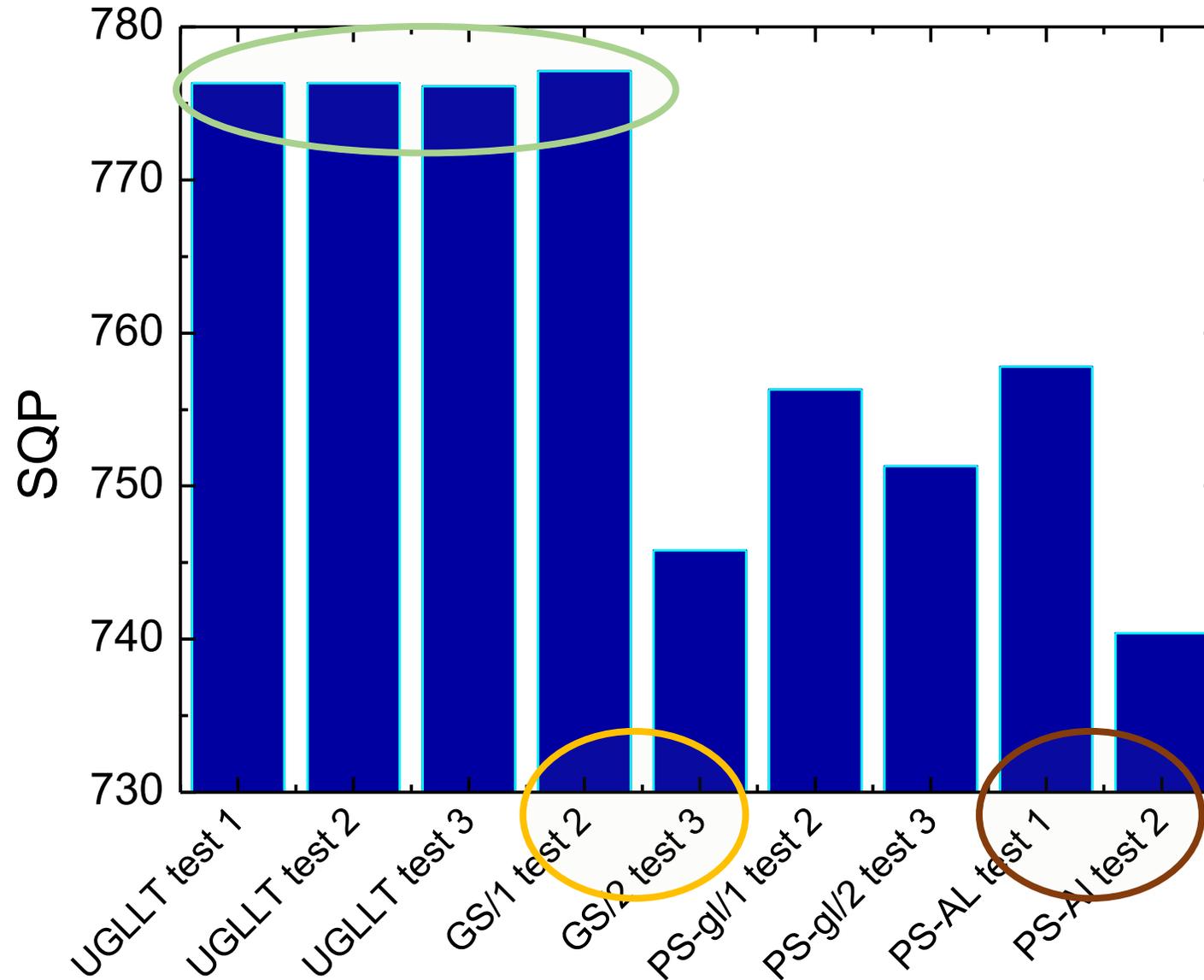


PS-Al yellowish, small bubbles – protective layer of Al container?

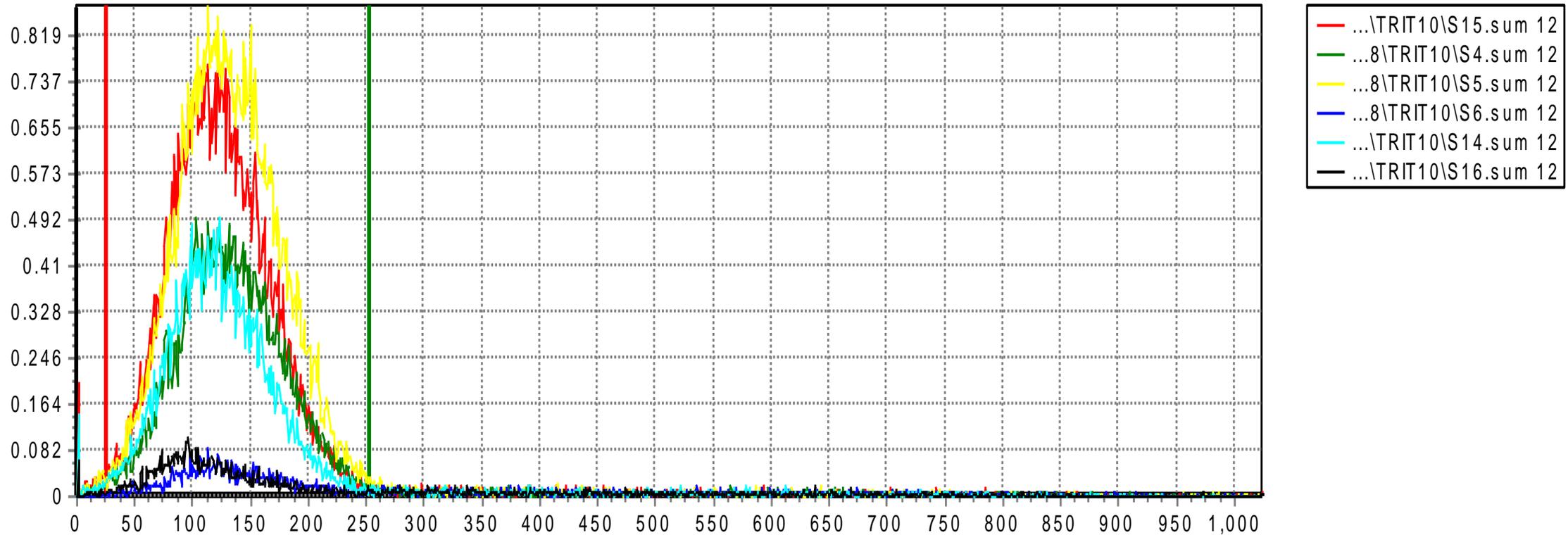


Tritium spectra of samples D, E and F prepared with the **UltimaGold LLT** cocktail (S24, S25, S26) and with the **Meridian GoldStar LT<sup>2</sup>** (S42, S43, S44)

# Standard quenching parameter



Sample Spectrum



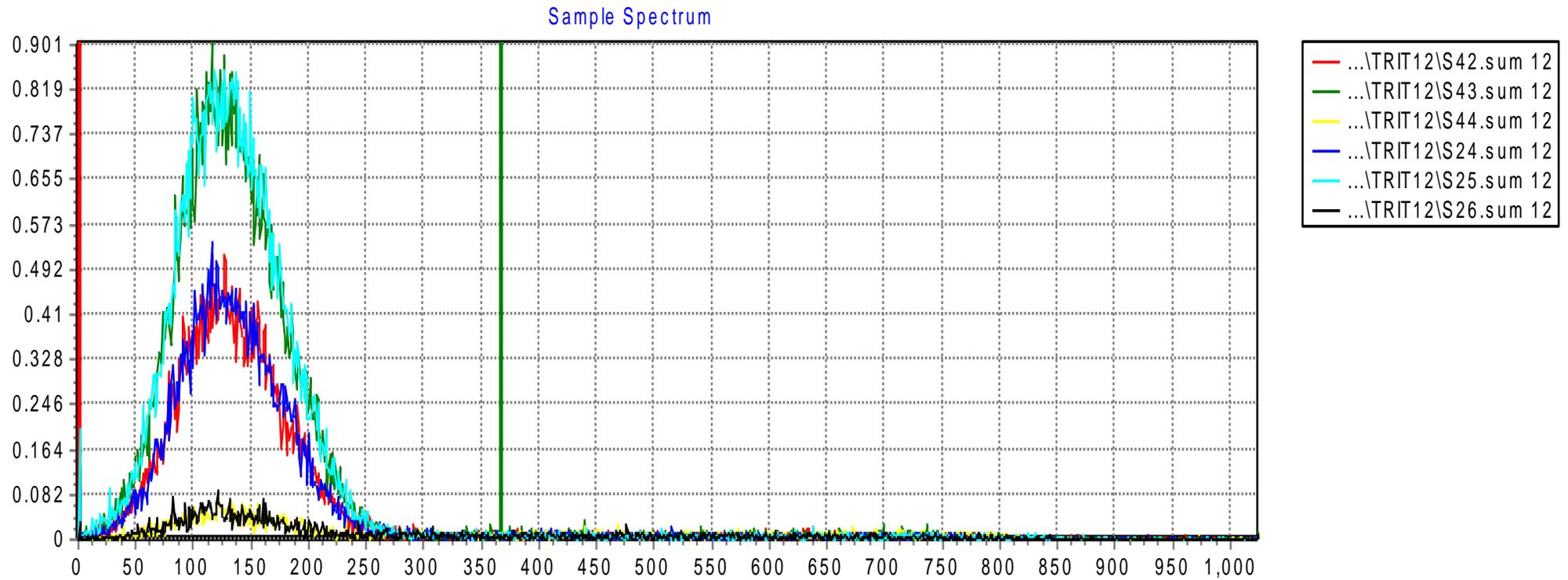
*Tritium spectra* (LSC Quantulus 1220, Easy View software)  
of 3 different  $^3\text{H}$  activity concentrations

