

Screening LSC method for monitoring ^{14}C activity in water samples

Todorović Nataša¹, Nikolov Jovana¹, Stojković Ivana², Krajcar Bronić Ines³

¹ University of Novi Sad, Faculty of Sciences, Department of Physics, Trg D. Obradovica 3, 21000 Novi Sad, Serbia

² University of Novi Sad, Faculty of Technical Sciences, Trg Dositeja Obradovica 6, 21000 Novi Sad, Serbia

³ Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia

INTRODUCTION

Radiocarbon is naturally occurring radioisotope, often found in radioactive waste, since it is being continuously generated in nuclear reactor operations, spent fuel reprocessing and radioisotope production. Environmental studies and monitoring program for radiocarbon (^{14}C) in the vicinity of nuclear facilities are important since its relatively long half-life (5730 y), high potential for mobility in geological systems and presence in food chains.

Precise determination of ^{14}C content in waters demands time-consuming chemical procedures and expensive analytical equipment since its natural levels are very low. The necessity to detect elevated ^{14}C levels in water in case of nuclear emergency has triggered an investigation of a possibility to quantify ^{14}C content without any chemical preparation of samples.

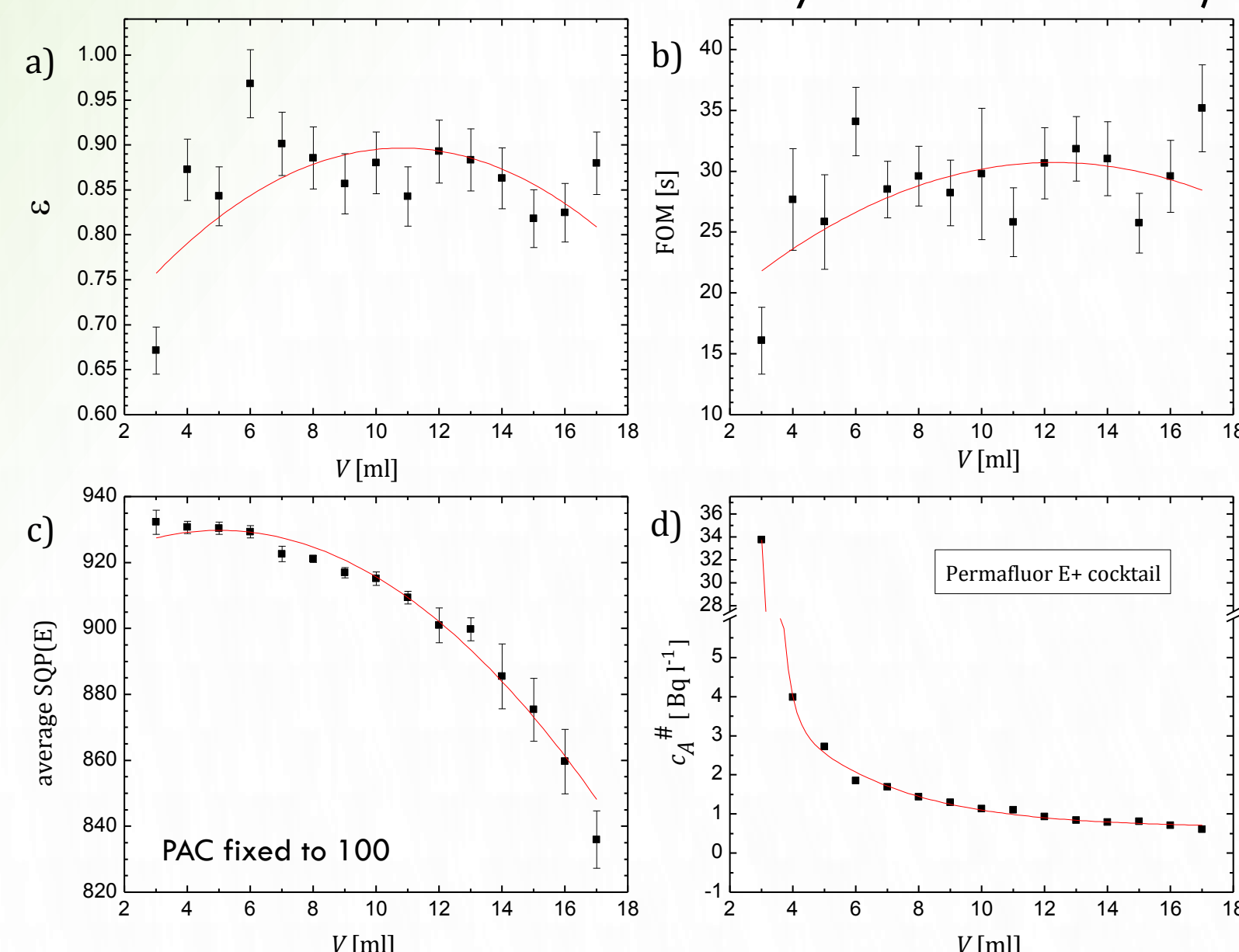
We present a development of a direct method for the effective, simple, inexpensive and rapid estimation of ^{14}C level in waters via Liquid Scintillation Counting (LSC) technique, defining its possibilities and limitations.

