Standard and validated method for determination of tritium on Liquid scintillation spectrometer

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***Abstract*—Tritium concentrations in water samples were analyzed. The aim is to compare methods: standard method (direct method): according to ASTM D 4107-08 and validated method: which applies electrolytic enrichment. Low level tritium concentration in natural waters required measurement after enrichment. One set of samples, which contain 16 samples including spike water were enrichment and compared with 4 samples measured by direct method. For this analysis liquid scintillation spectrometer was using. In general, analysis with enrichment is more applicable for samples with low activity. Also, validated method with enrichment reduced minimum detectable concentration.**

***Index Terms*—tritium, liquid scintillation spectrometer, water samples, enrichment.**

I. Introduction

Tritium (^3H), radioactive isotope of hydrogen, has half life of 12.3 years. ^3H has low beta energy with maximum of 18 keV and a mean energy of 5.7 keV. Its origin is naturally, from the upper atmosphere (stratosphere) where arises by interaction between fast neutron and nitrogen atoms, and artificially (produced from the nuclear reactor, atmospheric thermonuclear tests, nuclear weapons testing, nuclear reactors, fuel reprocessing plants, heavy water production facilities and commercial production for medical diagnostics, radiopharmaceuticals, luminous paints, sign illumination, self-luminous aircraft, airport runway lights, luminous dials, gauges and wrist watches) [1]. It can enter in hydrological cycle from precipitation and can enter in surface water and groundwater. From that reason, monitoring of tritium in natural water is necessary.

In water samples, tritium can be measured directly, after distillation, or after electrolytic enrichment of samples. Based on the fact that nowadays, concentration of tritium in natural water is low, it is necessary to concentrate the samples through enrichment. In the case of the assumption that the concentration is high, enrichment is not required.

This paper presents the comparison between different preparations of water samples which means using of standard method – direct method and validated method – method with electrolytic enrichment.

II. The Method

Total number of 15 water samples were collected in order to analyze tritium concentrations: 1 drinking water, November 2020, 9 precipitations (3 from referent meteorological station Zeleno Brdo in Belgrade (ZB), September, October and November 2020; 3 from station in Vinča Institute of Nuclear Sciences Site Center (CS), September, October and November 2020; 3 from station in Vinča Institute of Nuclear Sciences Meteo stub (MS), September, October and November 2020), 5 surface water (Sava, September and October 2020; Danube, October 2020; Mlaka Creek in Vinča Institute of Nuclear Sciences, October and November 2020).

Approximately 300 ml of each composite monthly sample are distilled to remove dissolved salts and organic impurities. The various ions that are naturally found in water (Cl^-, SO^{-4}, CO_3, Mg^{++}, Na^+, K^+, etc.) could interfere with the electrolysis process [2].

In the case where the direct method is applied the ASTM D 4107-08 standard method [3] is used. After preliminary distillation an aliquot of 8 ml of distillated samples is mix with 12 ml scintillation cocktail ULTIMA GOLD LLT in polyethylene vial (volume of vial is 20 ml).

In the case where validated method is applied [4], preliminary distillated samples must be enriched. Enrichment unit contains electrolytic cells, constant current supply unit and cooling unit. In one electrolysis run, a set of 16

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electrolytic cells is connected in series and connected to a direct current source. Each enrichment run contains 16 samples, including 1 spike water (water of known tritium activity concentration used for enrichment factor determination). Each cell contains 250 ml of initial volume of the distillated sample. As an electrolyte, Na_2O_2 is used. In order to achieve approximately 10-15 ml of final volume of the samples, system works on 5 A. The enrichment operated with 5 A current could enrich approximately 1.7 g of water samples per hour. This means 5 days is necessary to enrich from 250 ml to 10-15 ml of water samples according to Faraday's factor.

An enrichment samples must be distilled again to remove electrolyte. After the second distillation an aliquot of 8 ml of the samples mix with 12 ml scintillation cocktail ULTIMA GOLD LLT in polyethylene vials.

For both methods, standard and validated, ultra-low-level liquid scintillation counter Quantulus 1220 is used. Measuring time of each sample is 300 min. Beside the samples, *dead water DW* (tritium free water) is also measured for background, as well as water of known tritium activity (*BEFORE BE*). *BEFORE*, after enrichment calls *SPIKE SW* water. Their ratio determines cell enrichment factor.