**UltimaGold LLT (S4, S5, S6)**

**SQP = 776**

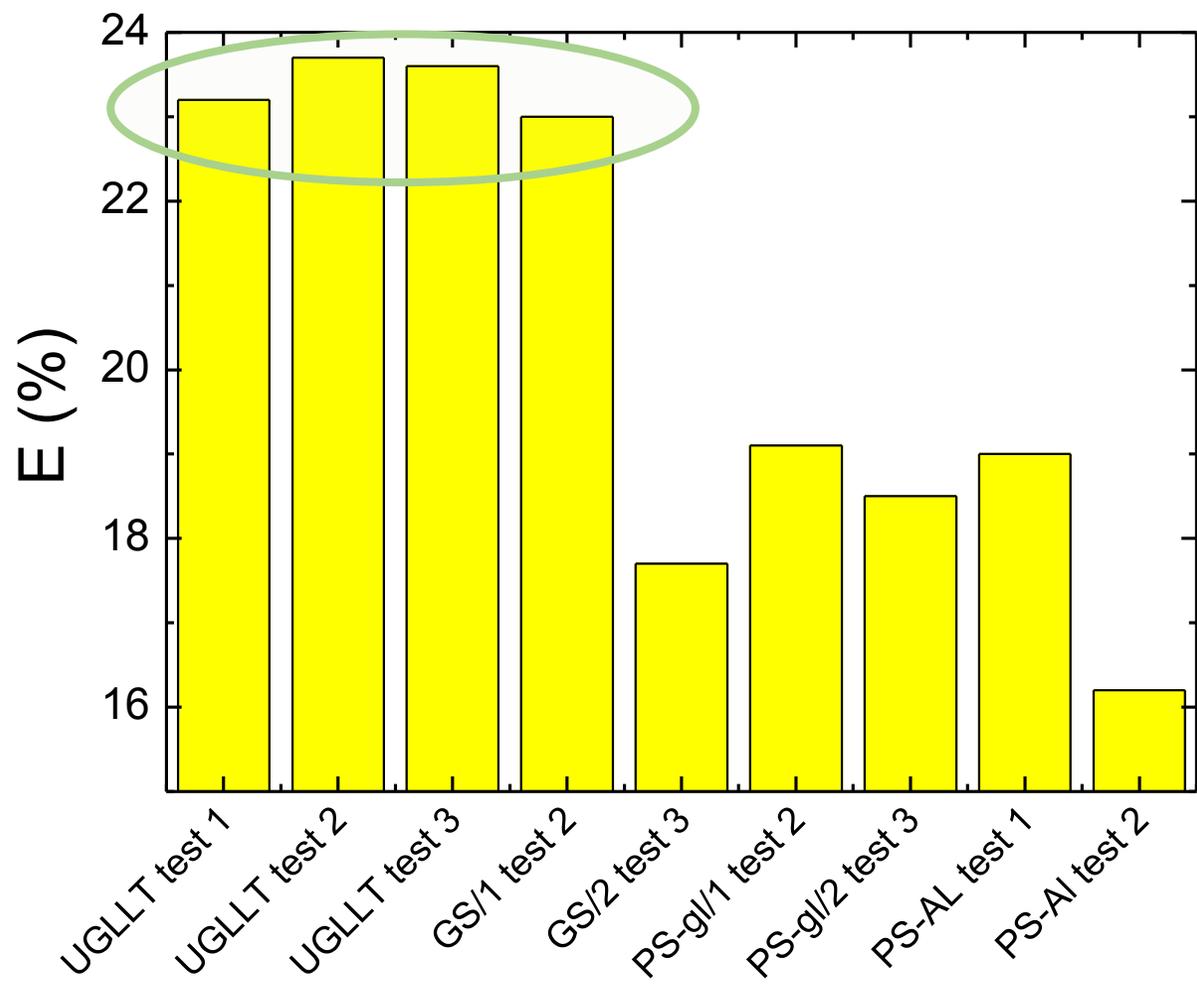
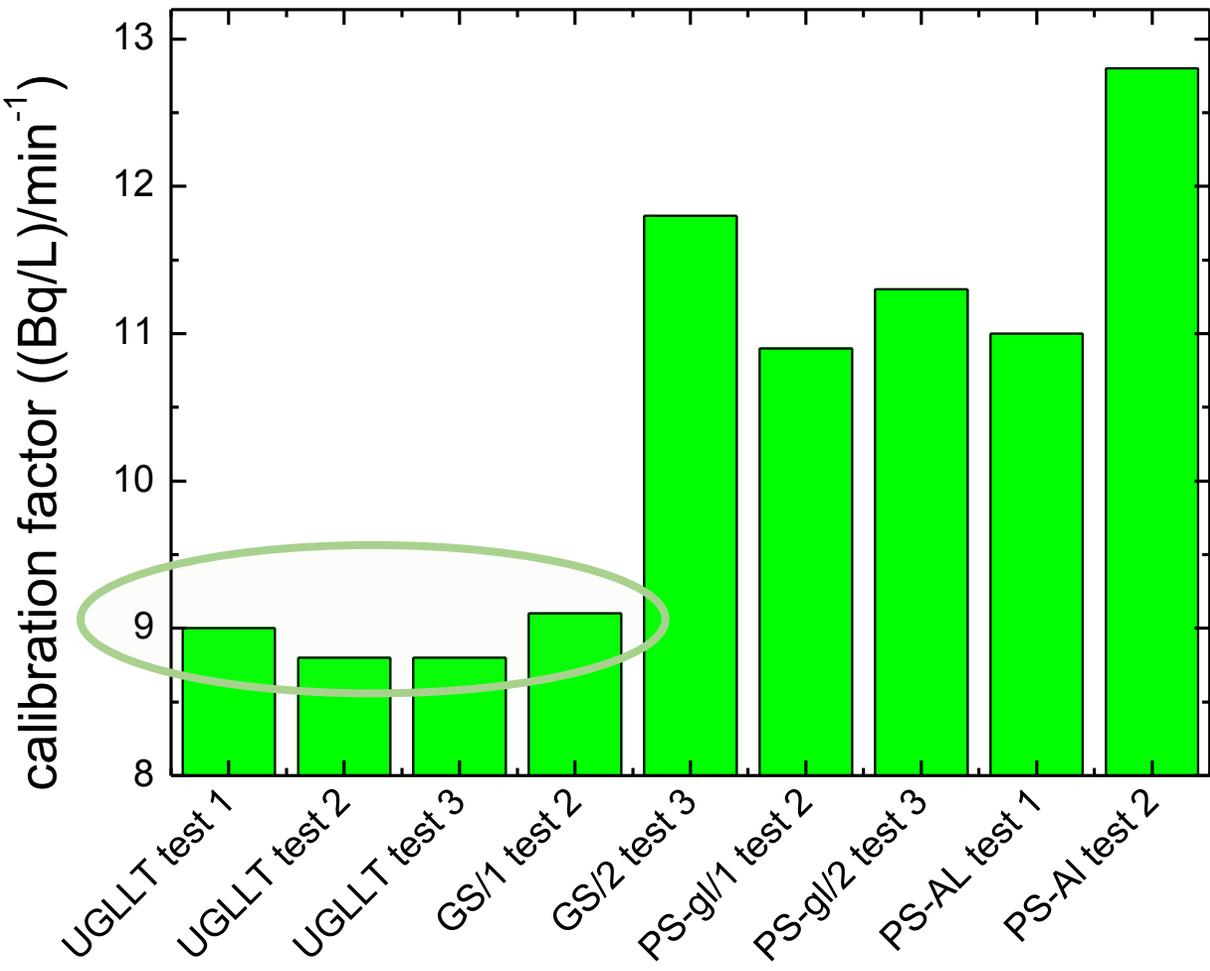
**ProSafe LT+ PS-AI (S14, S15, S16)**