CALIBRATION PROCEDURE

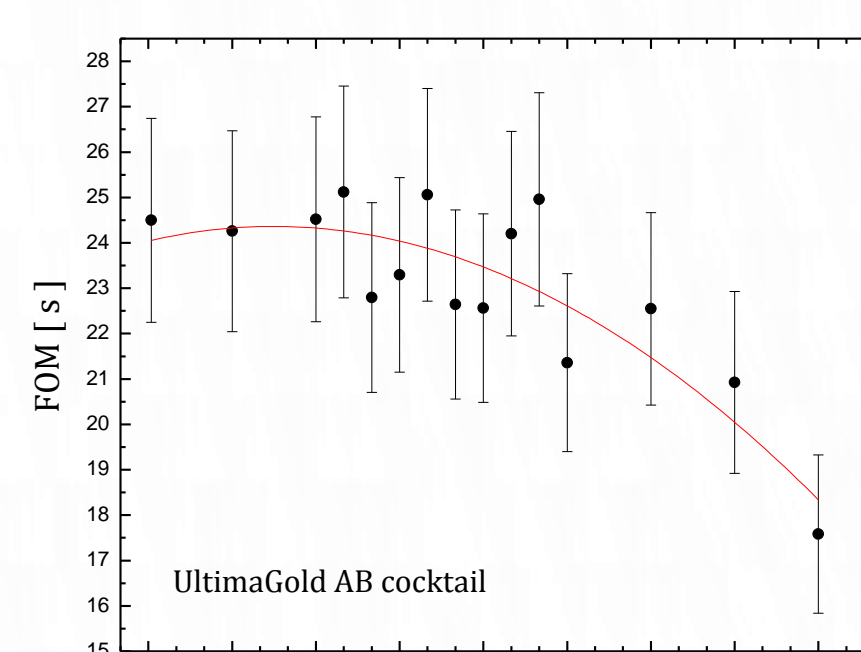
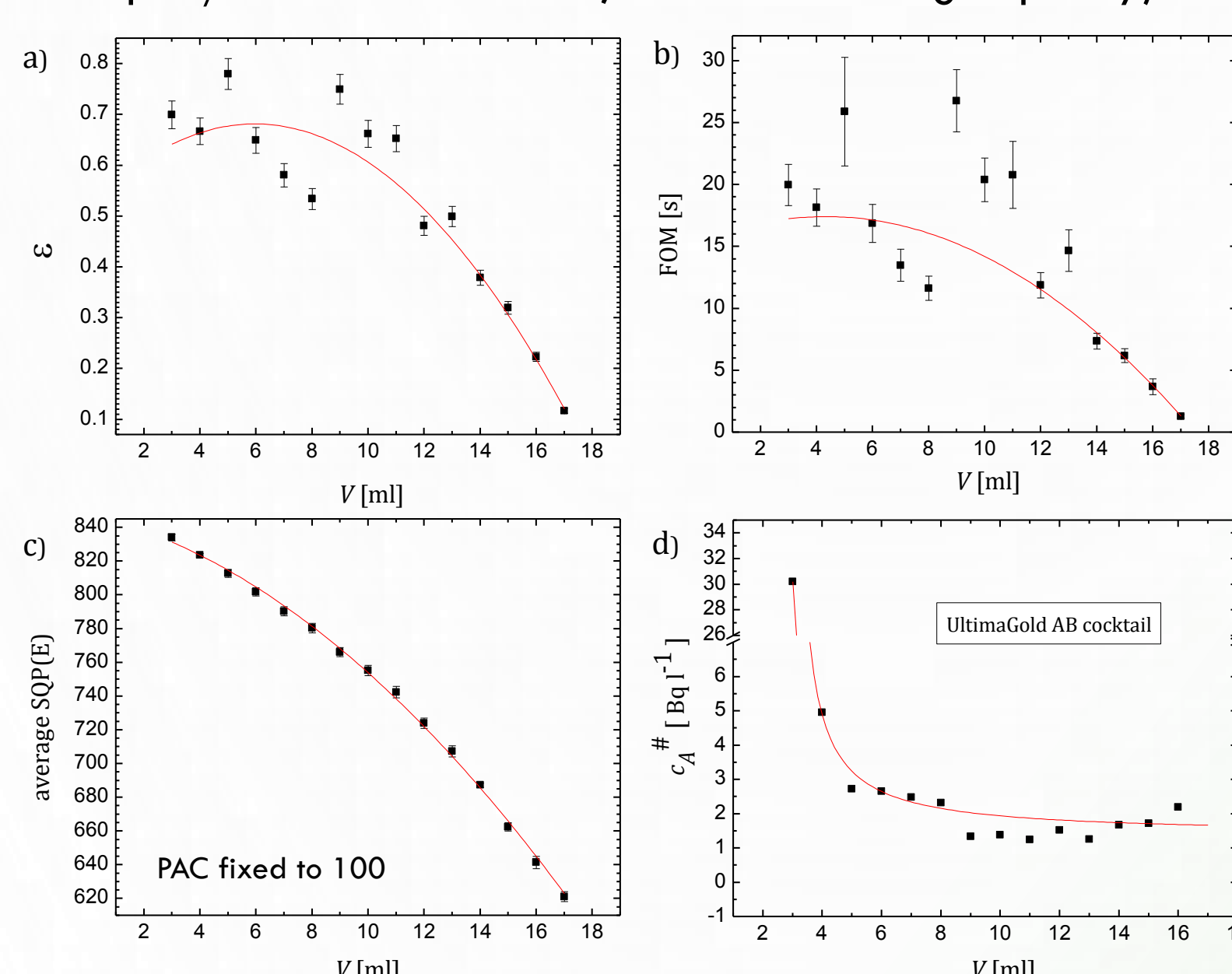
Method's optimization (sample:cocktail ratio, PAC adjustment) was carried out to