Counting efficiency is determined according to standard method [3]. For determination of efficiency, standard tritium solution ^{3}H 9031-OL-548/13 Czech Metrology Institute Type: ERX with activity 5.060 MBq on day 1.10.2013 is used. The tritium measurement uncertainty is expressed as the expanded measurement uncertainty for the factor k=2, which corresponds to a normal distribution with a confidence level of 95 %.

Minimum detectable activity (*MDA*) is measured using the following equation:

$$MDA = \frac{2,71 + 4,65\sqrt{R_b t_b}}{60 \varepsilon V t_b} \quad (1)$$

where R_b is background count rate (cps), t_b is background counting time (min), ε is efficiency (%) and V is volume of the *DW* (l). In case with enrichment, above equation is further divided by the electrolysis enrichment factor Z.

III. Section Title (e.g. Main Results)

For 15 natural water samples, validated method with electrolytic enrichment was performed in order to determined tritium activity. The obtained results are presented in Table 1. 1 drinking water, 9 precipitation samples and 5 surface water samples were analyzed. For the results shown from one electrolysis, it took 695 Ah to reduce initial volume of the samples to 13 ml (5.8 days at 5A). Calculated enrichment factor, Z, for this electrolysis is 13.2. Calculated *MDA* for this electrolysis is 0,23 Bq/l for background counts of 0.035 cps. Efficiency obtained by calibration of the spectrometer is 27.9 %.

Results for tritium activity in drinking water and precipitation from the reference meteorological station Zeleno Brdo are similar regardless of the month of sampling. Results obtained for precipitation at two locations in Vinča Institute of Nuclear Sciences, CS and MS are higher than results obtained for precipitation at ZB. This is in accordance with earlier results for tritium activity in precipitation for these locations [5-7]. In surface water samples, obtained results are different in relation to precipitation. Results for Sava and Danube are similar with values obtained for precipitation at MS. On the other hand, results for Mlaka Creek at location in Vinča Institute of Nuclear Sciences present higher values than surface water in Belgrade outside the Institute. These results are in accordance with previously results [5-7].

TABLE I

Tritium activity concentrations in water samples

Sample	Location	^{3}H (Bq/l) with enrichment	^{3}H (Bq/l) without enrichment
Drinking water	Belgrade	0.7 ± 0.2	
Precipitation	ZB IX 2020	1.2 ± 0.2	
	ZB X 2020	0.8 ± 0.2	5.4 ± 1.9
	ZB XI 2020	0.8 ± 0.2	
	CS IX 2020	3.1 ± 0.3	
	CS X 2020	3.0 ± 0.3	
	CS XI 2020	3.0 ± 0.3	
	MS IX 2020	1.6 ± 0.2	
	MS X 2020	1.7 ± 0.2	
	MS XI 2020	1.7 ± 0.2	
Surface water	Sava IX 2020	1.4 ± 0.2	
	Sava X 2020	1.2 ± 0.2	5.0 ± 1.9
	Danube X 2020	1.7 ± 0.2	5.0 ± 1.9
	Mlaka X 2020	5.4 ± 0.5	9.5 ± 2.0
	Mlaka XI 2020	5.4 ± 0.5	

For 4 samples: one precipitation, ZB, X 2020, and 3 surface water, Sava, X 2020, Danube, X 2020 and Mlaka Creek, X 2020 direct method for tritium analysis is performed. Results are presented in Table 1. As can be seen from the Table, values obtained for these samples which were measured directly are higher than values obtained for the same samples which were measured after enrichment. For this method, calculated *MDA* is 2.9 Bq/l for background counts of 0.033 cps. Efficiency is the same, 27.9 %.

For low level tritium activity it is evident that it is better to apply validated method, which also reduces the detection limit. In case it is certain that the activity of tritium is high the standard direct method can be applied. Especially because it is necessary to take into account that in case of expected high tritium values, contamination of the electrolysis system may occur.

In Serbia, legislation defines permitted values for tritum activity only for drinking water (100 Bq/l) [8]. In relation to this allowed value, all analyzed samples meet the criteria given by rulebook.

IV. CONCLUSION

Comparing standard and validated method for tritium determination in natural water samples, it can be concluded that validated method with electrolytic enrichment is more applicable for samples with low level tritium concentrations. Standard – direct method gives higher values and can be acceptable for expected high values of tritium. Method with enrichment also reduced minimum detectable activity. Liquid scintillation counting has proven to be irreplaceable in environmental tritium monitoring and for analysis of low level activity.

ACKNOWLEDGMENT

The research was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia.

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