**SQP = 757**

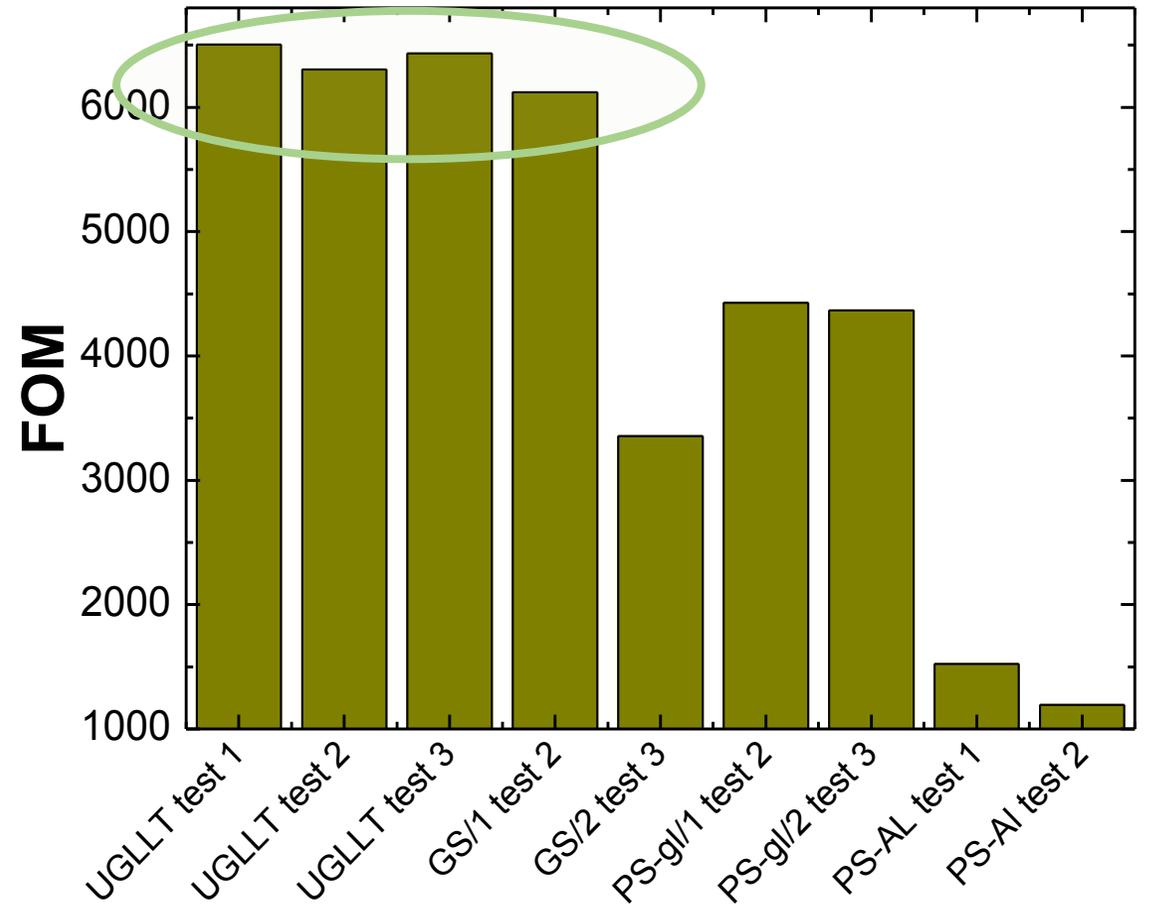
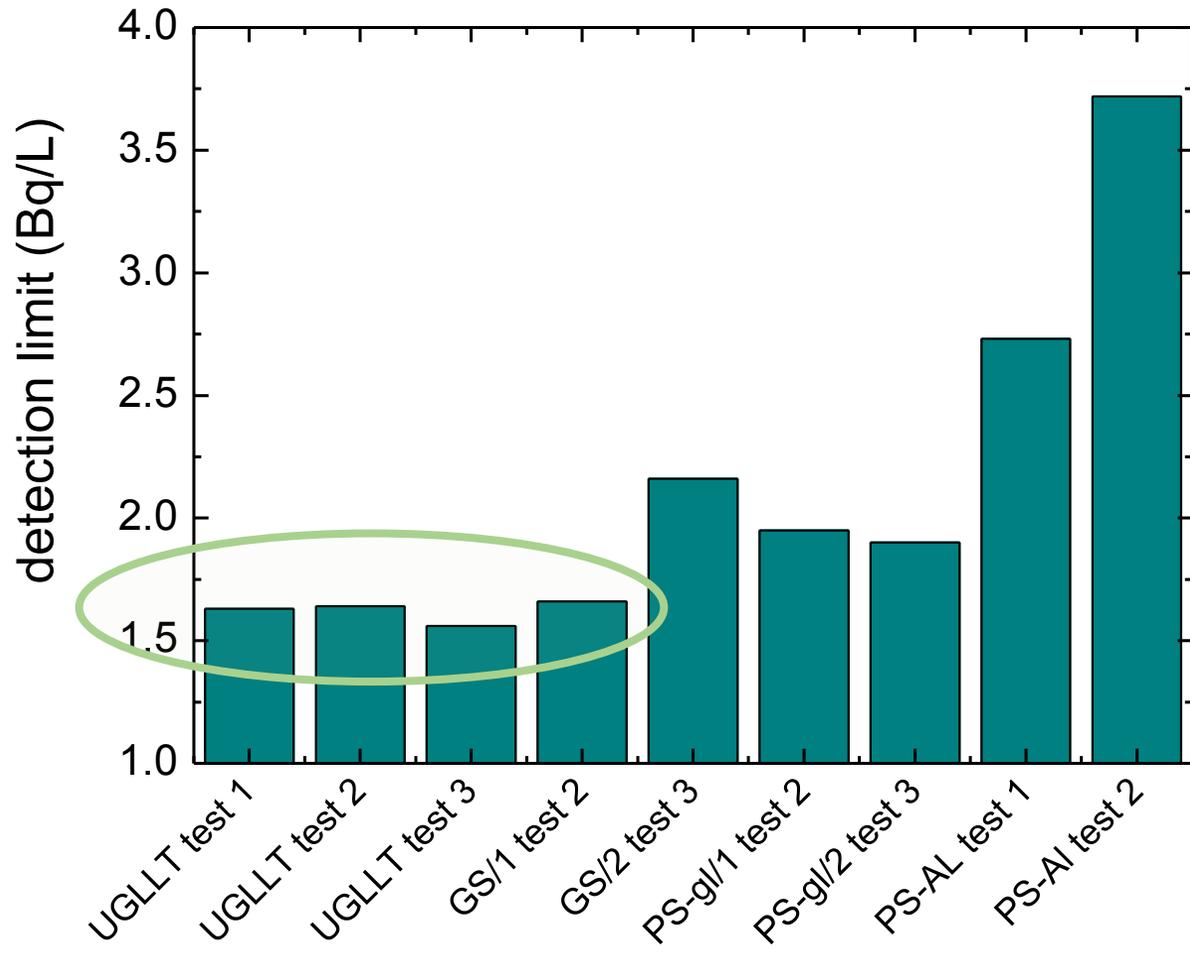


*Tritium spectra* (LSC Quantulus 1220, Easy View software)  
of 3 different  $^3\text{H}$  activity concentrations  
UltimaGold LLT (S24, S25, S26)  
GoldStar LT<sup>2</sup> GS/1 (S42, S43, S44)

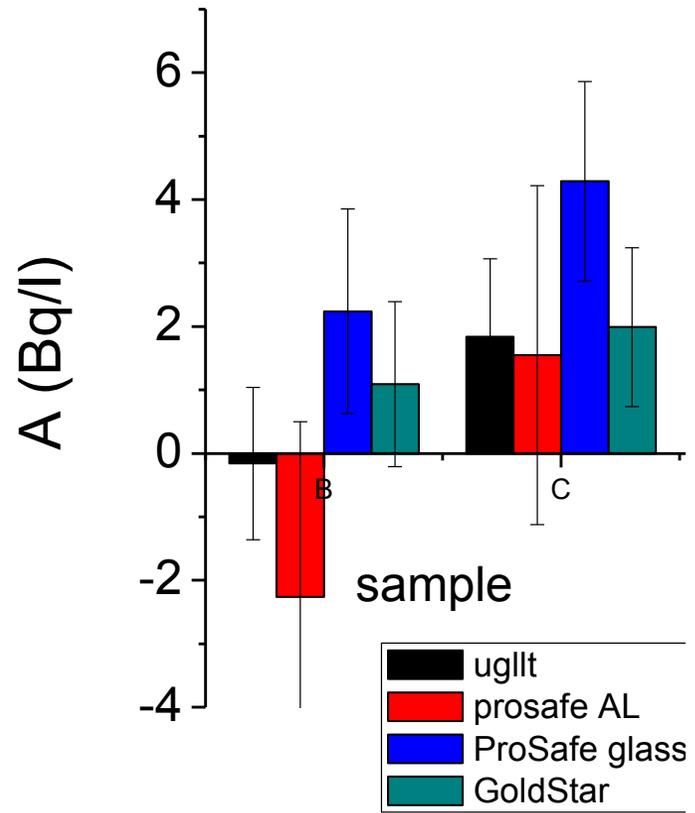
# Calibration factor ( $w$ ) and efficiency



