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Efficiencies of Tritium (3H) bubbling systems

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ABSTRACT

Bubbling systems are among the devices most used by nuclear operators to measure atmospheric tritium activity in their facilities or the neighbouring environment. However, information about trapping efficiency and bubbling system oxidation is not accessible and/or, at best, only minimally supported by demonstrations in actual operating conditions. In order to evaluate easily these parameters and thereby meet actual normative and regulatory requirements, a statistical study was carried out over 2000 monitoring records from the CEA Valduc site.

From this data collection obtained over recent years of monitoring the CEA Valduc facilities and environment, a direct relation was highlighted between the 3H-samplers trapping efficiency of tritium as tritiated water and the sampling time and conditions of use: temperature and atmospheric moisture. It was thus demonstrated that this efficiency originated from two sources. The first one is intrinsic to the bubbling system operating parameters and the sampling time. That part applies equally to all four bubblers. The second part, however, is specific to the first bubbler. In essence, it depends on the sampling time and the sampled air characteristics. It was also highlighted that the water volume variation in the first bubbler, between the beginning and the end of the sampling process, is directly related to the average water concentration of the sampled air. In this way, it was possible to model the variations in trapping efficiency of the 3H-samplers relative to the sampling time and the water volume variation in the first bubbler.

This model makes it possible to obtain the quantities required to comply with the current standards governing the monitoring of radionuclides in the environment and to associate an uncertainty concerning the measurements as well as the sampling parameters.

1. Introduction

Tritium is the natural radioactive isotope of hydrogen. It is therefore able to integrate any environmental medium under various chemical species (Diabaté and Strack, 1993), starting with tritiated water (HTO), its most common species (Jacobs, 1968; UNSCEAR, 2008; Weaver et al., 1969), and tritiated hydrogen (HT), usually present in the vicinity of tritium-emitting facilities (Philippe and Besnus, 2010). In surroundings of plants that emit tritium, organic forms of tritium are also commonly observed (see for example Le Goff et al., 2016 for terrestrial ecosystems, Eyrolle-Boyer et al., 2015 for aquatic continental ecosystems or McCubbin et al., 2001 for marine ecosystems) as a result of integration of tritium by living organisms in their own matter during their metabolisms.

Nuclear plants that emit tritium into the environment usually do either as HTO in their liquid effluents, so that it can be quickly diluted, or as HT or HTO in their gaseous effluents (Philippe and Besnus, 2010). In the latter case, given the very high mobility of such states in the atmosphere (Jacobs, 1968; Murphy, 1990; NCRP, 1979), operators monitor the impact of their discharge on their nearby environment (see (Devin and Deguette, 2010; Guétat et al., 2013) for example).

Whether measuring ambient working conditions in the facilities, air emissions or the environmental impact, nuclear operators have different means at their disposal to measure atmospheric tritium (Belovodski et al., 1985; Vogl and Gesewskv, 2012; Wood et al., 1993):

- Direct measurement of the β radiation of tritium in the atmosphere using gaseous counters (Osborne and Coveart, 1977), i.e. large circulation chambers, without discriminating the HT and HTO species, for concentration activity over 5 $kBq \cdot m^{-3}$
- Trapping atmospheric water vapor in dry traps (silica gel (Iida et al., 1995; Patton et al., 1997), zeolites (Caldeira Ideias et al., 2017; Momoshima et al., 2007; Okai and Takashima, 1989; Uda et al., 2006) or on cold spots (Phillips and Easterly, 1982; Tircot, 1982), in order to measure tritium activity in its HTO state;
- Isotopic equilibrium of initially non-tritiated water as is the case in

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bubbling systems (AFNOR, 1999; Osborne, 1973).

The last technique is certainly the most common, because of its simplicity of operation, the ability of most bubbling systems to discriminate between several chemical species of tritium (HTO and HT at least), its low decision threshold and the good repeatability of results. Nevertheless, bubbling is inconvenient because sampled tritium gets diluted in the exchange water (Belovodski et al., 1985). As a consequence, in the case of very low atmospheric activity such as environment monitoring, the activity in the bubbler water is often below the usual detection limits, including those obtained through the measurement technique of liquid scintillation with low background. Similarly, the tritium trapping efficiency of these systems as well as the uncertainty due to this sampling technique are put into question.

In order to address such questions and bring forth solutions making it possible to express atmospheric tritium activity even if one bubbler shows concentration activity lower than the detection limit, records were analysed from several years of monitoring of atmospheric tritium at the facilities of the CEA Valduc site (Burgundy, France) as well as at its environmental stations located around the site.

2. Material and method

The CEA Valduc uses the same tritium sampling devices by bubbling, hereinafter designated as 3H-Samplers, to monitor tritium emissions into the atmosphere and measure its environmental impact. 3H-Samplers are used to sample tritium from the atmosphere, discriminating its water vapor species (HTO) from other chemical species, of which the HT species is considered the most common (IRSN/DEI, 2010). The other species, such as CH_3T, T_2O, T_2 or Organically Bound Tritium, may also exist in proportions we shall consider here as negligible (Belot et al., 1996).

