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Tritium Determination in Danube River Water in Serbia by Liquid Scintillation Counter

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***Abstract*—**Tritium activity concentration in Danube river water in Serbia has been determinate using a liquid scintillation counter Quantulus 1220. During December 2010, water samples were taken along the entire course of Danube through Serbia, from Hungarian-Serbian to Romanian-Serbian border. This investigation is very important because of the nearness of nuclear reactor Paks in Hungary. Sample preparation was performed by standard test method using Optiphase HiSafe 3 scintillation cocktail. We used a rapid method for the preparation of environmental samples, without electrolytic enrichment.

***Keywords*—**detection limit, liquid scintillation counter, low-level tritium analysis, monitoring.

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I. Introduction

TRITIUM analysis has been useful in many areas such as hydrogeology, nuclear industry monitoring, dosimetry and health-risk assessment and some special topics such as false labeling of alcoholic beverages [1]. It is well known that nuclear power plants (NPP) have become a significant source of tritium in the environment. But tritium is also a naturally occurring radionuclide, mainly due to interactions of cosmic rays with the atmosphere.

Common methods for determination of low-level tritium activity concentrations are liquid scintillation counting (LSC) and gas-proportional counting (GPC). For analyzing natural water samples, it is better to use LSC because in this method water sample is directly combined with an appropriate aqueous scintillation cocktail, required pre-treatment is minimal and the counting efficiency is higher than that of GPC [2].

Despite the relatively low radiotoxicity of tritium, monitoring of tritium activity concentrations in the environment is necessary in order to follow its circulation in the hydrosphere and biosphere [3]. Taking into account the tritium low level in the environment, special conditions have to be fulfilling in order to obtain reliable and accurate tritium measurements. It is important for counting system to have a high and stable overall efficiency for the detection of low energy β particles together with a low and stable background. These conditions are very well fulfilled in LSC Quantulus 1220.

When tritium concentration is low, that is less than 10 T.U. (tritium unit, 1 T.U. = 0.118 Bq/l), electrolytic enrichment is necessary to determine the tritium activity [1].

The Danube is Europe's second longest river (after the Volga). It is classified as an international waterway. The river originates in the Black Forest in Germany as the much smaller Brigach and Breg rivers which join at the German town of Donaueschingen. After that point it is known as the Danube River and it flows southeastward for a distance of some 2850 km, passing through four Central and Eastern European capitals, before emptying into the Black See via the Danube Delta in Romania and Ukraine. This river flows through or acts as part of the borders of ten countries: Germany (7.5%), Austria (10.3%), Slovakia (5.8%), Hungary (11.7%), Croatia (4.5%), Serbia (10.3%), Bulgaria (5.2%), Moldova (1.6%), Ukraine (3.8%) and Romania (28.9%) (The percentages reflect the proportion of the total Danube basin area), shown on the Figure 1. Major cities along the Danube include the three national capitals of Vienna (Austria), Budapest (Hungary) and Belgrade (Serbia). Along its course (Figure 1), the Danube is a source of drinking water for about ten million people. But most states find it difficult to clean the water because of extensive pollution.



Fig. 1 Map of Danube River

The main purpose of this work was to establish a rapid method to measure low-level activity concentrations of tritium in natural water samples. Because of this, we used fresh water samples, without electrolytic enrichment (we made an assumption that tritium concentration in analyzed samples will be higher than 1.18 Bq/l). The used method is low background liquid scintillation system detector Quantulus 1220 (Perkin Elmer). We measured tritium levels in the samples from Danube River, along its entire course through Serbia, in order to test this rapid method. This is the first monitoring of tritium activity concentration in Danube River water in Serbia. This investigation is important because in our neighbor country Hungary, there is a Nuclear Power Plant Paks. Also, on October 7, 2010, a toxic red sludge that burst out of a Hungarian aluminum factory's reservoir entered the Danube, threatening an ecological disaster. This event may also

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contribute to the quality of water in Danube.

II. Experimental Procedure

A. Equipment

In our laboratory we performed a rapid tritium activity determination method by LSC (Liquid Scintillation Counter) Quantulus 1220 (Perkin Elmer). This technique involves mixing the sample with a proper detection cocktail to be counted in a liquid scintillator. This instrument has its own background reduction system around the vial chamber, which consists of both, active and passive shield. Passive shield is made of lead, cooper and cadmium and active shield is based on a mineral oil scintillator. In the construction of Quantulus low activity materials are used, so it is useful for measuring a low level radiation activity. The system is provided with two pulse analysis circuits that are accessible for the users: a pulse shape analysis (PSA) and pulse amplitude comparator (PAC) circuit. There is also a delayed coincidence circuit (DCOS) inside the Quantulus, which is useful in correction of the chemiluminescence. Delayed coincidence pulses are routed to a MCA (multi-channel analyzer) and stored as a chemiluminescence spectrum. There are also a second MCA, and the rest of the pulses are routed to it and stored as the tritium spectrum. In order to determine the counting window for tritium measurements we collected spectra of tritium and background and the window was set to maximize the figure of merit. In our measurements the tritium window is fixed to channels 1-250. Quenching was quantified with the external standard quenching parameter, SQP(E), which was used to determine the counting efficiency of the system with appropriate calibration curves.

