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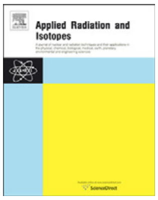

Different methods for tritium determination in surface water by LSC

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HIGHLIGHTS

- ▸ 3 methods of water sample preparation for low-level tritium measurement have been compared.
- ▸ All prepared samples were measured by LSC Quantulus 1220.
- ▸ The most novel is that Sample Oxidizer is used as one method for sample preparation.
- ▸ Paper presents MDA values for each presented method.
- ▸ For environmental monitoring all three methods give comparable results.

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ABSTRACT

The main aim of this paper was to compare different methods of preparing water samples for tritium analysis by ultra-low-level background liquid scintillation counter, Quantulus 1220. Three methods of sample preparation for low-level tritium measurement have been implemented in the Nuclear Physics Laboratory in Novi Sad: electrolytic enrichment, direct method without electrolytic enrichment and sample Oxidizer 307 method. The examined fresh water samples were rainfall collected during 6 months and water from a stream in the Vinča nuclear research center collected over 3 months. The obtained results using these three methods showed satisfying agreement. The appropriate measuring time by LSC for each sample prepared according to different methods has been determined.

1. Introduction

Tritium is a radioactive isotope of hydrogen with a physical half-life of 4500 ± 8 days (Lucas and Unterweger, 2000) that behaves like stable hydrogen and is usually found attached to molecules replacing hydrogen (Varlam et al., 2011). This radionuclide occurs in nature, originating from natural and anthropogenic sources. Natural tritium is produced in the atmosphere from the interaction of cosmic radiation with atmospheric nitrogen (Madruga et al., 2008). Anthropogenic production has disturbed the natural levels of tritium by nuclear weapons tests and, in addition to that tritium is being released into the atmosphere through weapons manufacturing, the operation of nuclear power plants and reprocessing of nuclear fuels (Pujol and Sanchez-Cabeza, 1999).

Tritium most commonly enters the environment in gaseous form (T_2) or as a replacement for one of the hydrogen atoms in water (HTO, called “tritiated water,” instead of ordinary, non-radioactive H_2O). Tritiated water can replace ordinary water in living cells (approximately 70% of the soft tissue in the human body is water). Once in living cells, tritium can replace hydrogen in the organic molecules in the body. Thus, despite tritium’s low radiotoxicity in gaseous form and its tendency to be released from the body rather rapidly as water; its effects on health are made more severe by its property of being chemically identical to hydrogen (Varlam et al., 2011).

As tritium is a very soft beta-emitter (maximum energy = 18.6 keV), the common methods for low-level counting of tritium are either gas-proportional counting (GPC) or liquid scintillation counting (LSC). For analyzing natural water samples, it is better to use LSC because in this method the water sample is directly combined with an appropriate aqueous scintillation cocktail, the required pre-treatment is minimal and the counting efficiency is higher than that of GPC (Noakes and De Filippis, 1988).

The primary objective of all sample preparation methods is to obtain a stable homogeneous solution suitable for analysis by Liquid Scintillation Counting (LSC). There are no absolutes in sample preparation; whichever method produces a sample that lends itself to accurate and reproducible analysis is acceptable.

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However, there will be occasions when more than one method will be both suitable and available and the selection of either method will depend on other factors (Oxidizer Application Note, 2002).

According to the European Commission, the upper limit for tritium in water is 100 Bq l^{-1} (European Commission, 1998). This value is not based on health effects relative to its consumption but more as a monitoring value. A tritium activity of 100 Bq l^{-1} could indicate that leakage or a release occur on a power plant and further analysis are then realized to check if other radionuclides are present in water. In considering health concerns, the activity value that is commonly used as a limit is the one from the World Health Organization (10,000 Bq l^{-1} for a man of 70 kg who drinks 2 l of water per day) published in the 4th edition of their guidelines for drinking water (WHO, 2011).

Three methods (electrolytic enrichment, direct method and oxidizer/LSC method) for tritium concentration determination in water samples have been compared in this paper.

The water samples were taken from the Mlaka creek which passes through the Vinca Institute of Nuclear Science in Belgrade, Serbia. The Mlaka creek is 5 km long with an average water flow of only 10 l s^{-1}. The sampling point was situated near the discharge from research reactor RA (Miljevic et al., 2000). The increases in content can be attributed to a tritium contribution due to liquid release through infiltration from the reactor target storage basins into the catchments area. The other sampling location was the Zeleno Brdo reference meteorological station (44°47′N, 20°32′E, altitude 243.2 m) for collecting rainfall samples. Vinca Institute of Nuclear Sciences (VINS) is situated on the Danube, 7 km SE of Belgrade which is potential source of environmental dispersal of anthropogenic tritium primarily as HTO from the long-established nuclear facilities. In spite of the cessation of normal reaction operations at VINS in 1986, this is potentially still a source of tritium which will continue to disperse into the open environment (Miljevic et al., 2000). The last published results were before the year 2000; this paper will also provide a new data of activity concentration of tritium in precipitation and in the water from Mlaka creek and that could indicate a future need for continual monitoring of this area.

