ENVIRONMENTAL MONITORING FOR TRITIUM AT TRITIUM SEPARATION FACILITY

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ABSTRACT

The Cryogenic Pilot is an experimental project in the nuclear energy national research program, which has the aim of developing technologies for tritium and deuterium separation by cryogenic distillation. The experimental installation is located 15 km near the highest city of the area and 1 km near Olt River. An important chemical activity is developed in the area and the Experimental Cryogenic Pilot’s, almost the entire neighborhood are chemical plants.

It is necessary to emphasize this aspect because the sewerage system is connected with the other three chemical plants from the neighborhood. This is the reason that we progressively established elements of an environmental monitoring program well in advance of tritium operation in order to determine baseline levels.

The first step was the tritium level monitoring in environmental water and waste water of industrial activity from neighborhood. In this work, a low background liquid scintillation is used to determine tritium activity concentration according to ISO 9698/1998. We measured drinking water, precipitation, river water, underground water and waste water. The tritium level was between 10 TU and 27 TU that indicates there is no source of tritium contamination in the neighborhood of Cryogenic Pilot. In order to determine baseline levels we decide to monitories monthly each location.

In this paper a standard method is presented which it is used for tritium determination in water sample, the precautions needed in order to achieve reliable results, and the evolution of tritium level in different location near the Experimental Pilot Tritium and Deuterium Cryogenic Separation.

1 INTRODUCTION

There are several aspects related to the topic of tritium in the nuclear fuel cycle: e.g. its source, its behavior when released to the environment, its management, conditioning, storage and disposal. Nuclear power plant and fuel reprocessing facilities are the major sources of tritium release to the environment, and with the continuing development of nuclear power, increasing attention will be given to improved treatment method for the tritium. The amount of tritium that will be produced and handled in future fusion reactors is several orders of magnitude greater than that produced during the generation of an equivalent amount of energy from fission reactors. Much of the technology now being developed for handling tritium produced by fission reactions will be applicable to fusion installations.

The Cryogenic Pilot is an experimental project in the nuclear energy national research program, which has the aim of developing technologies for tritium and deuterium separation...
by cryogenic distillation. The process, used in this installation, is based on a combined method for liquid-phase catalytic exchange (LPCE) and cryogenic distillation. In the liquid-phase catalytic exchange tritium transfer process the isotopic exchange reaction is carried out between liquid water and deuterium gas rather than water vapor. The use of a hydrophobic catalyst developed in our institute [1] enables the reaction to be carried out using liquid water, thus providing a counter-current process and avoiding the necessity of evaporation, superheating and condensation of the feed. The tritiated deuterium is purified by the removal of oxygen, nitrogen and other gaseous impurities and is then fed to the cryogenic distillation system using nitrogen and hydrogen like refrigeration agents. The detritiated deuterium gas from the first cryogenic distillation tower is recirculated to the LPCE front-end. Concentrated tritium is bled off periodically from the bottom of the last distillation tower and packaged for storage or disposal. In this process concentrated tritium is handled in its elemental state and the maximum tritiated water concentration handled is that of the heavy water feed. Total radioactive source, for normal working conditions, is contained in installation and it is equal with tritium inventory of process fluid. There are two ways that Cryogenic Pilot can interact with the environment: by atmospheric release and by sewage.

Until now, the simulation of the process described above was made with heavy water, but now we intend to fulfill the exigency of national regulations for nuclear facilities. This is the reason that we progressively established elements of an environmental monitoring program well in advance of tritium operation in order to determine baseline levels. The first step was the tritium level monitoring in environmental water and wastewater of industrial activity from neighborhood.

In this paper is presented standard method used for tritium determination in water sample, the precautions needed in order to achieve reliable results, and the evolution of tritium level in different location near the Experimental Pilot Tritium and Deuterium Cryogenic Separation.