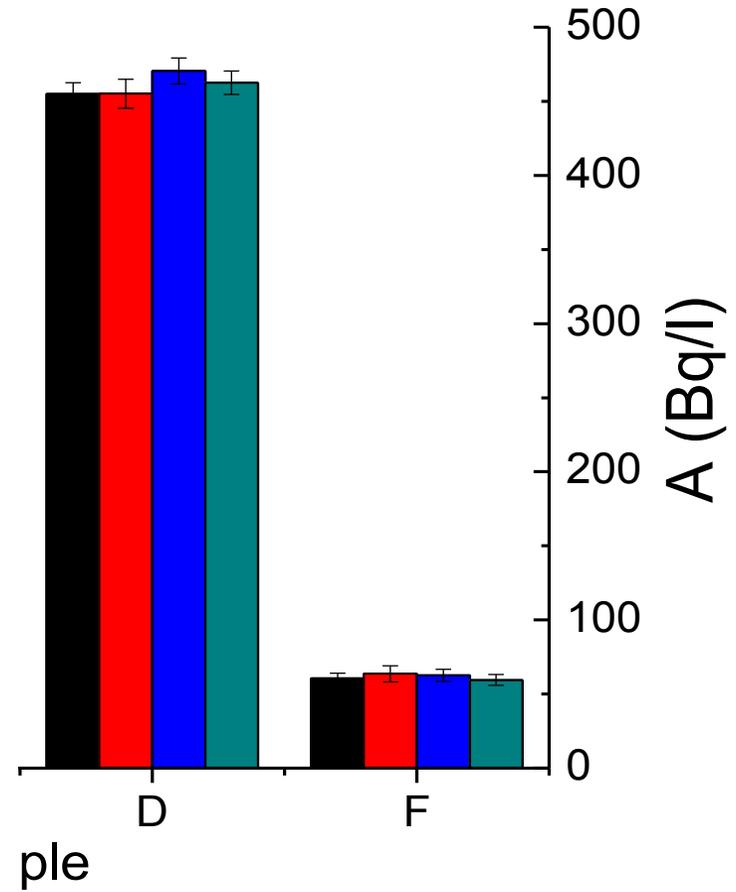
# Detection limit and FOM



## Low-activity samples



## High-activity samples



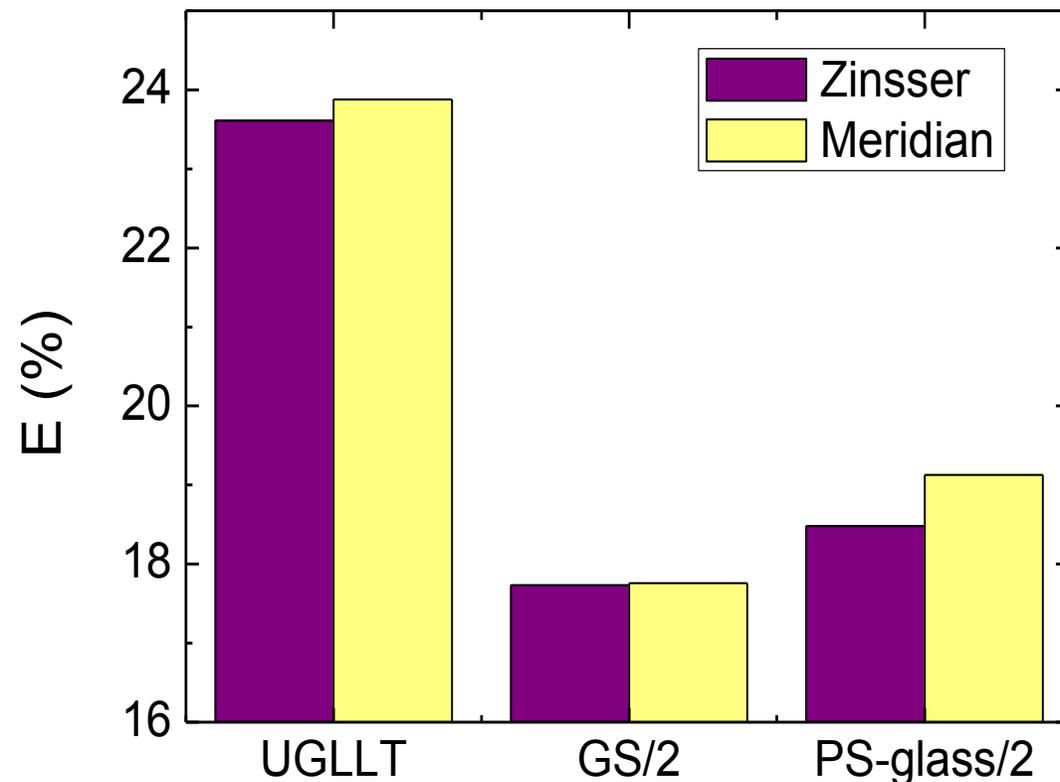
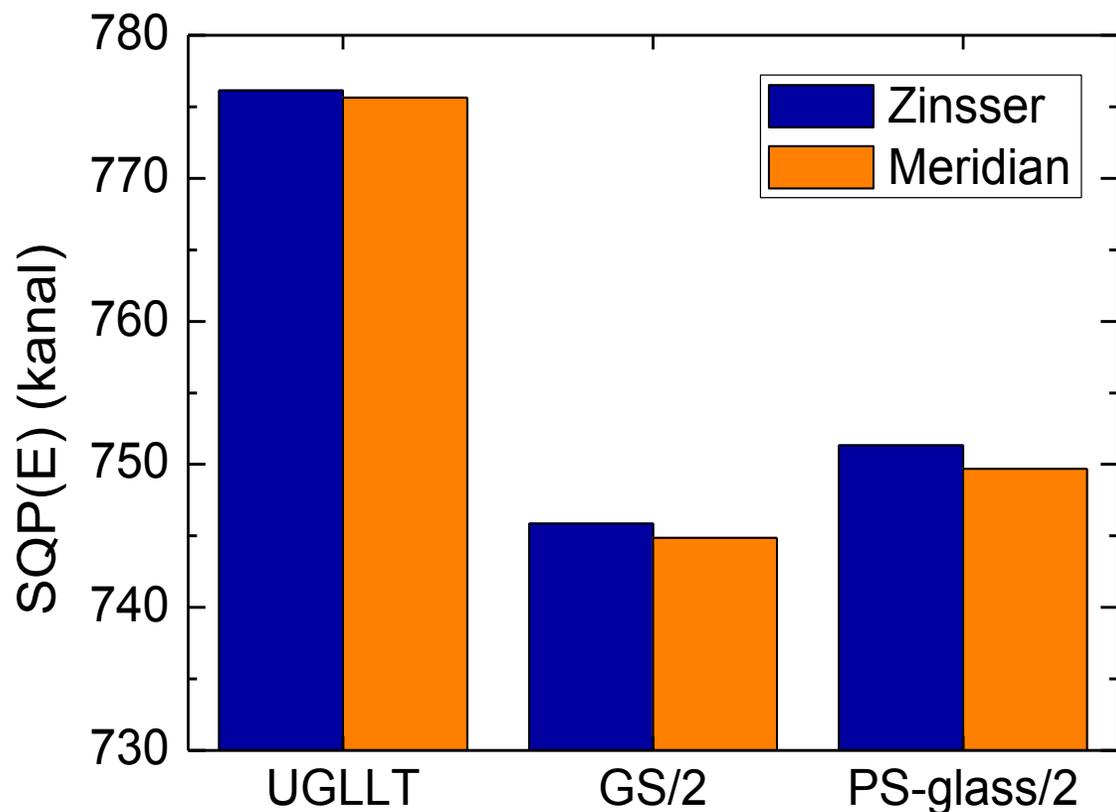
## Summary of the results

- Background count rate is practically the same for UGLLT, GS and PS-glass scintillation cocktails.
- PS-Al cocktail results in higher background count rate (peak at low channels)
- Calibration factor  $w$  is practically the same ( $\approx 9$ ) for UGLLT and GS, as well as for PS-Al test 1 and PS-glass ( $\approx 11$ ).
- SQP(E) values the same for UGLLT and GS ( $\approx 777$ ), and for PS-Al test 1 and PS-glass ( $\approx 757$ ).
- Detection limit is practically the same ( $\approx 1.6$  Bq/L) for UGLLT and GS, followed by PS-glass and finally PS-Al.
- Figure of merit follows the same order: the best values for UGLLT and GS, followed by PS-glass and finally PS-Al.
- Efficiency is  $\approx 23$  % for UGLLT and GS; for PS-Al test 1 and PS-glass  $\approx 19$  %.
- PS-Al showed deterioration of all parameters in test 2 comparing to test 1.
- SQP(E), CF and E values are the same for PS-Al test 1 and PS-glass, but the background count rate is lower for PS-glass, resulting in lower DL and higher FOM values.

## Conclusions – regarding scintillation cocktails

- UGLLT and GS show comparable performance and can be used for relatively low  $^3\text{H}$  activities (for very low  $^3\text{H}$  activities electrolytic enrichment should be performed)
- PS-glass can safely be used for relatively high  $^3\text{H}$  activities.
- PS-Al should not be used because it has different colour, and the storage in Al container causes further deterioration of its performance during longer storage time.

# Vials



3 cocktails (UGLLT, GS/2 i PS-glass/2) in two types of vials (anti-static PV1AS-HDPE **Meridian**, **Zinsser** POLYVIALS® cat.no 3071401).

Best characteristics. UGLLT in both vials, earlier it was shown also for PE vials.

Characteristics do not depend on vial type.

New batch GS/2 worse characteristics than UGLLT and PS-glass/2.

# CONCLUSIONS

- UltimaGold LLT (PerkinElmer) showed best characteristics in all tests.
- UGLLT and GS/1 similar, but GS/2 not so good.
- ProSafe LT+ (Meridian Technologies) also good characteristics
- ProSafe LT+ from Al container – worst characteristics, deterioration with time
- Not observed difference among 3 types of vials – additional issue: cost.
- Activity concentrations of unknown samples (well above DL) comparable, if the appropriate *B* and *CF* are used.

## Acknowledgement

- Zinsser Analytic – for sample vials
- Meridian Biotechnologies for PS and GS cocktails and vials

## IAEA Intercomparison TRIC2008

2 measurements of each sample with two scintillation cocktails

All results accepted as satisfactory

	A [Bq/L]	$\pm u$	A [Bq/L]	$\pm u$	Diff LLT-GS %	z score
	UGLLT		GS			
<b>T32</b>	5.13	1.25	4.27	1.31	16.835	0.689
	6.50	1.34	5.72	1.38	12.083	0.585
<b>T33</b>	16.38	1.75	13.56	1.77	17.234	1.617
	17.10	1.79	17.12	1.89	-0.097	-0.009
<b>T34</b>	59.7	2.7	58.8	2.8	1.5	0.4
	62.8	2.8	62.2	2.8	0.93	0.2
<b>New UGLLT</b>	60.08	1.81				
	60.00	1.81				

## Important notes

- Sample preparation depends on the sample type and the radioisotope to be determined - the preferred method of sample preparation depends primarily on the nature of the sample and the number of samples that need to be processed (and the required precision)
- Choose the appropriate scintillation cocktail
- Choose the appropriate vial
- Choose the proper „Geometry” – ratio sample:scintillation cocktail, total volume/mass,
- Be consistent in the scintillation cocktail and vial type
- Include referent material/standards, background samples

## Applications of tritium

Tritium („bomb peak”) has been widely used for studying time scale of hydrologic processes in the last decades of the 20th century.