2. Measuring technique

2.1. Liquid scintillation counter Quantulus 1220

All prepared samples were measured by a Quantulus 1220 liquid scintillation counter, which is a low-level background liquid scintillation counter (LSC) manufactured by Perkin Elmer, Finland (Quantulus, 1220,2002). This instrument has its own background reduction system around the vial chamber, which consists of both an active and passive shield. The passive shield is made of lead, copper and cadmium and the active shield is based on a mineral oil scintillator. Low-activity materials were used in the construction of the Quantulus, so it is useful for measuring 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 for the correction of chemiluminescence. The Quantulus 1220 has two multichannel analyzers (MCA), one is used for active shield and the second one is used for spectra record. Those MCA's are divided in two halves, 1024 channels each. The tritium configuration of the MCA's setting eliminates the random noise of phototubes, inhibits the coincidence pulse from the guard and the sample, and monitors the random coincidence by DCOS in a half of the MCA, the whole sample spectrum being recorded in the other half of the MCA. 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 (Pujol and Sanchez-Cabeza, 1999). We determined the counting windows for each of the three methods according to the results obtained by measuring standard samples.

3. Sample preparation

3.1. Method of electrolytic enrichment

After collecting 500 ml of water, samples were distilled to remove any impurities, to reduce quenching and to prevent the introduction of other radionuclides which might adulterate the results.

In order to increase the tritium concentration to an easily measurable level, electrolytic enrichment must be applied (Kaufman and Libby, 1954). When the water is decomposed by electrolysis, the deuterium and tritium content in the resultant hydrogen is lower than in the electrolyte and, as the electrolysis proceeds, the tritium concentration in the remaining electrolyte increases (Cameron, 1967). The enrichment process was conducted in an apparatus containing electrolytic cells with co-axial stainless steel electrodes. In each cell, 250 ml of previously distilled water with 1 g of Na_2O_2 (an electrolyte which forms NaOH in water and yields an alkaline medium favorable to electric conduction and hence to the reaction of water electrolysis) was electrolyzed. Each electrolysis run comprised 2 reference dilutions of tritiated water and the rest were the samples. Electrolysis was carried out at a current of 5 A (voltage of 48 V across each cell) until the volume of electrolyte was reduced to 25–30 ml. All runs were carried out at a temperature of 2–5° C to prevent the loss of tritiated water molecules by evaporation. After electrolysis the samples were distilled to separate the water from the electrolyte.

An aliquot of 8 ml from the second 10 ml fraction of the distillate was placed in a 20 ml polyethylene scintillation vial, and mixed with 12 ml of OptiPhase HiSafe scintillation cocktail from Perkin Elmer. Neither glass vials nor Teflon-cooper vials were used because of their relatively high background in the tritium window and their high cost for routine monitoring (Kaihola, 1993). The tritium activity of water samples was determined by LSC Quantulus 1220. The counting time was 90 min in 5 cycles for each sample and the tritium activity was calculated by averaging the results. The measurement of the background noise is very important when counting samples of low activity. As a background sample, distilled raw water (deep well water) was used. With each set of samples a counting blank was included. Spiked water of known tritium activity concentration is used to determine the enrichment factor. The enrichment factor, *f*, for electrolytically concentrated samples is defined as the ratio of the concentration after enrichment, SW (spiked water), of a standard and the concentration before enrichment (BE) (Sauzay and Schell, 1972).

Tritium activity concentration of each enriched sample is calculated according to the following expression (Madruga et al., 2008):

$$A\left(\mathrm{Bq\ l^{-1}}\right) = \frac{R_a - R_b}{\varepsilon \times V \times e^{-\lambda t}} \frac{1}{\left(V_{sBE}/V_{sf}\right)^f} \tag{1}$$

where R_a—count rate of the sample (cps), R_b—count rate of the background (cps), ε—counting efficiency, V—volume of the sample in the container vial (l), V_{sBE}—volume of the sample before enrichment (ml), V_{sf}—volume of the sample after enrichment (ml), f— enrichment factor, λ is decay constant for tritium