Comparison of two techniques for low-level tritium measurement – gas proportional and liquid scintillation counting

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Abstract

Measurement of low-level tritium activities in natural/non-polluted waters, e.g. in precipitation and groundwater, requires special techniques for water pretreatment and detection of low-level radioactivity. Two methods for low-level tritium measurement have been developed in Zagreb Radiocarbon and Tritium Laboratory: gas proportional counting (GPC) and liquid scintillation counting (LSC). Method of electrolytic enrichment of water samples with tritium followed by measurement by LSC *Quantulus 1220* has been developed in 2008. Here we present the comparison of the two measurement techniques.

Our Laboratory participated in the intercomparison study organized by the IAEA, TRIC2008. The data evaluation of six samples revealed that all results measured by LSC are accepted, as well as four GPC results, while two GPC results of samples with low tritium activity (<2 TU) are in the warning level.

Introduction

Atmospheric thermonuclear tests during 1950es and 1960es introduced large amount of anthropogenic tritium into the atmosphere. The peak of tritium activity with up to 10 000 TU has been reached in 1963 in a monthly rain in North America. The anthropogenic tritium has been used as a global tracer in hydrogeology and meteorology studies (Rożanski at al. 1991). Tritium activity in surface, groundwater and precipitation was measured by a gas proportional counting (GPC) technique, and later on by liquid scintillation counting (LSC). However, the present tritium activity almost approached natural levels (5 – 10 TU), and measurement of samples without tritium enrichment is not precise enough any more.

In Zagreb Radiocarbon and Tritium Laboratory two measurement techniques of low-level tritium activities in natural/non-polluted waters, e.g. in precipitation and groundwater, have been used: gas proportional counting (GPC) and liquid scintillation counting (LSC). GPC technique for measurement of non-enriched samples has been used since 1978. A method of tritium measurement by LSC *Quantulus 1220* using electrolytic enrichment of water samples has been developed in 2008.

Material and methods

CH_4 is used as a counting gas in a multi-wire GPC. It is obtained by reaction of water (50 ml) with aluminium carbide at 150°C (Horvatinčić, 1980). The counting energy window is set to energies between 1 keV and 10 keV to obtain the best figure of merit. Gas quality control has been performed by simultaneous monitoring of the count rate above the tritium channel, i.e., above 20 keV (Krajcar Bronić et al. 1986). The limit of detection is 2.5 TU.

System of electrolytic enrichment consists of 20 cells of 500 ml volume (anodes: stainless steel, cathodes: mild steel) and equipments for primary and secondary distillations. The first step of sample pretreatment is primary distillation. If conductivity of distilled samples is <50 µS/cm, samples are ready for the enrichment procedure. Otherwise, samples have to be distilled again. For each enrichment run 3 spike and 2 dead-water (DW) samples are used for system control. Enrichment procedure lasts for 8 days (1420 Ah). Final volume of water sample after electrolysis is 19±1 ml. The enrichment factor (E) and the enrichment parameter (P) for each electrolysis run have been calculated using initial and final mass of water in cells and individual count rates of spike water before and after enrichment. The average enrichment factor (E) of several electrolysis runs is 21.4 ± 0.9, and the P parameter reached a value of 0.95.

Mixture of 8 ml of water and 12 ml of scintillation cocktail *Ultima Gold LLT* in plastic vials is used for counting in LSC. The measurement run contains 15 samples, 3 enriched spikes, 2 enriched DW samples, 1 non-enriched spike, 2 non-enriched DWs and a standard sample (activity 11 552 TU on 7.7.2008). The limit of detection is 0.3 to 0.5 TU, depending on the measurement duration.

Results

The results of GPC and LSC measurements of IAEA TRIC2008 intercomparison samples are presented in Table 1. The results were evaluated with the z-score and Final score evaluations. The z-score values were calculated using measured laboratory values (A_{lab}) and their sigma values (σ_{lab}) and IAEA true values (A_{IAEA}):

$$z = \frac{A_{lab} - A_{IAEA}}{\sigma_{lab}}$$

The Final score evaluations were determined by the evaluation criteria for both trueness and precision of the measurements (Gröning et al, 2009). In the final evaluation, both scores are combined and a result must obtain 'Acceptable' score in both criteria to be assigned final score 'Acceptable'.