2.1. Tritium sampling system

The 3H-Samplers used to monitor tritium emissions (SDEC, 2005–2014) are set up inside the facilities, near the emitting channel in order to sample gas flowing through the stack, using a sampling pipe.

The 3H-Samplers used to monitor the environment are identical. They are set up inside the sampling stations situated within a perimeter less than or equal to 7 km around the emitting channels of the Valduc site. The room temperature inside the sampling stations is regulated to (23 ± 6) °C. Ambient air sampling is done by means of a sampling head located at 1 m above the roof ridge, i.e. 3 m above the ground. The sampling heads are adapted to the local climatic conditions. They guarantee the non-contamination of samples by the rain and prevent the risk of the sampling lines freezing during winter.

Fig. 1 shows the flow diagram of the 3H-Samplers deployed. 3H-Samplers consist of:

- four trapping bubblers for atmospheric tritium $B_{i=1,\ 2,\ 3\ and\ 4}$,
- an alumina-supported palladium oxide catalytic furnace to convert other species of tritium into HTO,
- an airflow system composed of a dust filter, a controlled flow pump, a mass flow meter and four bubble generators $Bg_{i=1,\ 2,\ 3\ and\ 4}$,
- a bubbling water cooling system and
- a LCD display of sampled air volume, flow rate, cooling and furnace temperatures, in real time.

There are two distinctive sampling units. The first one is specific to the HTO tritium species. It consists of bubblers B1 and B2. The second one consists of bubblers B3 and B4. It traps the residual HTO species not collected by the first sampling unit and the HT converted into HTO by the furnace.

Under normal operating conditions, the four trapping bubblers are hermetically isolated from the ambient air of the room where the 3H-Samplers is set up. Each trapping bubbler contains a reference water volume V_{ref}. The average of V_{ref} is equal to (165 ± 2) mL (k = 2). In this study, the reference water is Volvic mineral water (below 5 $Bq{\cdot}L^{-1}$ of tritium) cooled to a temperature ranging from 3 to 7 °C. The air volume in the trapping bubbler atmosphere is in the range of 100 mL. The dust filter upstream blocks out solid aerosols with a particle size above 4 μm until 2007 and above 11 μm from 2008. The mass flow meter is calibrated annually according to ISO 10780 standard (ISO, 1994). The pump downstream samples the ambient air, of which the moisture rate H% varies with the seasonal climatic conditions. The system enables a wide range of flow rates, ranging from 10.0 $L{\cdot}h^{-1}$ to 120$L{\cdot}h^{-1}$. Under normal operating conditions, the ambient air flow Φ flowing through the trapping bubblers is 30.0 $L{\cdot}h^{-1}$ with a tolerance of 10% and the temperature setting of the catalytic furnace is 450 °C.

The distance covered by the bubbles from the generator to the interface with the trapping bubbler atmosphere depends on the water volume when the bubbles are emitted. When the water volume is nominal (i.e. equal to V_{ref}) the working distance covered by the bubbles is around 7 cm. The clearing height, i.e. the water height under the bubble generator, is around 2 cm. During normal operation, the minimum working water height is not tolerated below 4 cm. Under these conditions, the minimum volume V_{min} will be around 90 mL. Besides, the bubbler design implies a maximum volume V_{max}. In our case, this maximum volume is 220 mL.

Fig. 2 shows the flow diagram of the series connection of the two 3H-Samplers used to determine furnace oxidation efficiency. This experiment determines the furnace oxidation efficiency by subjecting the residual HT species at the output of the first 3H-Samplers to a second oxidation process, supposing the two furnaces were built identically. Bubblers B3, B4, B5 and B6 then collect the HT tritium species turned to HTO and the residual tritium species as HTO species not collected by bubblers B1 and B2. After going through the second oxidation furnace (Furnace 2), bubblers B7 and B8 collect the HT species, oxidized in Furnace 2, as well as the residual HTO part not collected by the upstream bubblers.

This system made it was possible to conduct two experiments at the facility under normal sampling conditions, over a period of 7 days in 2013.

2.2. Origin and treatment of data

2.2.1. Trapping efficiency

The data used to determine the tritium trapping efficiency in bubbling water were extracted from the CEA Valduc site facilities monitoring of air emissions and environmental monitoring.

Data concerning the facilities were acquired in the time period of 2005–2015. Data concerning the environment were acquired in the time period of 2008–2015. The data retained for this study were selected under the following pertinence criteria:

- sampling times between 5 and 15 days,
- air sampling rates at (30.0 ± 0.8) $L{\cdot}h^{-1}$,
- significant concentration activity values for bubblers B1 and B2, with expanded relative uncertainties, at a 95% confidence level, strictly under 15% for facilities data and strictly under 20% for environmental data.
- concentration activity values for bubblers B2 and B4, respectively lower, taking into account uncertainties of measurement, than the concentration activity values for bubblers B1 and B3.

This sorting method has selected 2085 of 2613 experimental values from the facilities and 90 of 1528 experimental values from the environment. The vast majority of rejections among the environmental values is explained by uncertainties greater than the selection criteria because there is often very low activity levels in the samples from bubblers B3 and B4.