obtain maximal Figure of Merit, $\text{FOM} [\text{s}] = \frac{\varepsilon^2}{r_0 [\text{s}^{-1}]}$ value

PermaFluor E+ cocktail (based on pseudocumene, widely used in conventional radiocarbon techniques, available in laboratories that already measure ^{14}C levels)



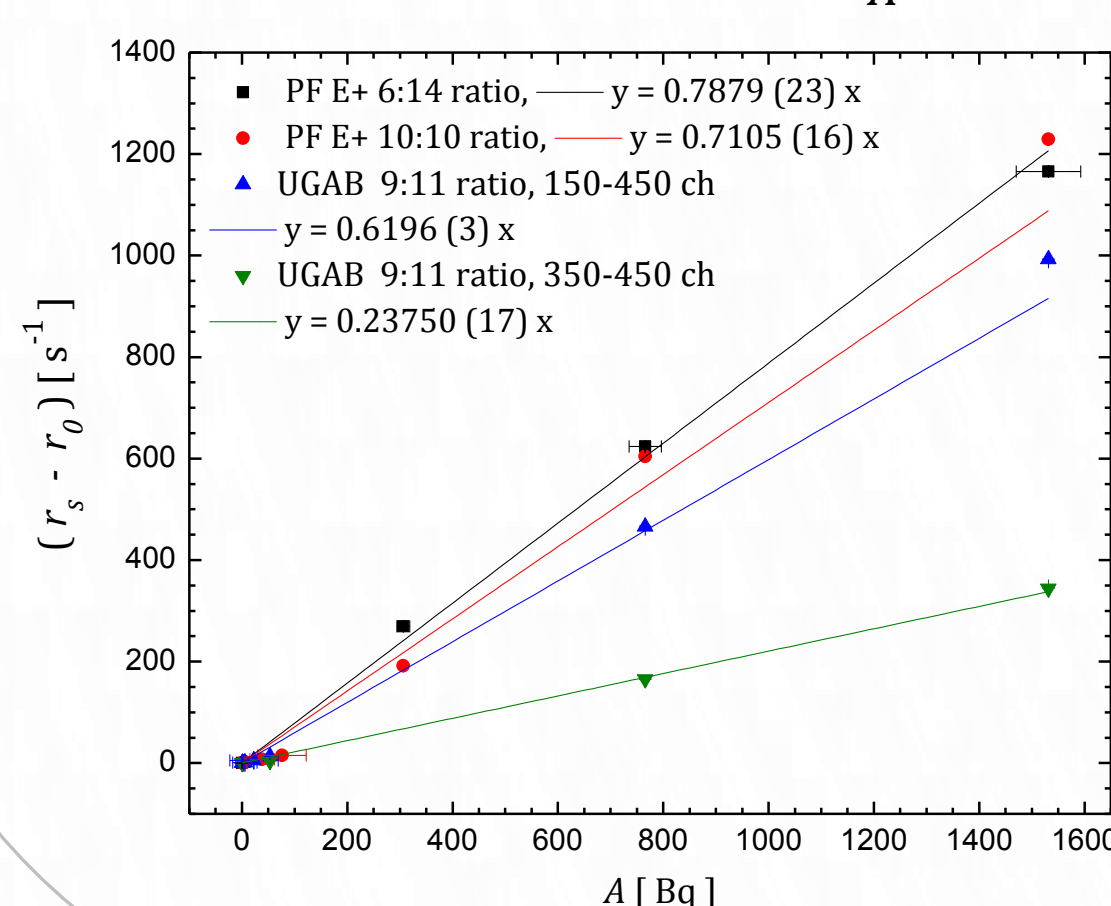
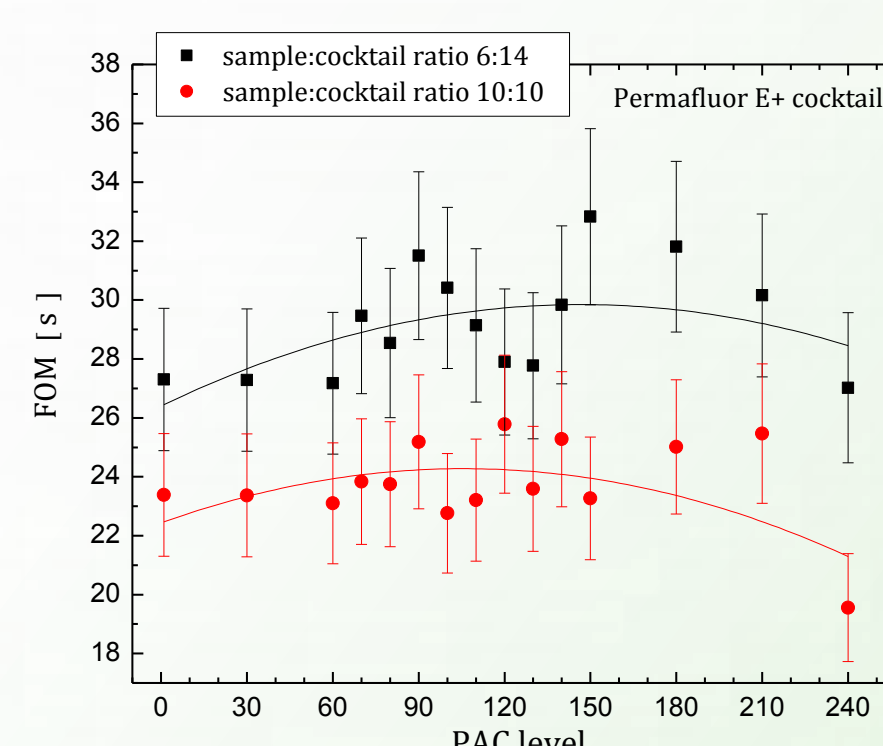
Ultima Gold AB cocktail (general purpose, effective alpha/beta discrimination, excellent holding capacity)