According to the Final score evaluations all our LSC results are acceptable while two GPC results of samples T14 and T15 with low tritium activity are in warning level. The z-score evaluations showed that most of GPC results are lower than the IAEA true values (mean z-score is -0.44) and in the case of LSC results the deviations from the IAEA true values is smaller (mean z-score is -0.29). The comparison of both GPC and LSC results with the IAEA true values is presented in Fig.1.

Table 1. Comparison of GPC and LSC values measured in our Laboratory with IAEA TRIC2008 intercomparison results. The z-score and Final score evaluations are presented for both methods (A – acceptable, W – warning)

IAEA code	IAEA true value (TU)	GPC				LSC			
		Lab. code	Lab value (TU)	z-score	Final score	Lab. code	Lab value (TU)	z-score	Final score
T14	1.54 ± 0.05	T-3867	0.21 ± 0.81	-1.64	W	T-3906	1.25 ± 0.3	-0.97	A
T15	4.07 ± 0.05	T-3868	3.50 ± 0.96	-0.59	A	T-3907	4.11 ± 0.3	0.13	A
T16	7.74 ± 0.06	T-3869	6.60 ± 0.99	-1.15	A	T-3908	7.42 ± 0.3	-1.06	A
T17	14.46 ± 0.08	T-3870	14.23 ± 0.67	-0.34	A	T-3909	14.44 ± 0.4	-0.05	A
T18	0.67 ± 0.05	T-3871	0.03 ± 0.82	-0.78	W	T-3910	0.57 ± 0.3	-0.33	A
T19	568.7 ± 2.3	T-3872	579.24 ±5.70	1.85	A	T-3911	576.0 ± 13	0.56	A

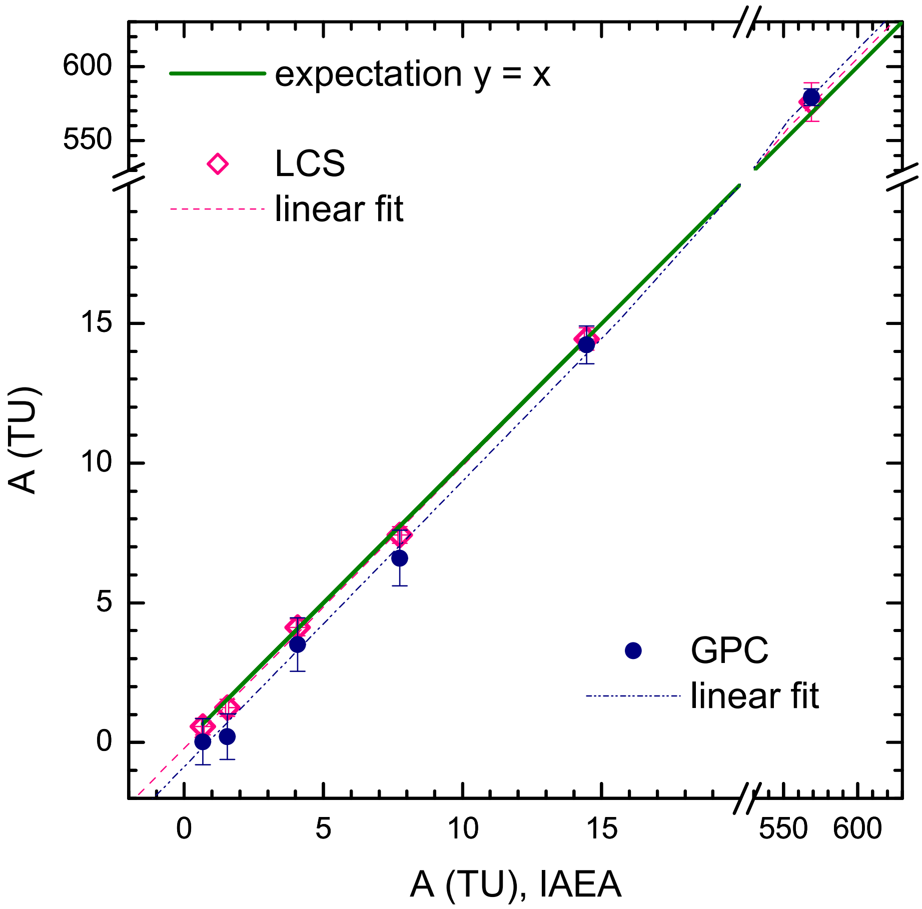

Fig. 1. The comparison of tritium activities of TRIC2008 intercomparison samples measured by GPC and LSC techniques with the IAEA true values