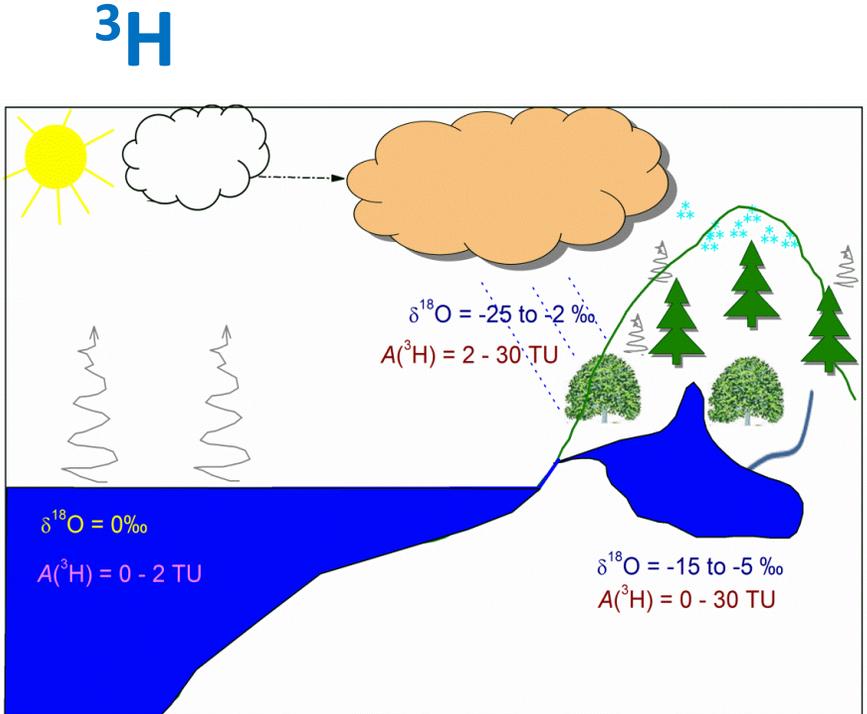
GNIP database (Global Network of Isotopes in Precipitation)

Organized by IAEA and WMO

<https://www.iaea.org/services/networks/gnip>

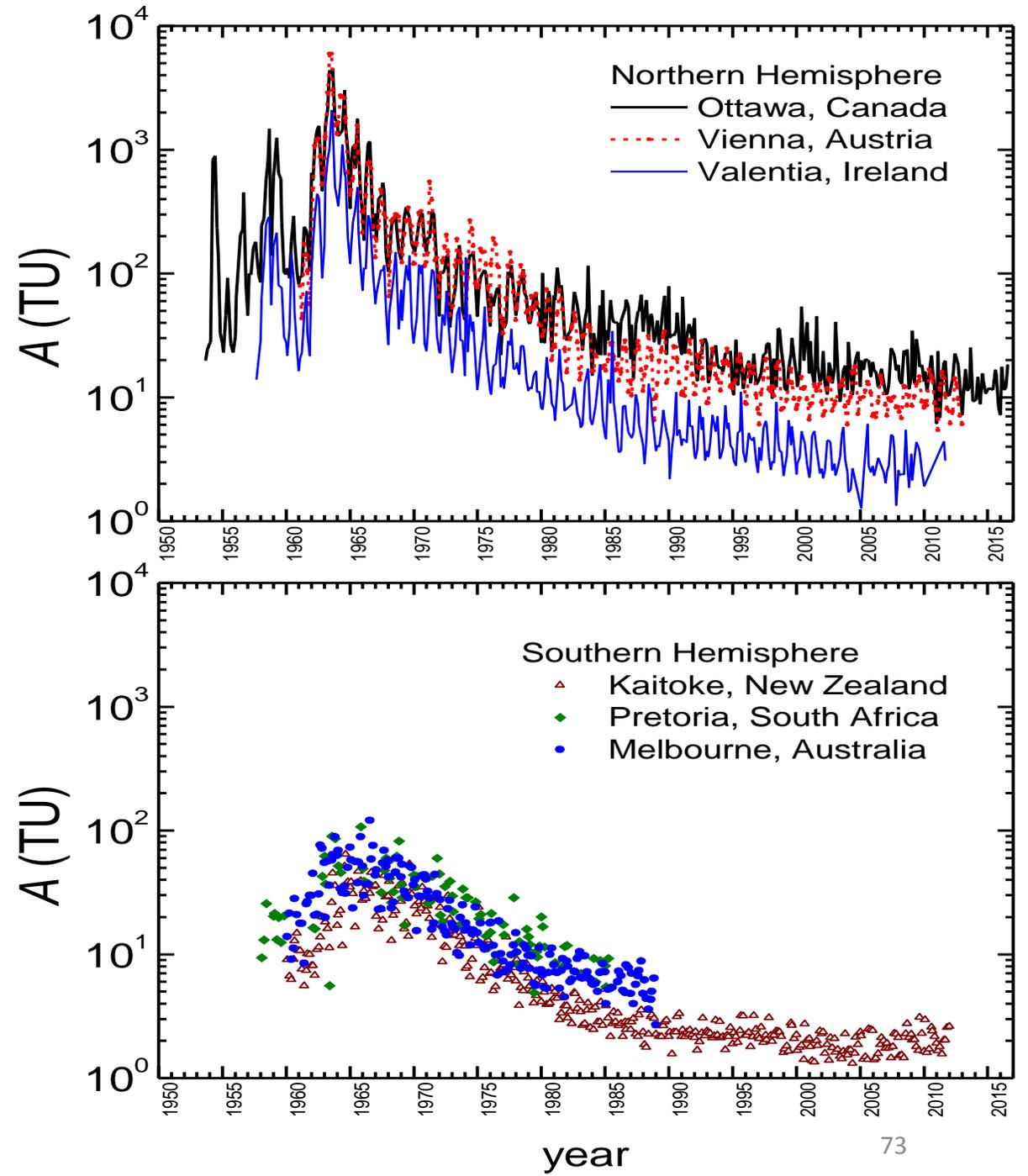
<https://www.iaea.org/resources/network/global-network-of-isotopes-in-precipitation-gnip>

Present scientific value of tritium for hydrological applications has significantly declined.



Schematic simplified representation of the hydrological cycle. Characteristic “isotopic fingerprints,” i.e.,  $\delta^{18}\text{O}$  and tritium activity concentration  $A$ , are shown for sea water, precipitation and surface waters

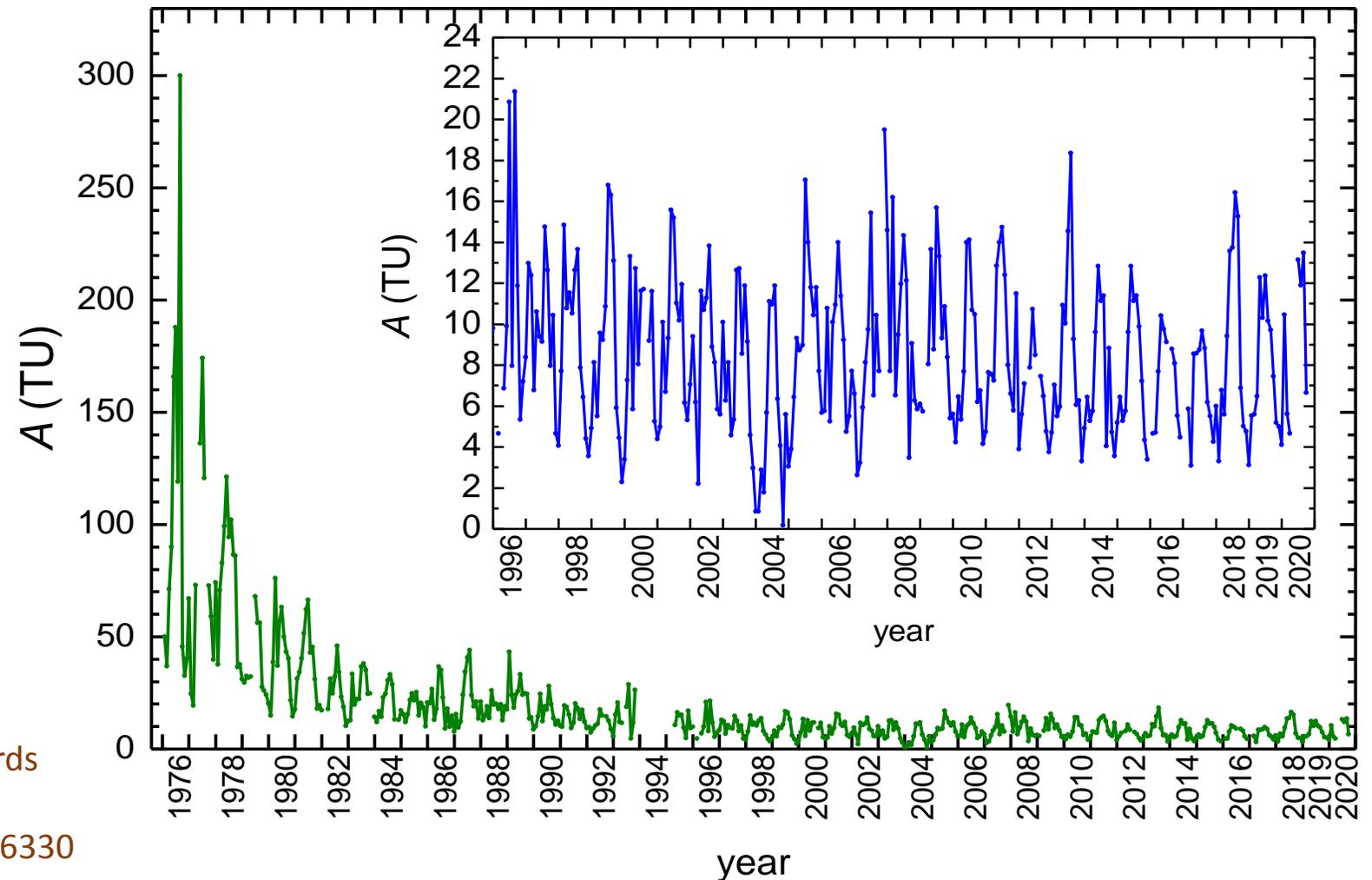
Tritium activity concentration  $A$  in monthly precipitation period 1950 – 2016.