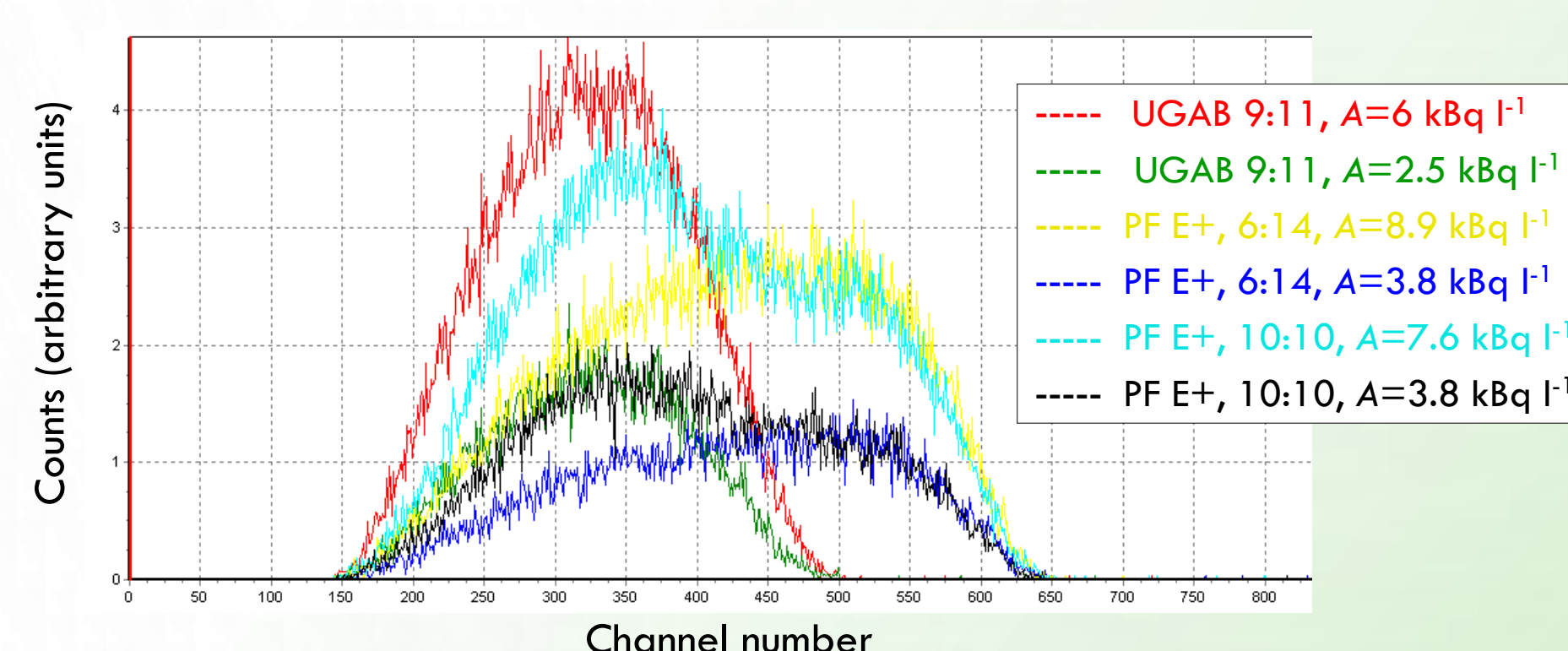
PF E+ optimal ratio 6:14 since maximal FOM/ε and low quench level; optimal $\text{PAC}=150$, $c_A^{\#} = 1.05 \text{ Bq l}^{-1}$ for $t_0 = 300 \text{ min}$, $\varepsilon=(78.79 \pm 0.23)\%$

PF E+ other tested optimal ratio 10:10 since more conservative, simpler in laboratory practice, close to the plateau of FOM/ε fitting curves so small changes/errors in volumes during sample preparation would not significantly influence the measured results; optimal $\text{PAC}=120$, $c_A^{\#} = 0.68 \text{ Bq l}^{-1}$ for $t_0 = 300 \text{ min}$, $\varepsilon=(71.05 \pm 0.16)\%$

UG AB optimal ratio 9:11 since lower detection limit, high FOM/ε and moderate quench level; optimal $\text{PAC}=70$, $c_A^{\#} = 0.88 \text{ Bq l}^{-1}$ for $t_0 = 300 \text{ min}$, $\varepsilon=(61.96 \pm 0.03)\%$