For additional testing of both systems we measured tritium activity in several precipitation and groundwater samples by both GPC and LSC techniques. The results are presented in Fig. 2. Here we can see that all LSC results have smaller errors then GPC results. For the samples with low tritium activity (<10 TU, mostly groundwater) the GPC results are mainly lower then the LSC results while for the higher tritium activities (precipitation samples) the GPC results are lower than the LSC results. If we take into account also the IAEA intercomparison results obtained by both methods, we can conclude that for the low tritium activity the GPC system is not acceptable because of higher/worse detection limit (2.5 TU). LSC system with detection limit of 0.3 – 0.5 TU and with better precision (Table 1) is more suitable for most natural water samples including precipitation and groundwater samples.

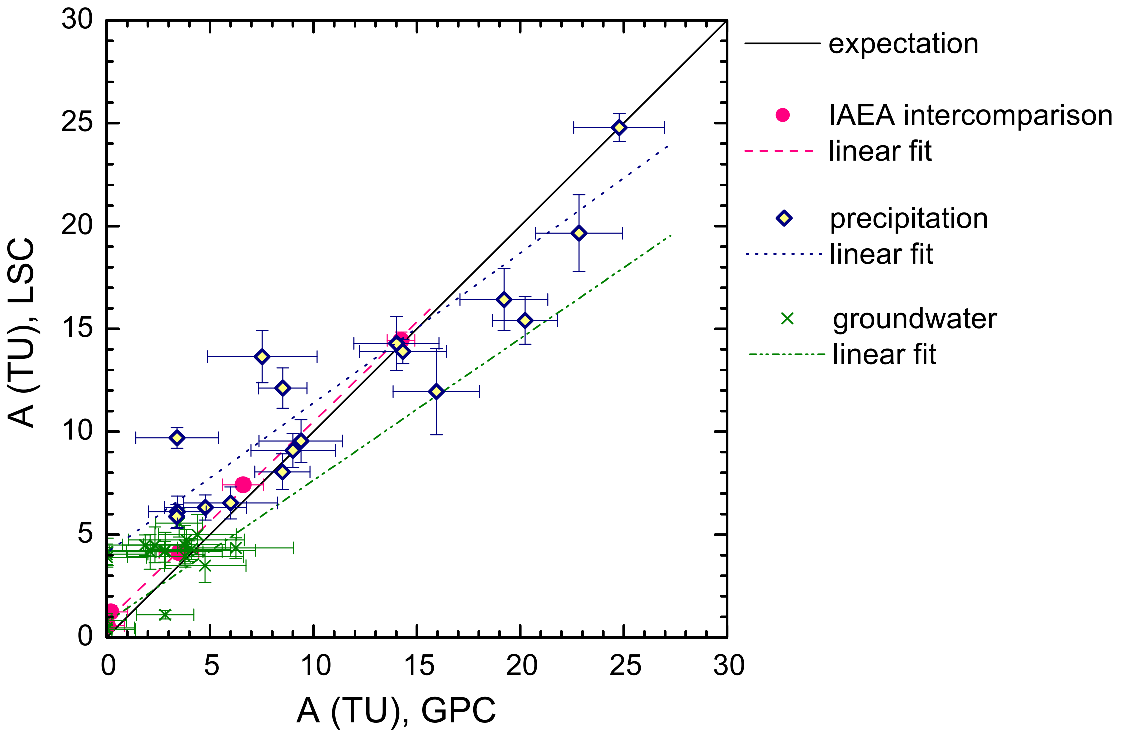

Fig. 2. Comparison of GPC and LSC results of groundwater and precipitation samples, as well as TRIC2008 intercomparison samples.

Conclusion

The data evaluation of six TRIC2008 samples (IAEA intercomparison) revealed that all results measured by LSC are accepted, and for GPC results four results are accepted and two results of low tritium activity (<2 TU) are in the warning level. Measurements of groundwater and precipitation samples show that GPC values are still valid for higher tritium activities (>10 TU), while lower activities can not be measured properly without enrichment and followed by LSC measurement.

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