Pure Beta Emitters in Water Samples from Neutron Irradiation Facilities: Activity Determination Via Vacuum Distillation and Liquid Scintillation Counting


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Abstract—In the decommissioning of nuclear facilities, it is necessary to assess the radioactivity inventory for waste classification and management. For nuclear fusion experiments or accelerator-driven neutron sources, the main contribution to the radiological inventory comes from activation products and tritium. When water is used as coolant of components, it may be activated by neutrons with the consequent production of tritium, and short-lived oxygen and nitrogen isotopes. In most cases several chemical elements may be in solution or suspension in water, because of metallic pipes corrosion when occurring, or functional reasons, e.g. chemical conditioning, addition of antifreeze agent, etc. In this case other activation products could be present and need to be characterized. In this case study, a sample of the coolant of the ENEA Frascati Neutron Generator (FNG) has been radiologically, chemically and physically characterized. In such a facility, during the operation, a beam of deuterons is accelerated up to 300 keV and impacts on a tritiated target for producing 14 MeV neutrons exploiting the fusion reaction T(d,n)α. To avoid overheating in the area around the target, a water-cooling loop is used. After several years of operation, a sample of the fluid has been extracted to undergo a qualitative and quantitative analysis of the radionuclides inventory. Gamma spectrometry has not shown any presence of gamma emitters. On the other hand, Liquid Scintillation Counting (LSC) has provided evidence of the presence of beta emitters. It is known that tritium is expected to occur in the sample because of releases from the tritiated titanium target. This work concerns the development of a method to discriminate the tritium contribution with respect to the total beta activity within the FNG coolant. Since it is known that an unspecified percentage of an unknown anticorrosive agent was added to the water coolant, vacuum distillation has been used to extract purified water (containing only tritium) from the coolant sample leaving any (activated) non-volatile compound in the undistilled fraction. After distillation, any fraction has been investigated by Raman spectroscopy, to determine: a) the chemical composition of the colored anticorrosive agent, b) the efficiency of the separation. Afterwards, both fractions have been analysed by means of LSC, and results showed that the main contribution to sample activity is due to tritium and the activity values are consistent with the theoretical H atomic concentration in both fractions.

Keywords — Liquid Scintillation Counting, Tritium, distillation, neutron generator

I. INTRODUCTION

During the decommissioning of a nuclear facility, it is necessary to determine the activity of various radionuclides to assess the total radiological inventory. In nuclear fusion experiments with accelerator-driven neutron sources, the main contribution to the inventory comes from activation products and tritium [1]. When water is used as a coolant for components, it could be activated by neutrons, resulting in the production of tritium and short-lived isotopes of oxygen and nitrogen, or contaminated by gaseous tritium that has a high capacity to permeate through metals. Additionally, various chemical elements may be present in solution or suspension in water due to potential corrosion of metallic pipes or for functional reasons, such as chemical conditioning or the addition of refrigerant agents. It is crucial to find a simple and convenient way to assess the contribution of tritium with respect to any other radionuclides when advanced technologies and equipment are not available.

Among the various techniques used for tritium separation from aqueous solutions, the easiest and most inexpensive method is the vacuum distillation [2]. In this study, a sample of water from the ENEA Frascati Neutron Generator (FNG) cooling system was analyzed. Specifically, this work illustrates a method for discriminating the contribution of tritium from the total beta activity of the FNG cooling water.

II. MATERIALS AND METHODS

FNG target consists of a 50 mm diameter copper plate with a titanium substrate on which tritium is adsorbed. During operations, a beam of deuterons impacts on the tritiated surface to produce 14 MeV neutrons through the fusion reaction T(d,n)α. To prevent overheating of the target, a 150-liter water cooling loop is used. A simplified scheme of the circuit is shown in Fig.1. An unspecified percentage of a colored anticorrosive agent was added to the cooling water. The formulation of this additive was initially unknown. After 30 years of operation without changing or refilling the water, a sample was collected and characterized through qualitative and

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quantitative analyses of the chemical content and radionuclide inventory.

Before any treatment, a preliminary non-destructive analysis through low-background gamma spectrometry on the original sample was performed to quantify, if present, gamma emitter radionuclides. The sample was then analyzed to determine the composition of the colored anticorrosive agent, considering parameters such as alkalinity, viscosity, refrigeration power, and water miscibility. These characteristics led to consider the presence of diols in the sample. To confirm this hypothesis, the sample was initially subjected to a vacuum distillation to obtain a complete separation of the sample into water and colored anticorrosive agent residue. The determination of the density of the residual sample, compared with the mixture before distillation, allowed to characterize the colored anticorrosive agent and its percentage in the aqueous mixture. Raman analysis was performed to determine the chemical composition of the anticorrosive agent. LSC analysis on both fractions, distilled water and residue, was then carried out to assess the radioactivity distribution after distillation.

To investigate the nature of the anticorrosive agent used in the FNG cooling circuit and the quantity added to the water to obtain the coolant solution, the following steps were followed. A sample of the coolant solution was taken and weighed using an analytical balance. Additionally, the volume of the sample was measured with a calibrated pipette. Twenty measurements were performed to obtain a statistical average. The sample was then subjected to distillation using the distillation apparatus shown in Fig. 2, where a refrigerant cooled the water to 4 °C through a chiller. During distillation, the system was connected to a vacuum pump.