Detection efficiency determination



Obtained spectra of ^{14}C standard spiked in distilled water mixed with two different scintillation cocktails in different sample: cocktail ratios

LSC METHOD

ISO 13162:2011(E) [1] assumes direct mixing of a scintillation cocktail and water sample the 20 ml polyethylene/glass vial.

$$\varepsilon = \frac{r_s - r_0}{A}$$

ε - the detection efficiency, A [Bq] - the activity of the calibration source

$r_g / r_0 / r_s [\text{s}^{-1}]$ - sample/background/calibration standard count-rates

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

c_A [Bq l⁻¹] - sample activity concentration, V [l] - sample volume analysed

f_q - quench factor (=1 for the unquenched sample)

$$c_A^* = k w \sqrt{\frac{r_0}{t_g} + \frac{r_0}{t_0}}, \quad c_A^{\#} = \frac{2 c_A^* + (k^2 w)/t_g}{1 - k^2 u_{rel}^2(w)}$$

c_A^* [Bq l⁻¹] - the decision threshold, $c_A^{\#}$ [Bq l⁻¹] - the detection limit

$k = 1.65$, $u_{rel}(w)$ - relative uncertainty of w

$t_g [\text{s}] / t_0 [\text{s}]$ - the sample/background counting times

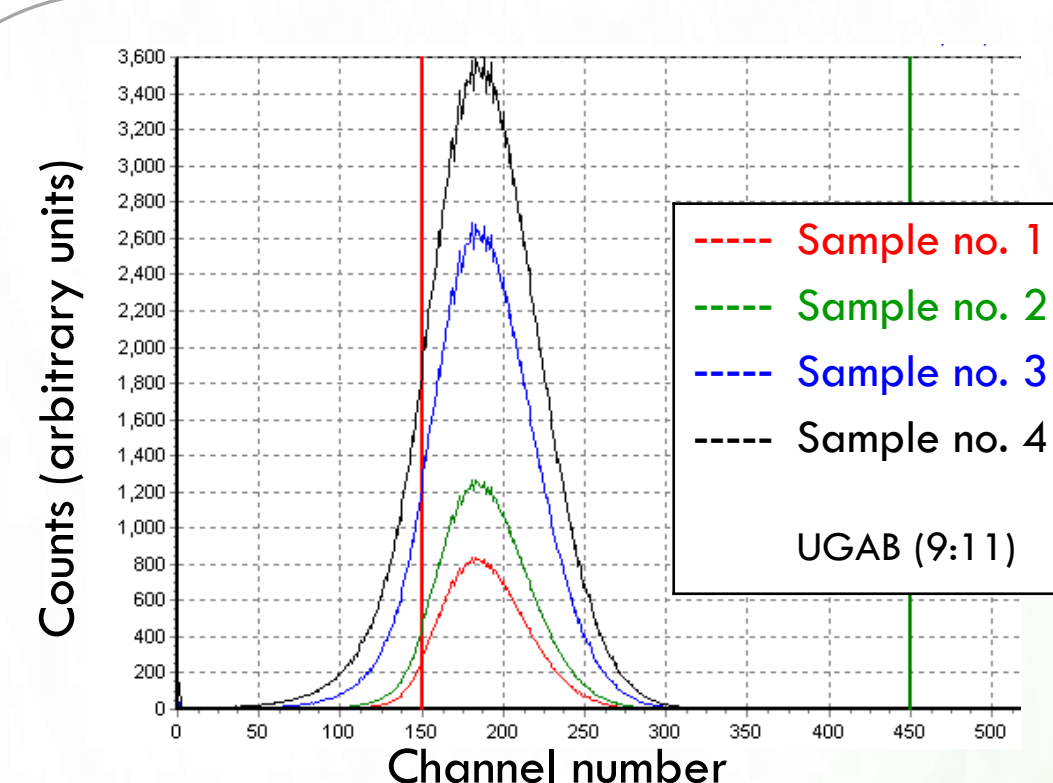
EQUIPMENT AND MATERIALS

- Ultra Low Level Liquid Scintillation Spectrometer Wallac 1220™ Quantulus:
- a) Two PMT's are used for background event detection and two separate ones for coincident sample counting. The sample detector operates in anticoincidence with the guard detector
- b) PAC (Pulse Amplitude Comparator) circuit decreases the background component produced by the optical crosstalk
- c) Quench level was monitored via quench indicating parameter SQP(E), Spectral Quench Parameter of the External Standard. Samples with higher quench level have lower SQP(E) values
- d) The spectra were acquired by WinQ and analyzed by EasyView software
- Polyethylene vials – chosen for experiments since they are less expensive than the glass ones and induce lower background