B. Sample Treatment and Measurement

As a background sample we used distilled raw water (deep well water) prepared according to the Standard Test Method. We used the commercial standard of tritium activity from Perkin Elmer, and prepared it with scintillation cocktail. The preparation method of background and standard should be the same as the preparation of samples. In every set of measurement it is important to measure background and standard, in the aim of the same measuring conditions.

We took water samples from eight different locations along the course of Danube River (Figure 2), during December 2010. All samples were prepared according to ASTM Standard Test Method [4]. Each water sample was filtered through a slow depth filter and then distilled. After the distillation, the samples were mixed with the scintillation cocktail Optiphase HiSafe 3.



Fig. 2 Sampling locations from Danube River in Serbia

In this study we used standard 20 ml polyethylene vials. Neither glass vials nor teflon-cooper vials were used because of their relatively high background in the tritium window [5] and their high cost for routine monitoring. According to Standard Test Method, the recommendation for our scintillation cocktail is to mix 10 ml of distilled sample with 12 ml of scintillation cocktail. The volume of the used polyethylene vial is 20 ml, so we used appropriate volumes of sample and scintillation cocktail, which are 9 ml of distilled sample and 11 ml of scintillation cocktail. That is in correspondence with Ref.[1], in this paper authors suggested that the optimum sample volume to use for liquid scintillation analysis is 9 ml.

We noticed that reduced detection efficiency may result from quenching in the sample scintillator mixture. The main reasons for quenching are different types of impurities in the sample, which can inhibit the transfer of energy, or by colored materials, which may absorb some of the emitted light. This is especially the case with direct methods, like the method we used, without electrolytic enrichment. There are two ways to make corrections for quenching, one is the use of internal standards and the other one is so-called ratio method. According to our test method [4], distillation after alkaline permanganate treatment, eliminates quenching substances, as well as radionuclides which might be present in a volatile chemical form such as radioiodine or radiocarbon.

The minimum detectable activity (MDA), achieved was 3.1 Bq/l for a total counting time of 300 minutes. The aim was to perform a rapid method so we used the total counting time of 90 minutes for each sample, and the obtained MDA for that interval of time was 5.8 Bq/l (as shown on Figure 3). For calculating of MDA we used the following relation:

$$MDA = \frac{2.71 + 3.29 \cdot \sqrt{R_b \cdot t_a \cdot \left(1 + \frac{t_a}{t_b}\right)}}{\varepsilon \cdot t_a \cdot F \cdot V \cdot e^{-\lambda t}} \quad (1)$$

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The L_C value (critical activity), also called *detection limit*, for the total counting time of 90 minutes was 2.8 Bq/l (as shown on Figure 4). For calculating of L_C value we used the following relation:

$$L_C = \frac{1.65 \cdot \sqrt{R_b \cdot t_a \cdot \left(1 + \frac{t_a}{t_b}\right)}}{\varepsilon \cdot t_a \cdot F \cdot V \cdot e^{-\lambda t}} \quad (2)$$

In the previous two relations, R_b is the background aliquot count rate (s^{-1}), t_a is the counting time of sample (s), t_b is the counting time of background (s), ε is the detection efficiency (the obtained efficiency of our system is 23.25%), F is recovery factor (in our measurements it was 0.9), V is volume of the sample aliquot (9 ml), λ is decay constant for tritium ($\lambda = \ln 2 / t_{\frac{1}{2}}$; $t_{\frac{1}{2}} = 4500\ days$, half life of tritium).

The tritium activity concentrations in measured samples were calculated according to the formula from ASTM Standard Test Method:

$$AC = \frac{R_a - R_b}{\varepsilon \cdot F \cdot V \cdot e^{-\lambda t}} \quad (3)$$

Where R_a is the sample aliquot gross count rate (s^{-1}), R_b is the background aliquot count rate (s^{-1}), ε is the detection efficiency (the obtained efficiency of our system is 23.25%), F is recovery factor (in our measurements it was 0.9), V is volume of the sample aliquot (9 ml), λ is decay constant for tritium ($\lambda = \ln 2 / t_{\frac{1}{2}}$; $t_{\frac{1}{2}} = 4500\ days$, half life of tritium) and t is elapsed time between sampling and counting (in days).