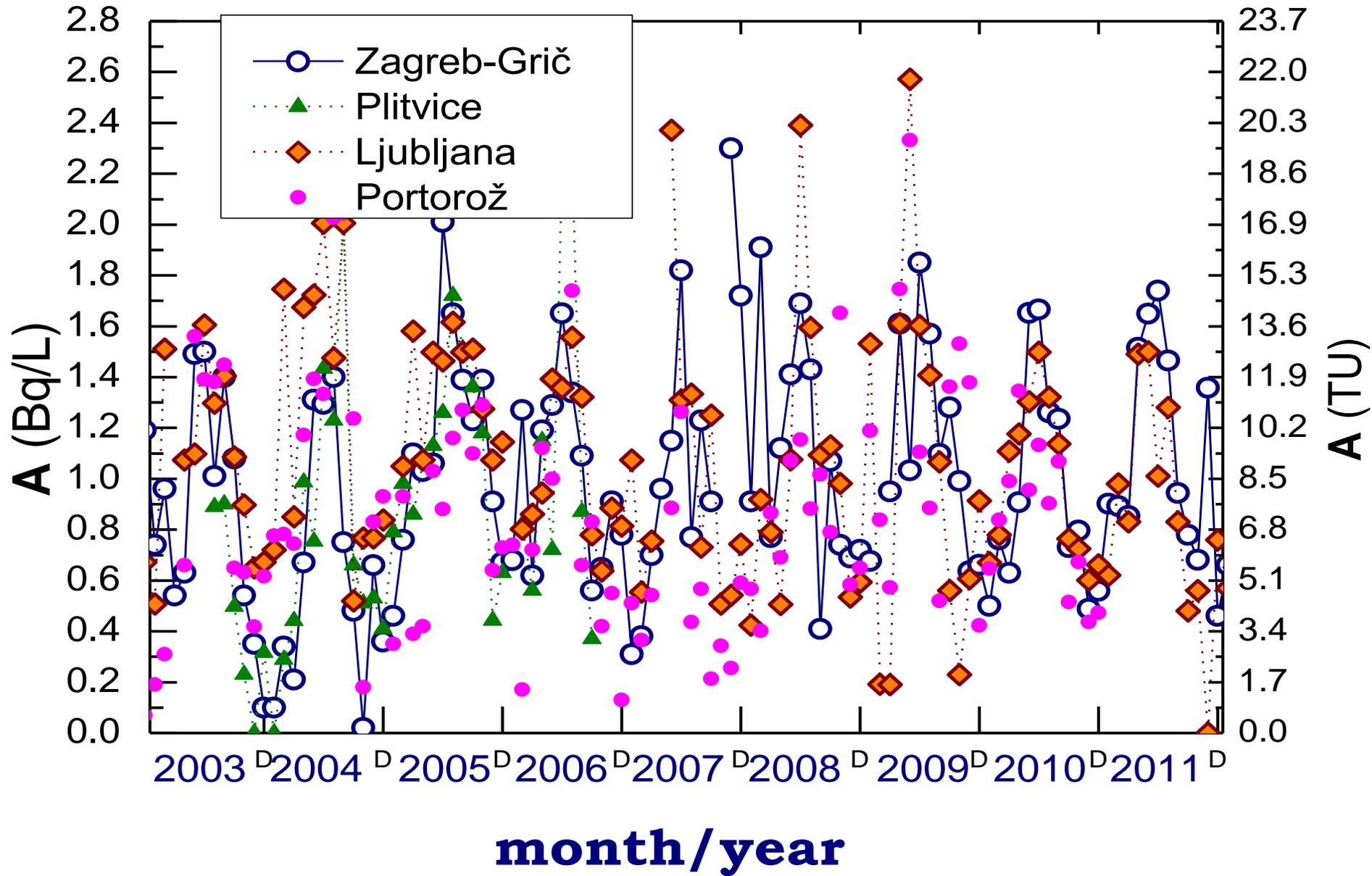


Seasonal variations were superposed on the basic decreasing trend of mean annual values until approximately 1996.

Between 1996 and 2019 no significant decrease has been observed (mean about 8 TU).

Seasonal variations remained observable, with winter activities close to the natural pre-bomb  $^3\text{H}$  activity concentrations.





Various continental stations in Croatia and Slovenia

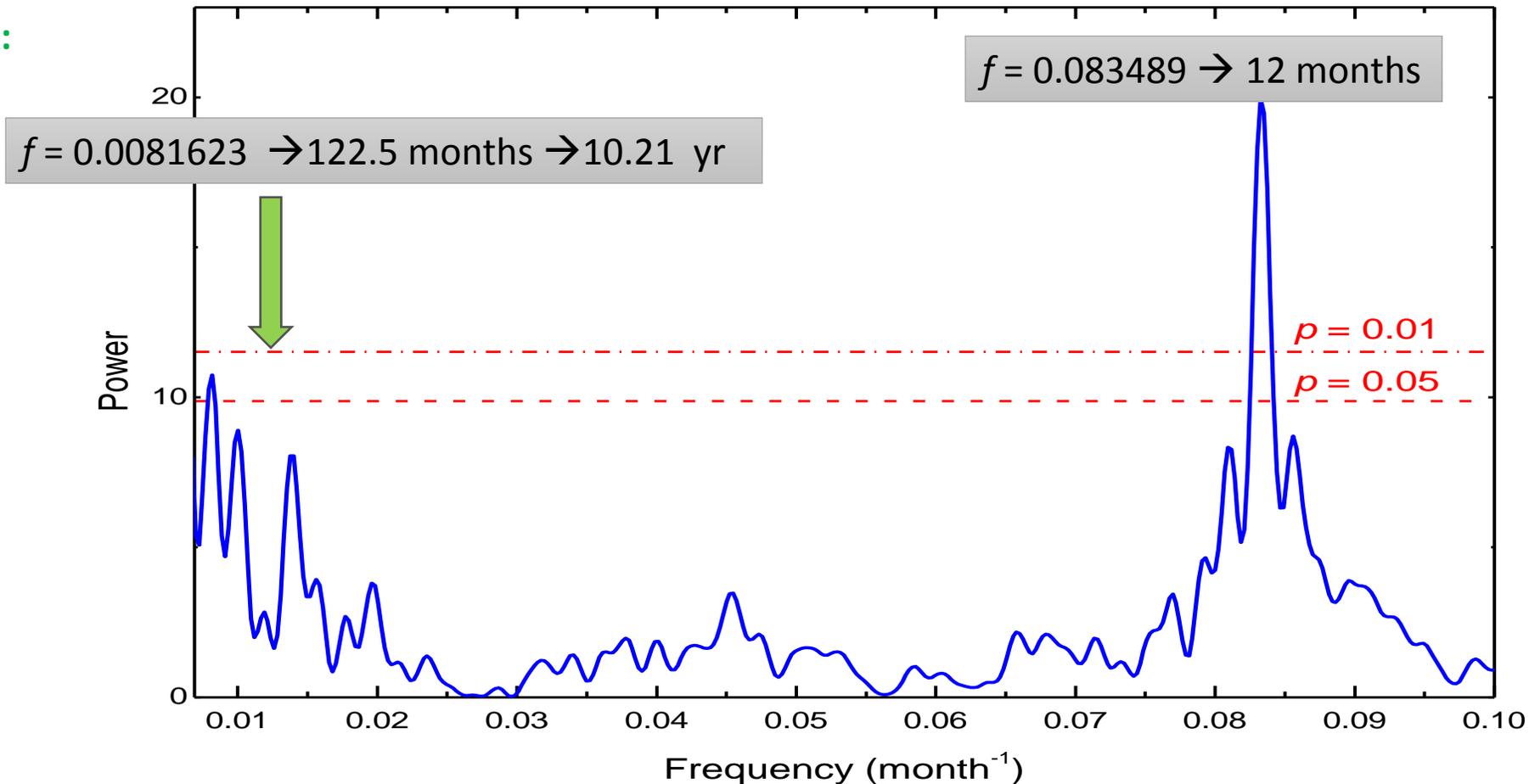
## RESULTS

Our long-term data were evaluated by applying frequency analysis (FA), wavelet analysis, and sinusoidal curve fitting.

Strong evidence of the correlation of tritium variation in precipitation with the 11-year solar cycle and so neutron flux is obtained.

