

TRITIUM DETERMINATION IN WATER

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Abstract. An analytical procedure for the determination of tritium in water is described in this paper. The determination is carried out in presence of other radionuclides, such as Fe-55, Ni-63, Mn-54, Zn-65, Co-60, Cd-109, Sr-90, Cs-134 and Cs-137. The method consists in a simple distillation stage prior to measurement by liquid scintillation counting. The samples containing beta and gamma emitters are conditioned with a $(\text{NO}_3)_2\text{Pb}$ solution and $\text{Na}(\text{OH})$ up to $\text{pH} = 7 - 8$. This produces lead hydroxide precipitation that allows fixing volatile elements, which could be transported together with tritium, and may increase the extinction degree of the sample or interfere with the counting process. Special attention must be paid if presence of Fe-55 ($E_{\text{max}} \sim 5.95 \text{ keV}$) is suspected as it might not be distinguished from tritium ($E_{\text{max}} \sim 18 \text{ keV}$), leading to an overestimation of tritium activity. Different tests were carried to obtain the optimum method conditions, to achieve the purification of the tritium and a pH near to 7 in the distilled. The detection limit (2σ) was 8.0 Bq/l and the distillation performance was 98.3% . This technique was applied to water samples containing Fe-55 and other gamma radionuclides in 1M hydrochloric acid media in successive Environmental Measurements Laboratory (EML), U.S. Department of Energy (DOE) intercomparison programs. The results obtained were very satisfactory and are presented in this paper.

KEYWORDS: *distillation, tritium, method.*

1. Introduction

Tritium (H-3) is mainly produced in PHWR reactors by neutronic activation of deuterium of heavy water moderator and coolant system. During normal operation some of the H-3 is released into the environment through liquid and gaseous discharges. Nuclear Regulatory Authority (ARN) performs analysis of H-3 on environmental samples from superficial and ground waters and also samples from liquid and gaseous discharges of nuclear power plants.

When large amounts of beta and gamma emitters are present in the samples, they could interfere in the H-3 measurement and it becomes necessary to distillate the sample to remove them. Under certain conditions, some elements could be transported to the distillate, especially when the distillation process reaches its final stage (dry), resulting in an inefficient separation. For example, when Fe is in hydrochloric acid media, the alkalization of the sample does not totally prevent Fe from passing to the distillate. However, the presence of Fe-55 in the distillate interfere in the H-3 measurement, due to its low energy ($E_{\text{max}} \sim 5.95 \text{ keV}$). Therefore it would be overlapped in the H-3 spectrum, increasing erroneously the counting.

The objective of this paper is to optimize the distillation process in order to achieve an adequate separation of H-3 from other volatile elements, adjusting work conditions in order to obtain a distillate with an adequate pH (within 7).

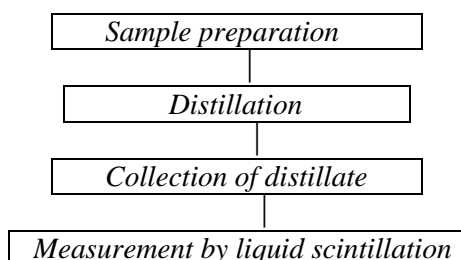
Several samples arising from the intercomparison exercises programs organized by EML contained some beta emitters. These samples were submitted to the distillation process and the absence of beta emitters was then confirmed in the distillate.

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2. Experimental stage

Tritium determination was carried out by following the scheme shown in Figure 1. The samples were finally measured in a Perkin Elmer Tri Carb 2770 TR / SL liquid scintillation equipment.

Figure 1: Scheme of the complete procedure



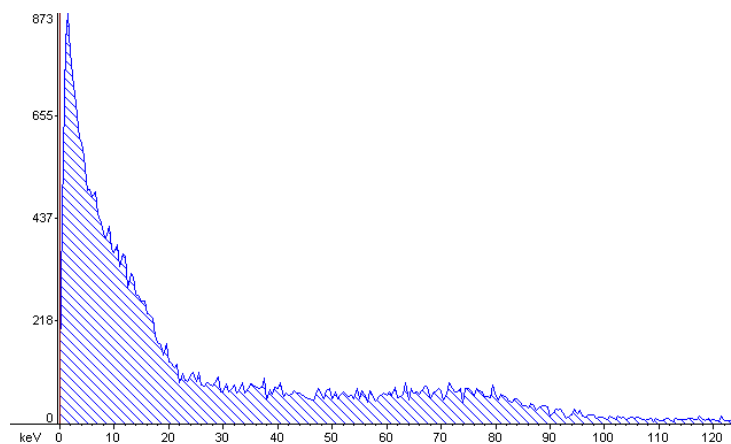
A batch of samples was prepared in 1M HCl media containing known and similar activities of H-3 and Fe-55. After that, the addition of 11,6 g of 5M Na(OH) and 20 g of Pb(NO₃)₂ was carried to reduce the alkali excess, forming a Pb(OH)₂ white precipitate. Finally, the distillation was performed up to dryness. The endpoint was indicated by the formation of PBO, a yellow precipitate [1-2].

Once the distillate was obtained, the final liquid was weighted and a 10 g aliquot was taken into a polyethylene vial containing 10 ml of Insta Gel XF as scintillation cocktail. The vials were left in darkness during 30 minutes and then measured during 150 minutes according to a predetermined protocol.