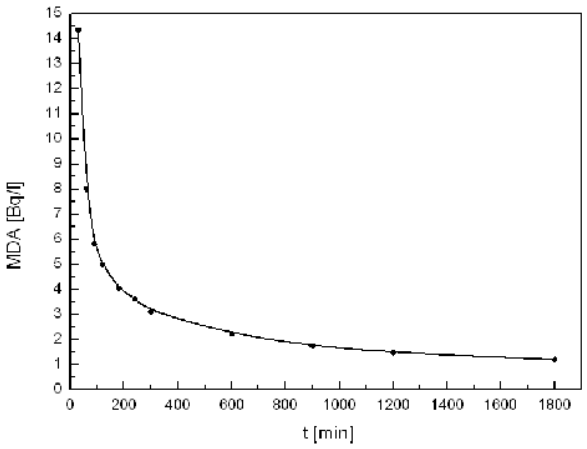


Fig. 3 Dependance of minimum detectable activity from measuring time

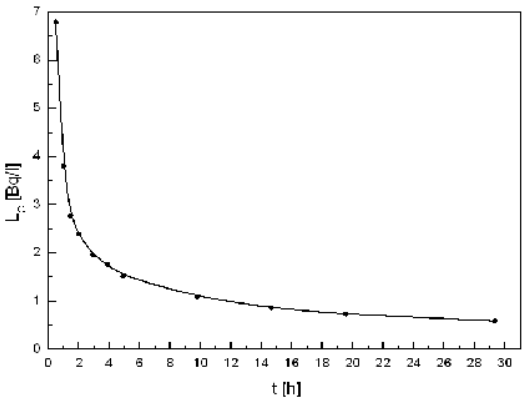


Fig. 4 Dependance of the critical activity value from measuring time

III. Results and Discussion

The obtained results are presented in the Table I. The samples are numerated starting from initial point of Danube entering Serbia, and the last water sample is taken on the point where the Danube is a border between three states: Romania, Bulgaria and Serbia.

TABLE I
Tritium Concentrations in Measured Water Samples from Danube River in Serbia

	Locations	Activity concentrations of ^3H	
		[Bq/l]	[TU]
1.	Danube near Apatin	3.0±1.0	25.7
2.	"Zimovnik" the branch of Danube near Apatin	2.7±1.2	22.5
3.	Danube port in Novi Sad	2.2±0.5	18.2
4.	"Strand" Danube beach in Novi Sad	1.6±0.7	13.5
5.	"Zemunski kej" beach in Belgrade	1.5±0.7	12.6
6.	Sava – Danube River delta	2.1±1.0	18.0
7.	"Kusjak" beach near Negotin, border between Serbia and Romania	2.5±1.1	21.2
8.	Border between Serbia, Bulgaria and Romania	2.1±1.0	18.0

We took water samples from the following locations: two samples were taken around Apatin (near Serbia-Slovenia border, Danube is coming from Hungary), after that we took two samples around Novi Sad, two samples around Belgrade and the last two samples were taken near border of Romania –

Bulgaria – Serbia. All the samples were taken during December 2010, and measured couple of days later after adequate chemical preparation.

All measured ^{3}H activity concentrations are higher than 10 TU (higher than 1.18 Bq/l), so we approve that for our samples it was not necessary to use electrolytic enrichment procedure. Varlam et al. published results of monitoring of tritium level along Romanian part of Danube River during different periods of the year [6]. They concluded that behavior of tritium concentration during the cold months of the year (like this December) with values higher than 10 TU proves the influence of nuclear activity developed along the Danube.

The measured values for tritium concentrations are far from any radioprotection concern (the highest value is around 3 Bq/l, which is much smaller than 100 Bq/l which is the recommended level by Council Directive 98/83/EC for drinking water). Tritium concentration average in the Danube River along the course in Serbia was 18.7 TU during December; our neighbor country Romania measured the averaged value of 16.2±2.2 TU in Danube in Romania [6].

IV. Conclusion

In most cases of environmental ^{3}H contamination pose no significant radiological risk, because the concentrations are far below the maximum permissible value for water. Anyway it is important to check the contamination dose that can cause an increase in environmental tritium concentrations, which are several orders of magnitude more than normal values.

The obtained values in this set of samples from Danube River in Serbia are smaller than detection limit, L_C, except the sample from the first location which is a little higher comparing to the detection limit.

If we want to do fast analysis of low level tritium activities in environmental samples, we can use this quick method of direct mixing of distilled water sample with scintillation cocktail following the Standard Test Method [4], without electrolytic enrichment, and measuring the obtained mixture in LSC Quantulus 1220. For more detailed investigation of this direct method, we should perform tritium in water analysis with and without electrolytic enrichment, and we should try to compare the results. Also, for the purpose of more detailed monitoring of tritium activity concentrations in Danube River in Serbia we should take more locations, to get more uniformly statistic and to do the analysis during different periods of the year, for example every month during one year which is the next step in our investigation.We didn't expect to find high level of tritium activity concentration because in Serbia there isn't any nuclear power plant, so the main contributor could be the Nuclear Power Plant Paks in Hungary and the cosmic radiation.

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