Interlaboratory comparison of tritium electrolytic enrichment systems at RBI (Zagreb) and JSI (Ljubljana)

krajcar@irb.hr

Jadranka Barešić[1], Ines Krajcar Bronić[1], Nada Horvatinčić[1], Bogomil Obelić[1], Andreja Sironić[1] and Jasmina Kožar-Logar[2]

[1]Ruđer Bošković Institute, Zagreb, Croatia
[2]Jožef Stefan Institute, Ljubljana, Slovenia

MOTIVATION

Tritium (3H) activity of natural waters (precipitation, groundwater, surface waters) has recently become too low to be directly measured by low-level liquid scintillation (LSC) techniques. It is therefore necessary to perform electrolytical enrichment of tritium in such waters prior to LSC measurements.

Electrolytical enrichment procedure has been implemented in the Laboratory for liquid scintillation counting at the Department of Low and Medium Energy Physics of the Jožef Stefan Institute (IJS) in Ljubljana, Slovenia, in 2007 and in the Radiocarbon and Tritium Laboratory at the Department of Experimental Physics of the Ruđer Bošković Institute (RBI) in Zagreb, Croatia, in 2008. Measurements of ^{3}H activity at RBI was performed by gas proportional counting technique between 1976 and 2009.

Both electrolysis systems were obtained from the same producer (AGH University of Science and Technology, Krakow, Poland). Both laboratories have Ultra-low-level LSC *Quantulus 1220* (Wallac, PerkinElmer) for measurement of ^{3}H activity.

The aim of this work is:

1. To compare electrolysis parameters
2. To perform interlaboratory comparison
3. To compare results of IAEA TRIC2008 intercomparison samples

Figure 1. Tritium electrolytic enrichment systems at RBI (left) and IJS (right). In-between: cells for electrolysis.

1. Comparison of electrolysis parameters

Since establishment 24 electrolyses have been completed at RBI (system has been stabilyzing during first 6 electrolyses) and 143 at JSI, where 75 were carried out under identical conditions. Most important parameters are compared in Table 1.

The mean enrichment factor E (a ratio between the final and initial ^{3}H activities) and the mean enrichment parameter P (which describes the process of water mass reduction during electrolysis) are shown in Figures 2 – 5.

Table 1. Comparison of various parameters of the two systems for electrolytic enrichment of water with tritium and of the counting systems at RBI and IJS

	RBI Radiocarbon and Tritium Laboratory Department of Experimental Physics	IJS Laboratory for Liquid Scintillation Counting Department of Low and Medium-Energy Physics (F-2)
PRIMARY DISTILLATION		
conductivity after distillation	<50 μS cm^{-1}	<25 μS cm^{-1} and 5 < pH < 8
ELECTROLYSIS		
producer	AGH University of Science and Technology, Krakow, Poland	
commencement	2008	2007
number of electrolyses performed	24	143
no. of electrolyses run under same conditions	18	75
number o cells	20	
total charge (per 8 days)	1420 Ah	1400 Ah
initial water volume	500 mL	
final water volume	(18 ± 1) mL	(18.2 ± 2.1) mL
number of unknown samples / spikes / backgrounds	15 / 3 / 2	15 / 3 / 2
enrichment factor E	(23.2 ± 2.3) 20.4 – 27.5	(17.0 ± 1.3) 14.4 – 20.7
enrichment parameter P	(0.951 ± 0.012) 0.934 – 0.979	(0.890 ± 0.013) 0.857 – 0.927
COUNTING SYSTEM		
liquid scintillation counter	Ultra low-level LSC *Quantulus 1220* (PerkinElmer)	
volume ratio sample : scintillator	8 mL sample : 12 mL scintillator	
scintillator type	UltimaGold LLT	HiSafe3 (UG LLT, UG uLLT)
measurement duration	6 – 10 cycles × 50 min	3 – 5 cycles × 100 min
counting window (channels)	25 – 187	5 – 200
background count rate	(0.95 ± 0.08) min^{-1}	(0.88 ± 0.08) min^{-1}
calibration factor	(71 ± 3) TU/(min^{-1})	56.8 ± 1.6 TU/(min^{-1}) HS 48.9 ± 0.6 TU/(min^{-1}) UG

HS = HiSafe 3 (mostly used)
UG = UltimaGold

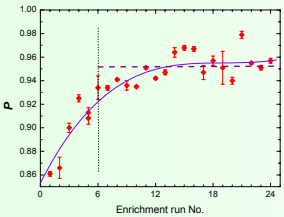

Figure 2. P at RBI.

Enrichment parameter P

The value of enrichment parameter P (which describes the process of water mass reduction during electrolysis) should be close to 1 for a stable and efficient electrolysis system.

The P values for first 6 electrolyses at RBI (Figure 2) increases, and later stabilizes around 0.95.

The corresponding value at IJS (after 75 electrolyses) is P_{IJS} = 0.890 ± 0.013 (Figure 3).