After distillation, both the distilled sample and the residue (anticorrosive agent) were weighed using the analytical balance. The volume was measured again using calibrated pipette. Again, twenty samples were taken, and a statistical average was calculated.

To evaluate the nature of the anticorrosive agent, both the distilled fraction and the residue were analyzed using a Raman spectrometer with a laser source at 535 nm coupled with a fiber optic probe. To quantify the beta activity concentration in the sample, both before and after distillation, a Hidex 300SL LS counter was used. A volume of 1 ml of each sample was diluted in 4 ml of distilled water, mixed with Ultima Gold AB scintillation cocktail in a 20 ml glass vial, and then counted for 3600 s. To evaluate any possible interference caused by the blue coloration of the sample in LSC measurements (color quenching), a preliminary study on the original sample was performed, using hydrogen peroxide as bleaching agent [ref] and carrying out LSC analysis on bleached and unbleached samples.

III. RESULTS AND DISCUSSION

A. Density evaluation

In Table I results from density evaluation are reported. The density of the original sample (1.063 g/ml) is consistent with the hypothesis that ethylene glycol was the anticorrosive agent, with a concentration of 40% by weight.

<table>
<thead>
<tr>
<th>Density (g/ml)</th>
<th>Before distillation Sample (water + anticorrosive agent)</th>
<th>1.063 ± 0.007</th>
</tr>
</thead>
<tbody>
<tr>
<td>After distillation</td>
<td>Transparent distilled fraction (water)</td>
<td>1.003 ± 0.007</td>
</tr>
<tr>
<td></td>
<td>Blue undistilled fraction (anticorrosive agent)</td>
<td>1.108 ± 0.003</td>
</tr>
</tbody>
</table>

B. Raman analysis

Raman spectra were performed on the different fractions of the distillation: the distilled fraction and the residue. We can assert
that the distillation was complete, and that the anticorrosive agent was definitely ethylene glycol. In fact, from the blue line in Fig. 3 the typical Raman spectrum of ethylene glycol (residue of the distillation) is observed while the red line highlights the typical Raman spectrum of water (distilled fraction). In Fig. 4-5 the spectra of pure substances ethylene glycol and distilled water are shown as reference. Therefore, the Raman analysis combined with density data confirms that the anticorrosive agent was ethylene glycol.

C. Activity evaluation through LSC

Before carrying out the LSC analysis, low-background gamma spectrometry was performed, and no gamma emitters were detected above the minimum detectable activity (about 0.02 Bq/ml).

Fig. 6 shows LSC spectra from HIDEX 300SL obtained in the preliminary study on the influence of the blue coloring of the sample before and after the bleaching with hydrogen peroxide. These graphs and activity evaluation are consistent within the uncertainty range, as shown in Table II, indicating that the blue coloration of the sample does not affect liquid scintillation results. In fact, the absorption of light photons by the blue solution occurs in the range from 490 nm to 800 nm, as shown by further analyses through UV-Vis spectrophotometer (Fig. 7). The region of greatest interest for LSC is between 300 nm and 400 nm, and it does not overlap with the sample absorption region.

![Fig. 3. Raman spectra: A) the blue line is undistilled fraction (anticorrosive agent), B) the red line is the water fraction.](image1)

![Fig. 4. Raman spectrum of pure ethylene glycol [3]](image2)

![Fig. 5. Raman spectrum of distilled water [4]](image3)

![Fig. 6. LSC spectra for bleached and unbleached sample](image4)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activity concentration (Bq/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unbleached sample</td>
<td>334 ± 53</td>
</tr>
<tr>
<td>Bleached sample</td>
<td>336 ± 51</td>
</tr>
</tbody>
</table>

![Fig. 7. UV-Vis spectra for bleached and unbleached (colored) sample](image5)
In Table III results from LSC analysis before and after distillation are reported.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activity concentration (Bq/ml)</th>
<th>Theoretical H atomic concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original sample</td>
<td>334 ± 53</td>
<td>64.1%</td>
</tr>
<tr>
<td>Transparent distilled fraction (water)</td>
<td>330 ± 50</td>
<td>66.7%</td>
</tr>
<tr>
<td>Blue distilled fraction (anticorrosive agent)</td>
<td>315 ± 47</td>
<td>60.0%</td>
</tr>
</tbody>
</table>

*evaluated considering an ethylene glycol concentration of 40% w/w

LSC outcomes suggest that the measured activity in the original sample is mainly due to tritium. The activity concentration of the distilled fraction (purified water) containing only tritium is in fact consistent with the theoretical H atomic concentration in the undistilled fraction and in the original sample.

IV. CONCLUSIONS

A rapid method to discriminate tritium content with respect to the total beta activity in water mixture, used as coolant of components operating in neutron fields, was established, by using a simple distillation apparatus. Several analyses were performed to assess the radionuclide content of the sample taken from the coolant of the Frascati Neutron Generator. First result seems to confirm that the main contribution is due to tritium. Since no complete radiochemical separation has been carried out and beta energies cover a broad region, it is not possible to discriminate among contributions from different beta emitters. For these reasons the presence of traces of other beta emitting radionuclides cannot be completely excluded.

REFERENCES