2  LOCATION AND SAMPLING POINTS

The Experimental Cryogenic Pilot is located 15 km near the highest city of the area and 1 km near Olt River, it is shown in Fig.1. An important chemical activity has developed in the area and almost all the neighbors of the Cryogenic Pilot are chemical plants. It is necessary to emphasize this aspect because the sewerage system is connected with the other three chemical plants in the neighborhood. Ground water flow is generally towards the river and liquid discharges are made into a drainage system which ultimate discharges into the river.

Olt River supplies water, needed in chemical processes, after a special treatment of purification. There are two sampling points, S1 and S2, upstream of chemical plants and passing the utility of water purification outflow respectively. The wastewater of industrial activity from neighborhood was surveyed by sampling points, S3 to S6, which are the entrance and the output of sewage on their territory. The sampling point S7 is one of the most important sampling points because this is the place were all sewage of chemical plants, including that from our Cryogenic Pilot, are collected. Other two sampling points were established after sewage treatment outflow of water utility, S8, and downstream of ultimate discharge point, S9. These are sampled monthly to measure tritium concentration.
Drinking water in the neighborhood, including the water from our Institute (D1 to D5), is supplied by a spring located 10 km far from the studied area. Lined boreholes pass through the sub-surface layer into the aquifer, which drains the area. The depth is approximately 6m and the water table is generally 1 to 2m below ground level. These are sampled quarterly for tritium.

Sampling of precipitation was made on a monthly basis in container avoiding the evaporation for tritium analysis. At the end of the month the container was shaken thoroughly and a sample of 1 liter was taken to measure in Tritium Laboratory.

3 MATERIALS AND METHODS

The specific activity of natural water samples is so low that to obtain accurate measurements any counting system must have a high and stable overall efficiency for the detection of low energy $\beta$ particles together with a low and stable background. In this work, a low background liquid scintillation system detector, Quantulus 1220 is used to determine tritium activity concentrations in water samples. The detector system background is reduced by placing a passive shield (made of lead, cadmium and copper) and an active shield (based on mineral oil scintillator) around the vial chamber. A computer is used to operate the system, to store and manipulate the resulting spectra.

It is a great advantage in low level counting to prepare unknown, references and background samples in the same way so as to maintain equal quench levels. In counting $^3$H water samples, distillation is an appropriate method to achieve uniform quenches level. There are two published standard methods for tritium measurement in water sample, one by International Standard Organization [2] and the other by APHA, AWWA and WEF in a standard collection [3] for the examination of water and wastewater. Basically the principle is the same. There are small differences between the two chemical treatments of water samples,
but the goal is to hold back most quenching materials by alkaline distillation, as well as radioiodine and radiocarbon.

There are a number of events, mainly originated during sample preparation, that interfere in liquid scintillation counting such as chemiluminiscence and photo-luminescence [4]. These interference must be corrected for soft beta-emitters such as tritium because they overlap its spectrum and produce false counts. This was confirmed for our counting conditions (Fig. 3).

![Figure 2: Tritium and chemiluminescence spectra for a natural water sample](image)

Water moves underground, and its salt of mineral contents is determined by all the soil and rock types it passes through. In our case, samples contain water with various constituents. All samples were prepared according to the two studied standards, and we observed at least two other parameters that were important for good scintillation measurement, pH and conductivity (table 1).

Mixing 8 mL water with 12 mL HiSafe 3 scintillation cocktail normally produces optimal figure of merit $EV/\sqrt{B}$ for lowest limit of detection. HiSafe 3 cocktail can well be used with standard polyethylene vials, for long time of counting, in our case 1000 min. Using those time of measurement, we were constrained to use ISO standard method that need a few hours waiting in the counter. The APHA – AWWA – WEF method provide better values for pH and conductivity, but the sample need at least 24 hours waiting period for a good stability of the measurement. The specific conditions used in our laboratory were: 20 mL polyethylene vial, OptiPhase HiSafe 3 scintillation cocktail, 8:12 mL ratio water: scintillate, 1000 minutes counting time, and a low limit of detection according to ISO standard method of 8,4 TU with 0,77 CPM background and efficiency of 24.37%.