CONCLUSIONS

- ✓ The idea to directly mix water with a scintillation cocktail without any chemical pre-treatment in order to detect ^{14}C content in a sample can be a reliable screening tool: it is a fast, simple and inexpensive method adequate for (very) high ^{14}C concentration measurements
- ✓ Presented method is ideal for ^{14}C monitoring purposes in case of a nuclear emergency when large number of samples should be screened as quickly as possible
- ✓ Even in the ^3H presence where ^3H spectrum overlaps with ^{14}C , this method can detect ^{14}C high activity (not precisely) if only high energy part of spectra is considered
- ✓ PAC value is not critical, has insignificant effect on FOM values
- ✓ Permafluor E+, although immiscible with water, still provides reliable and stable detection efficiency and can be used in this manner, but Ultima Gold AB is better choice since samples are homogeneous
- ✓ Plastic vials with Permafluor E+ should be stored safely after counting since wall diffusion of a cocktail. More suitable combination is Permafluor E+ with glass vials

METHOD'S LIMITATION – ^3H INTERFERENCE



Overlapping of ^3H and ^{14}C spectra of waste waters from nuclear power plant

Idea to overcome the problem of ^3H interference: cut off part of spectra with lower energies (with mixed ^3H and ^{14}C signals) and evaluate ^{14}C content from the remained high energy part of spectra (350-450 channels)

Comparison of method's parameters for the whole ^{14}C spectra consideration and for the high energy part only

Calibration parameters	Full energy window	The case of interference with ^3H
Energy window [channels]	150-450	350-450
ε [%]	61.96±0.03	23.750±0.017
r_0 [s ⁻¹] for $t_0 = 300 \text{ min}$	0.0185±0.0011	0.0080±0.0007
$\text{FOM} [\text{s}]$	207.5	70.5
$c_A^{\#}$ [Bq l ⁻¹] for $t_0 = 300 \text{ min}$	0.88	1.54
c_A^* [Bq l ⁻¹] for $t_0 = 300 \text{ min}$	0.42	0.73

Measurement results of waste waters

Sample no.	A (^3H) [MBq l ⁻¹]	A (^{14}C) [Bq l ⁻¹]	A (^{14}C) [Bq l ⁻¹] direct method (350-450 channels)
	LSC direct method	CO ₂ absorption	
1	5.92 ± 0.11	126.6 ± 2.3	247 ± 7
2	8.97 ± 0.19	201 ± 3	432 ± 3
3	20.8 ± 0.4	749 ± 16	924 ± 20
4	28.9 ± 0.6	230 ± 5	366 ± 9

- CO₂ absorption method: Radiocarbon Laboratory of the Ruđer Bošković Institute, Zagreb, Croatia [2,3] was used to measure ^{14}C content of waste water samples and to compare it with the results obtained by direct ^{14}C method
- ^3H content was determined by the direct LSC method [4].

REFERENCES

- [1] ISO 13162:2011(E), Water quality – Determination of carbon 14 activity – Liquid scintillation counting method, International Standard ISO 13162, First edition, 2011-11-01.
- [2] Krajcar Bronić, I., Horvatinčić, N., Barešić, J., Obelić, B., 2009. Measurement of ^{14}C activity by liquid scintillation counting. Appl. Radiat. Isot. 67, 800–804.
- [3] Horvatinčić, N., Barešić, J., Krajcar Bronić, I., Obelić, B., 2004. Measurement of low ^{14}C activities in liquid scintillation counter in the Zagreb Radiocarbon Laboratory. Radiocarbon 46(1), 105–116.
- [4] Jakonić, I., Todorović, N., Nikolov, J., Krajcar Bronić, I., Tenjović, B., Veskošić, M., 2014. Optimization of low-level LS counter Quantulus 1220 for tritium determination in water samples. Radiat. Phys. Chem. 98, 69-76.