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Canadian inter-laboratory organically bound tritium (OBT) analysis exercise

S.B. Kim [a, *], J. Olfert [a], N. Baglan [b], N. St-Amant [c], B. Carter [d], I. Clark [e], C. Bucur [f]

[a] CNL, Chalk River Laboratories, Chalk River, Canada
[b] CEA/DAM/DIF- F91297 Arpajon, France
[c] Canadian Nuclear Safety Commission, Canada
[d] Ontario Power Generation, Canada
[e] University of Ottawa, Canada
[f] Cernavoda NPP, Romania

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ABSTRACT

Tritium emissions are one of the main concerns with regard to CANDU reactors and Canadian nuclear facilities. After the Fukushima accident, the Canadian Nuclear Regulatory Commission suggested that models used in risk assessment of Canadian nuclear facilities be firmly based on measured data. Procedures for measurement of tritium as HTO (tritiated water) are well established, but there are no standard methods and certified reference materials for measurement of organically bound tritium (OBT) in environmental samples. This paper describes and discusses an inter-laboratory comparison study in which OBT in three different dried environmental samples (fish, Swiss chard and potato) was measured to evaluate OBT analysis methods currently used by CANDU Owners Group (COG) members.

The variations in the measured OBT activity concentrations between all laboratories were less than approximately 20%, with a total uncertainty between 11 and 17%. Based on the results using the dried samples, the current OBT analysis methods for combustion, distillation and counting are generally acceptable. However, a complete consensus OBT analysis methodology with respect to freeze-drying, rinsing, combustion, distillation and counting is required. Also, an exercise using low-level tritium samples (less than 100 Bq/L or 20 Bq/kg-fresh) would be useful in the near future to more fully evaluate the current OBT analysis methods.

1. Introduction

In many countries, there is increasing concern about the behavior of tritium in the environment and its potential impact on the public. Tritium decays to a stable form of helium by emitting an electron from its nucleus. These emitted beta particles can be a health risk if tritium is taken into the body because, despite their very low energy, these particles possess sufficient energy to ionize atoms and molecules. Tritium can be present in the environment in several forms. It can be gaseous, liquid or included within organic molecules as organically bound tritium (OBT) (Baglan et al., 2013; Korolevych and Kim, 2013; Kim et al., 2014). OBT is one of the important tritium species that can be measured in most environmental samples such as plants, animals and soils (Boyer et al., 2009; Baumgartner et al., 2009; Kim and Korolevych, 2013; Korolevych et al., 2014).

Monitoring of tritium in atmospheric and liquid releases is carried out worldwide, but few countries are measuring OBT in environmental samples. The reason for this is that OBT analysis is difficult and tedious. As a result, very few data are available to develop and validate models of OBT behavior, and this data has considerable uncertainty. Thus, OBT predictions using the current models cannot be tested in absence of quality assured experimental data (Galeriu et al., 2007, 2013).

Within the last decade, there has been more interest in OBT, with a focus on its behavior and also its analysis (Baglan et al., 2013; Galeriu et al., 2013; Kim and Roche, 2013). However, there are currently no certified reference materials (CRM) and no standard methods recommended by the International Organization for Standardization (ISO) for analysis of OBT (Baglan et al., 2013; Kim

* Corresponding author.
E-mail address: sangbog.kim@cnl.ca (S.B. Kim).

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and Roche, 2013; Baglan et al., 2015).

In the past, there have been differences in OBT analysis results between CANDU Owners Group (COG) member facilities (Kim et al., 2009). One possible reason for the discrepancies may be differences in the analytical methods used (Pointurier et al., 2004; Kim et al., 2008; Huang et al., 2014; Thompson et al., 2015). Therefore, a high priority should be given to the development of standard methods for measurement of OBT in the environment. Once the proper measurement methodology is established, then analyses can be performed on different media at different times/locations and better models can be developed.

Inter-laboratory comparisons of OBT analysis within the CANDU community are important and can provide a good opportunity for developing a standard OBT analysis procedure (Workman et al., 2005; Vikis, 2012). The international standard, ISO 5725 (ISO, 1994), which deals with the repeatability and reproducibility of measurements, is related to such inter-laboratory exercises. Repeatability relates to the similarity of independent measurement results obtained for identical test items in the same laboratory by the same operator using the same equipment within short intervals of time. Reproducibility relates to the similarity of measurement results obtained for identical test items in different laboratories with different operators using different equipment (Bartlett and Frost, 2008).