<table>
<thead>
<tr>
<th>Water sample</th>
<th>Initial pH</th>
<th>pH*</th>
<th>pH**</th>
<th>Initial conductivity [µs/cm]</th>
<th>Conductivity* [µs/cm]</th>
<th>Conductivity** [µs/cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation 1</td>
<td>7.22</td>
<td>6.28</td>
<td>6.89</td>
<td>18.5</td>
<td>2.9</td>
<td>1.4</td>
</tr>
<tr>
<td>Precipitation 2</td>
<td>7.18</td>
<td>6.38</td>
<td>6.94</td>
<td>47</td>
<td>2.3</td>
<td>1.8</td>
</tr>
<tr>
<td>Precipitation 3</td>
<td>7.30</td>
<td>6.18</td>
<td>7.01</td>
<td>34</td>
<td>2.1</td>
<td>1.7</td>
</tr>
<tr>
<td>River water S1</td>
<td>7.52</td>
<td>6.66</td>
<td>6.84</td>
<td>210</td>
<td>2.7</td>
<td>1.9</td>
</tr>
</tbody>
</table>
3 RESULTS

The input data, for every environmental tritium study, is precipitation. The tritium concentrations in precipitation before 1951 were estimated from 4 to 20 TU in the northern hemisphere [4]. The local tritium contents vary according to the distance from coast line and local temperature. Since large quantities of anthropogenic tritium first entered the water cycle in 1953, precipitation has contained concentrations of tritium that have been above the natural levels that existed prior to 1953. This value decreased rapidly following the enactment of the atmospheric test ban treaty [Fig. 3].

\[
\begin{array}{|c|c|c|c|c|c|c|}
\hline
 & 0 & 1 & 2 & 3 & 4 & 5 & 6 \\
\hline
\text{River water S2} & 7.84 & 6.51 & 7.07 & 220 & 2.3 & 1.8 \\
\text{River water S9} & 7.83 & 6.59 & 6.89 & 212 & 2.1 & 1.5 \\
\text{Wastewater S3} & 7.42 & 6.71 & 6.93 & 320 & 2.3 & 1.8 \\
\text{Wastewater S4} & 7.67 & 6.63 & 6.87 & 318 & 2.6 & 1.7 \\
\text{Wastewater S5} & 7.44 & 6.67 & 6.98 & 324 & 2.2 & 1.6 \\
\hline
\end{array}
\]

* after ISO distillation;
** after APHA-AWA-WEF distillation.

The tritium concentrations in precipitation vary seasonally with a maximum in late spring-early summer and a minimum in winter due to intense mixing across the tropopause level during the spring time. This tendency is recorded in measured precipitation at Cryogenic Pilot (Fig.4), with a minimum in March (9.7 ± 2.2 TU) and a maximum in June (27.1 ± 2.5 TU).

The same variation is in the river water, and it is illustrated in Fig.5, for the same period of sampling in S1 and S9 location. The minimum value (March, 14.9 ± 2.3 TU) and maximum value (June, 26.5 ± 2.5) are usually tritium contents in the surface water.
Sampled wastewater, for the chemical plants, shows the same variation of tritium content like river water (Fig.6). Small differences are in the range of reported uncertainty.

Tritium content in drinking water is lower than in surface water, which it is expected due the nature of the spring that has underground water in composition (Fig.7). The maximum value recorded is one month later than precipitation (July, 22.4 ± 2.3 TU).
The underground water had a very low tritium concentration, much lower than the limit of detection of Quantulus 1220. There is now a system for tritium electrolytic enrichment under construction.
4 CONCLUSION

The results of monitoring show that there is no source of tritium contamination in the neighborhood of Cryogenic Plant. Drinking water, precipitation, river water and wastewater present tritium values that are in natural range. Tritium level was between 10TU and 27TU, with a mean of the six months of observations around 22.6TU.

REFERENCES