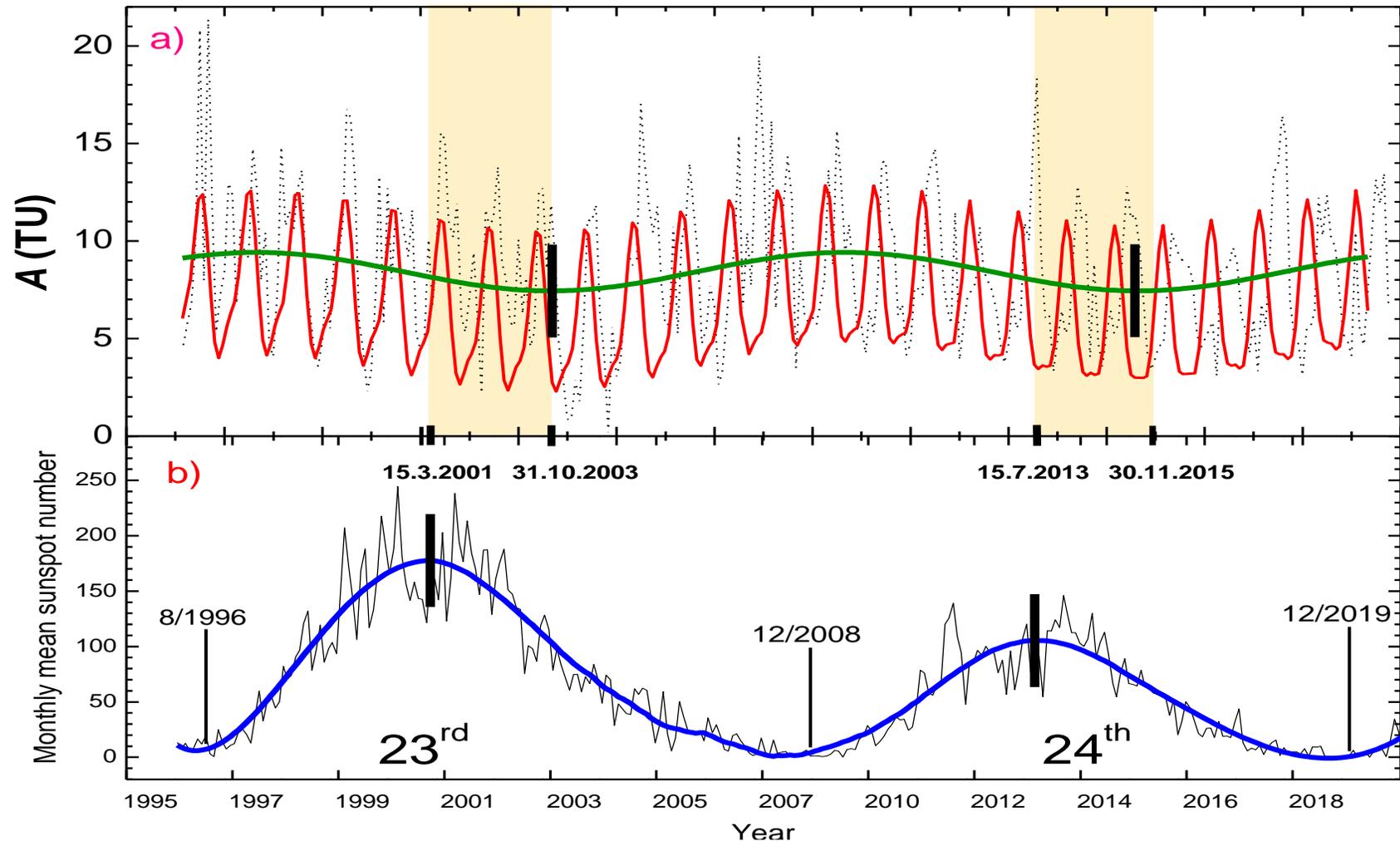
These findings support evidence of solar influence on meteoric tritium.

FA:



D. Borković, I. Krajcar  
Bronić, Solar activity cycles  
recorded in long-term  
data on tritium activity  
concentration in  
precipitation at Zagreb,  
Croatia.  
*Radiat. Phys. Chem.* 188  
(2021) 109646

## Comparison with the monthly number of Sun spots



The 23rd cycle lasted for 12 years and 4 months, and the 24th cycle for exactly 11 years  
Maxima in the sunspot number (minima in neutron flux) in March 2001 and July 2013

Minima in the tritium activity concentration observed in Oct. 2003 and Nov. 2005  
a delay of 31 months and 28 months

- We compared the maxima in the smoothed monthly sunspot number in the 23rd and 24th solar cycles and the minima in tritium activity concentration in precipitation
- A delay of about 30 months (31 and 28) between them was observed
- Plausible explanation – the residence time of cosmogenic tritium in the stratosphere before entering the troposphere
- Further observations may help in studying of exchange between the stratosphere and the troposphere and in determining the residence time of cosmogenic tritium in the stratosphere
- Continuation of the regular monitoring of tritium in environment recommended
- Local effects (technogenic  $^3\text{H}$ ) should be minimized or absent for this kind of studies
- Monitoring of  $^3\text{H}$  in environment important also for applied environmental protection – local technogenic sources, nuclear facilities, future fusion facilities

## OBT – Organically Bound Tritium

Organisms can contain tritium in the tissue water (TFWT—tissue free water tritium) and tritium bound in various organic compounds (OBT—organically bound tritium).

A part of OBT in the plant system, that does not exchange with the surrounding hydrogen atoms and has a long residence time, is referred to as non-exchangeable OBT, NE-OBT.

The NE-OBT is bound to carbon atoms through covalent bonds and is held firmly with the organic structure until the compound breaks down or is destroyed by combustion.

The exchangeable OBT, referred to as E-OBT, is bound to atoms other than carbon, i.e. nitrogen, sulphur and oxygen and is in equilibrium with HTO in the plant water.

The ratio between E-OBT and NE-OBT fractions may be different in different parts of the same biological sample or in different plants/animals from the same location.

Both E-OBT and NE-OBT are commonly studied and discussed together as OBT. This definition was used also in the OBT international intercomparison exercises.

# Importance of OBT

OBT has a longer biological half-life (than TFWT) of few weeks and is therefore of interest for radiological protection

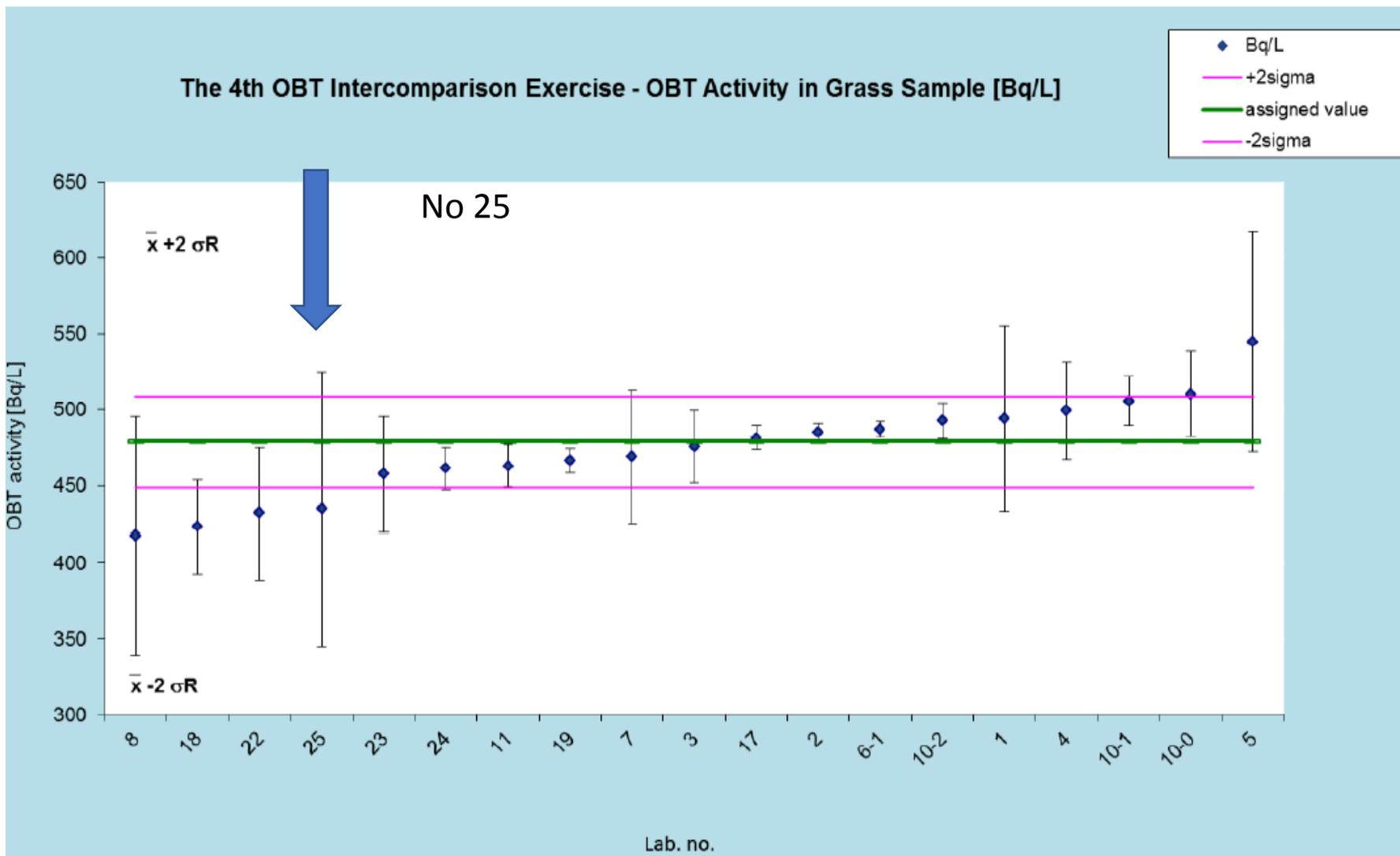
Measurements of the OBT activity are not considered mandatory under the routine environmental monitoring programmes around the NPPs in a majority of the countries.