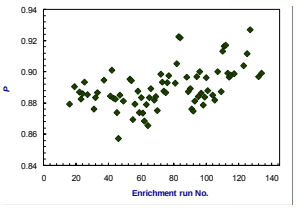

Figure 3. P at IJS.

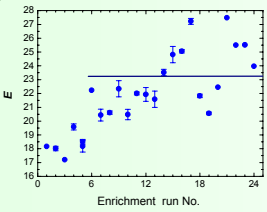

Figure 4. E at RBI.

Enrichment factor E

The mean enrichment factor E (a ratio between the final and initial ^{3}H activities) after stabilisation of the RBI system is E_{RBI} = 23.2 ± 2.3 (Figure 4).

The corresponding value at IJS (after 75 electrolyses) is E_{IJS} = 17.0 ± 1.3 (Figure 5).

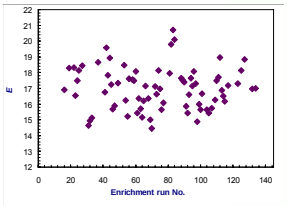

Figure 5. E at IJS.

2. Interlaboratory comparison

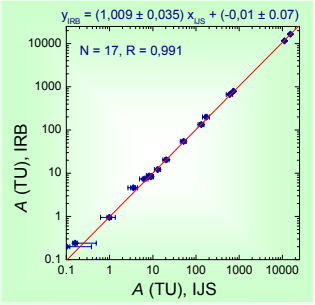

Figure 6. A set of water samples having ^{3}H activities in the range from 0 TU ("dead-water" samples) to 18 000 TU (1 TU = 0.118 Bq/L) were measured at both laboratories. Samples having ^{3}H activity <200 TU were enriched by electrolysis, while the others were measured directly in LSC.

3. Intercomparison IAEA TRIC2008

- Both laboratories participated in the IAEA TRIC2008 international intercomparison exercise.
- ^{3}H activities of 6 samples were measured (Table 2) in both laboratories
- For each sample the values of parameters z and u were determined
- The result is acceptable, i.e., without significant deviation from the "real" (IAEA) values, if $u < 1{,}64$

$$z = \frac{A_{lab} - A_{IAEA}}{\sigma_{lab}} \qquad u = \frac{|A_{lab} - A_{IAEA}|}{\sqrt{\sigma_{lab}^2 + \sigma_{IAEA}^2}}$$

$\sigma_{IAEA} << \sigma_{lab} \rightarrow u = |z|$

Table 2. Comparison of measured ^{3}H activities of IAEA TRIC2008 intercomparison samples

IAEA		IJS			RBI		
Sample code	$A_{IAEA} \pm \sigma_{IAEA}$ (TU)	Lab. code	$A_{IJS} \pm \sigma_{IJS}$ (TU)	z_{IJS}	Lab. code	$A_{IRB} \pm \sigma_{IRB}$ (TU)	z_{IRB}
T14	1.54 ± 0.05	TRIC08-T14-C1	1.68 ± 0.17	0.79	T-3906	1.25 ± 0.3	-0.97
T15	4.07 ± 0.05	TRIC08-T15-C1	4.20 ± 0.34	0.38	T-3907	4.11 ± 0.3	0.13
T16	7.74 ± 0.06	TRIC08-T16-C1	8.46 ± 1.03	0.70	T-3908	7.42 ± 0.3	-1.06
T17	14.46 ± 0.08	TRIC08-T17-C1	14.46 ± 0.95	0.00	T-3909	14.44 ± 0.4	-0.05
T18	0.67 ± 0.05	TRIC08-T18-C1	0.89 ± 0.18	1.18	T-3910	0.57 ± 0.3	-0.33
T19	568.7 ± 2.3	TRIC08-T19-C1	581 ± 26	0.47	T-3911	576 ± 13	0.56

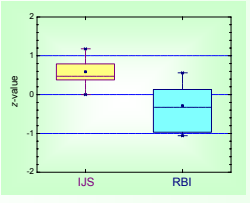

Figure 7. Comparison of z-values, box-plots.

All u values < 1.64 (u_{mean} = 0.51 for IRB and u_{mean} = 0.58 for IJS) → all results in both laboratories are accepted

CONCLUSION

- Electrolytic enrichment of water with tritium followed by counting in low-level liquid scintillation counter *Quantulus 1220* results in low detection limit (0.3 – 0.5 TU) and thus enables further application of tritium in hydrogeology, ecology and meteorology.
- Good agreement of results measured in two laboratories was obtained for a large range of ^{3}H activities, from 0 TU to 18 000 TU.
- Participation in the IAEA TRIC2008 intercomparison study showed acceptable results for all samples in both laboratories.

Acknowledgement: The work performed under the Project 098-0982709-2741 by the Ministry of Science, Education and Sport, Republic of Croatia and the Bilateral Croatian-Slovene project "Measurement of ^{3}H activity in natural waters with electrolytic enrichment". The authors thank to K. Kovačič (IJS), A. Rajtarić (RBI), R. Krištof (Ames d.o.o., Ljubljana), M. Centrih and M. Jerina for help in sample enrichment process and data evaluation.