This paper describes and discusses an inter-laboratory comparison study which was conducted over two years in order to help establish a consensus on OBT analysis methods to be used by COG members, based on the end use of the results.

2. Material and methods

2.1. Participants

Eight laboratories participated in this inter-laboratory OBT analysis exercise (Table 1). Six laboratories are in Canada, one is in Romania and one is in France. Four laboratories are members of COG and the others are volunteers.

2.2. Samples for analysis

At the OBT Workshop held at CRL in 2011, three environmental samples were chosen for the comparison by COG members. Table 2 shows all of the information for the samples, which were prepared by CRL. Fish (largemouth bass) was prepared in 2011 and two vegetables (potato and Swiss chard) were prepared in 2012.

Over 20 kg (fresh weight of fish) of largemouth bass (*Micropterus salmoides*) were collected from Maskinonge Lake at CRL according to the animal care protocol. All fish were frozen to remove water residue using a commercial freeze-drying system. Frozen fish were dried using freeze-drying for 2–3 days and oven drying at 55 °C for over 24 h. The average water content of flesh was determined to be 79.1 ± 0.8%. The dried fish flesh was ground using a mixer and packed with a vacuum saver to be distributed to all participants. The prepared fish contained many lipids and proteins, and was visually a greasy powder. Therefore, it was difficult to make homogenized samples.

Table 1
Participants in the inter-laboratory OBT analysis exercise.

Country	Organization	Remarks
Canada	Bruce Power (BP)	COG member
	Canadian Nuclear Safety Commission (CNSC)	Volunteer
	Chalk River Laboratories (CRL)	COG member
	Kinectrics	Volunteer
	Ontario Power Generation (OPG)	COG member
	University of Ottawa (UO)	Volunteer
Romania	Cernavoda NPP (SNN)	COG member
France	Atomic Energy and Alternative Energies Commission (CEA)	Volunteer

Harvested potatoes were stored frozen (−25 °C) in a low background laboratory. The potatoes were then slightly thawed, cleaned and cut. Then, the potatoes were freeze-dried over 3 days (Kim and Roche, 2013) and oven dried at 55 °C for over 24 h. The average water content of potato was determined to be 80.1 ± 0.6%.

Harvested Swiss chard was stored frozen (−25 °C) in a low background laboratory. Tissue free-water was extracted using a freeze dryer (Labconco, USA) over 2 days and oven drying at 55 °C for over 24 h. The average water content of Swiss chard was determined to be 90.7 ± 0.1%.

2.3. Analytical procedures

All participants were requested to perform 5 replicate measurements of OBT in the distributed samples. Each lab analyzed the samples based on their own protocols.

2.4. Consensus OBT values

Consensus OBT values were determined from the individual values using the methodology of the National Institute of Standards and Technology (Roelandts and Gladney, 1998). In order to calculate consensus values, aberrant data are excluded. Following these exclusions, an initial mean and standard deviation (SD) are calculated from the remaining data. Then, any data which is more than two standard deviations from the initial mean is dropped. A final mean and standard deviation are then calculated from the remaining data and are used as the consensus values.

3. Results

3.1. OBT concentration in the fish sample

Eight participants submitted the results of their analysis of the flesh sample (Table 3).

Two participants performed six replicates and two other participants performed four replicates. The other participants performed five replicates. The uncertainty of individual measurements ranged from 1.5% to 8.1%. The uncertainty of repeatability (standard deviation) ranged from 0.8% to 8.5%. The calculated total uncertainty (individual measurement + repeatability) ranged from 3.4% to 11.2%. Lab A did not follow suggested analytical procedures and completed the rinsing process before OBT combustion. Therefore, their values were not included in determining the consensus values. After these exclusions, the initial overall mean and standard deviation were 785 ± 89 Bq/L. Three values from lab H were also dropped as they were more than two standard deviations from the initial mean. The final consensus OBT values based on thirty-two submitted values were 804 ± 65 Bq/L. Fig. 1 graphically shows the results of the inter-laboratory comparison of OBT concentration in the fish sample.

Six laboratory mean values were within two standard deviations of the consensus mean and five were within one standard deviation. The highest laboratory mean was 107.7% of the consensus mean and the lowest was 76.5% of that mean.

3.2. OBT concentration in the Swiss chard sample

Seven participants submitted the results of their analysis of the Swiss chard sample on schedule (Table 4). One participant (Lab E) had issues with their equipment and could not measure the OBT concentration for this sample.