The exceptions are countries such as Canada, France, Romania, where CANDU reactor types are used and OBT measurements are included in environmental monitoring programs.

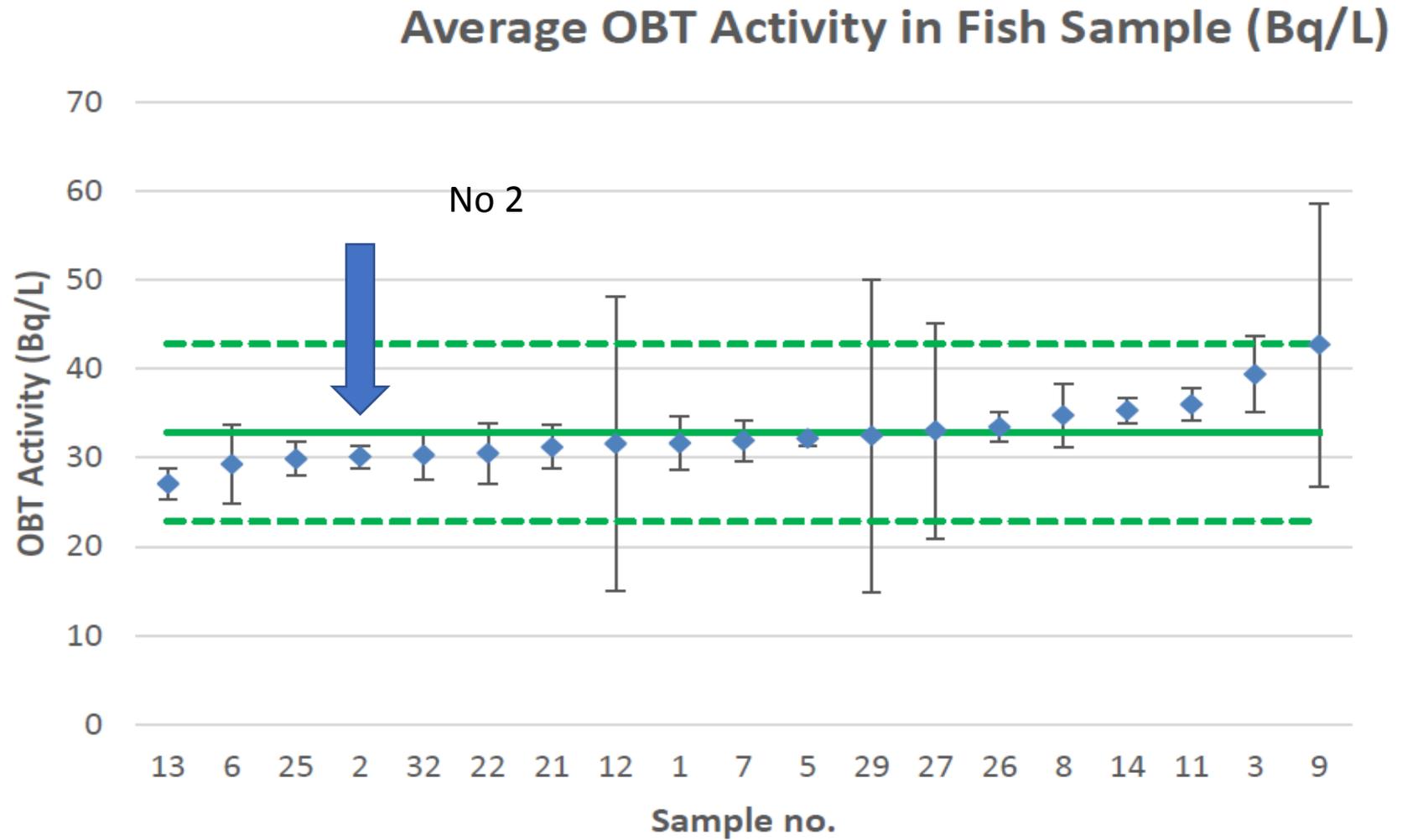
For a comparison of the OBT activity in the vicinity of NPP with a clean region and for determination of the Contribution of OBT to the total effective dose, a control site with minimal or no anthropogenic source of tritium should be identified.

A problem related to OBT determination is the fact that certified reference materials of environmental OBT samples are not available for the validation of the analytical methods.

# 4th OBT exercises



## 5th OBT exercises

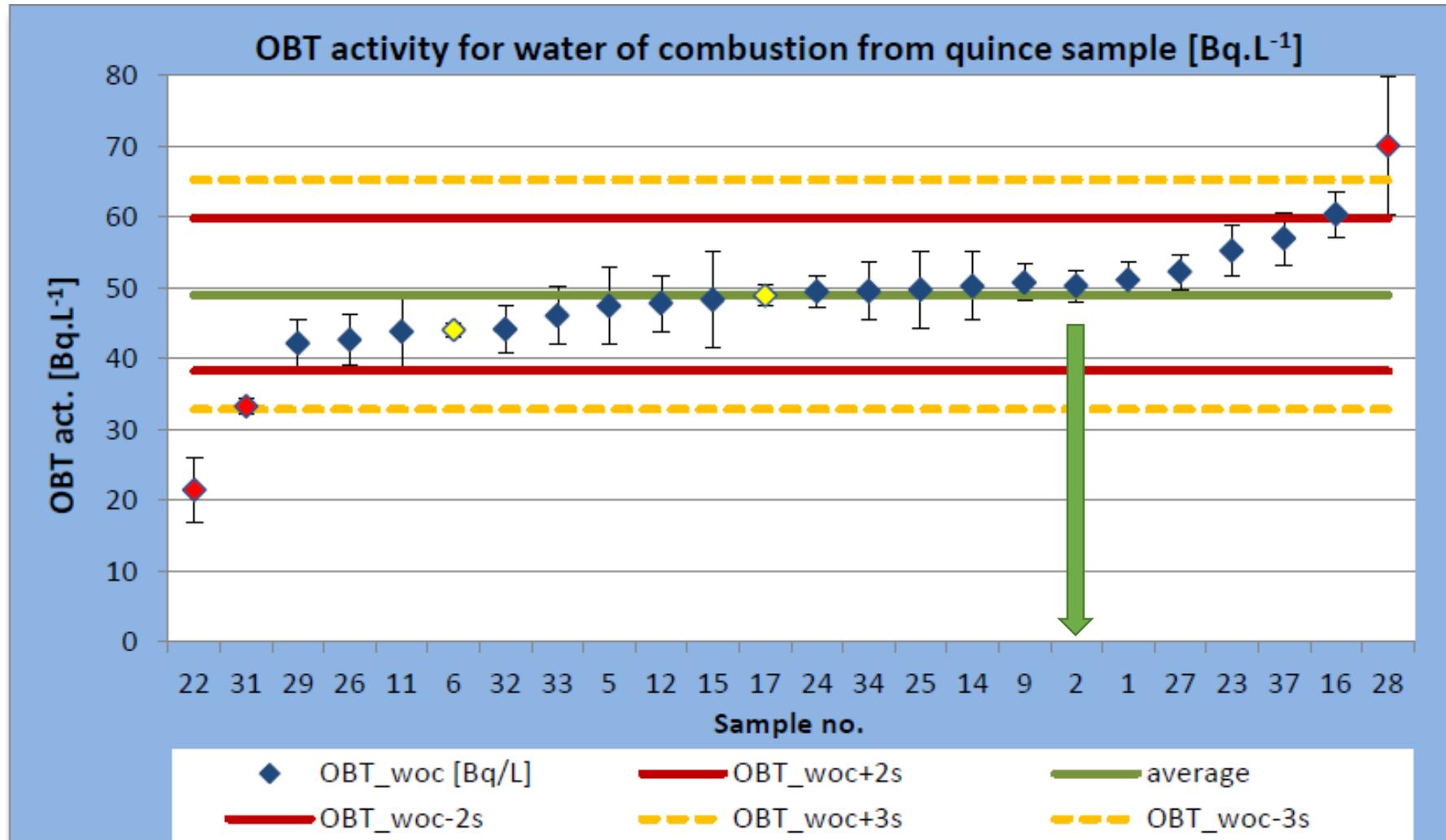


## 6th OBT exercises - quince



Figure 2. Combustion systems for sample preparation.

## 6th OBT exercises - quince



## Literature

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- L'Annunziata. M.F. 2012. *Handbook of Radioactivity Analysis*. Volume I: NUCLEAR RADIATION, ITS INTERACTION WITH MATTER AND RADIOISOTOPE DECAY. Academic Press, 3<sup>rd</sup> edition
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- Rozanski K., Gröning M. 2004. "Tritium assay in water samples using electrolytic enrichment and liquid scintillation spectrometry." In: *Quantifying uncertainty in nuclear analytical measurements*, IAEA-TECDOC-1401; 2004. p. 195-217.

Methodology of Tritium Determination in Aqueous Samples by Liquid Scintillation Counting Techniques , I. Stojković, N. Todorović, J. Nikolov, I. Krajcar Bronić, J. Barešić , U. Kozmidis Luburić, In *TRITIUM - ADVANCES IN RESEARCH AND APPLICATIONS*, ISBN: 971-1-53613-507-7 (e-Book), Nova Science Publisher 2018