3. Measurements by liquid scintillation counting

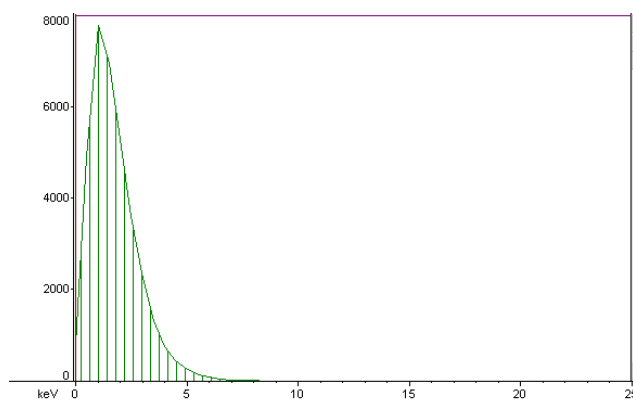
The sample spectrum (window from 0 to 120 keV) containing H-3 and several beta and gamma emitters (such as: Fe-55, Ni-63, Mn-54, Zn-65, Co-60, Cd-109, Sr-90, Cs-134 y Cs-137) is shown in Figure 2.

Figure 2: Spectrum obtained in a direct measurement of an intercomparison water sample



After the distillation, the sample spectrum can be observed in Figure 3.

Figure 3: Spectrum obtained by liquid scintillation, with previous distillation, of the same intercomparison water sample.



The results of H-3 recovery assays and the Fe-55 retention tests are shown in Table 1:

Table 1: Retention of H-3 and the retained amount of F-55 in the distillations

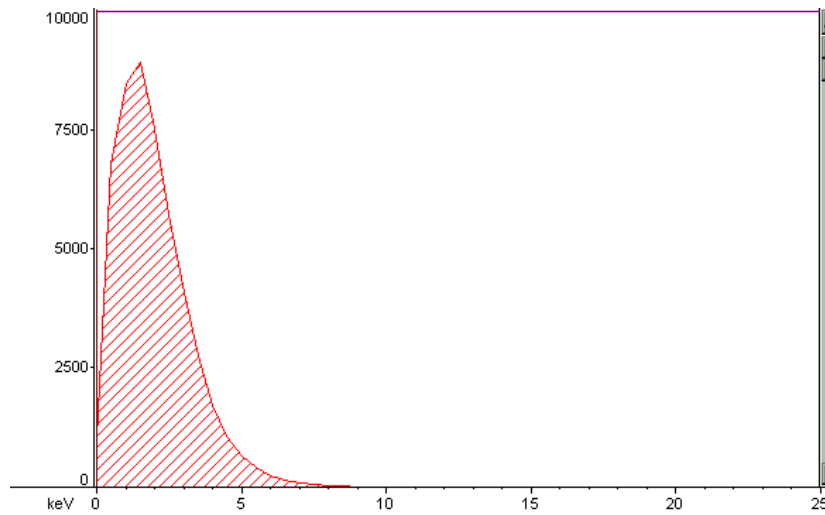
Number	H-3 Recovery (%)	Fe-55 Retention (%)
1	96.27	104.43
2	100.87	98.33
3	97.66	98.68
4	100.44	92.79
5	96.56	96.72
6	101.75	103.21
7	95.62	100.59
8	95.75	93.97
9	96.50	100.04
10	101.80	100.96

The average obtained was 98.3 % for tritium retention, with a $\sigma = 2.6$ %, whereas for Fe-55 retention, the average result was 99 % with a $\sigma = 3.7$ %.

In order to determine the distillation efficiency, several parameters were controlled, such as distillation time, boiling time, appearance of first drop of distillation and final volume collected.

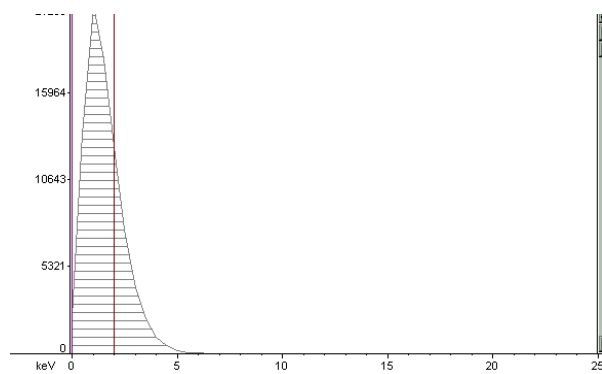
Figure 4 shows one of the spectra obtained in the recovery tests.

Figure 4: Distillation efficiency. Spectrum obtained according to the specified work conditions.



In Figure 5, it is shown a spectrum of Fe-55 (distillate waste), after the distillation of the sample, according to the mentioned conditions.

Figure 5: Fe-55 retained in the distillation flask. Spectrum obtained according to the work conditions.



The initial distilled quantity was 50 g. The measurements were performed in a Perkin Elmer Tri Carb 2770 TR / SL Packard Liquid Scintillation Analyzer Equipment, with a measure efficiency of 20 % in the 0 - 5 Kev region. Finally, a curve of extinction with 10 points was performed in order to determine the activity.

4. ARN results in the Quality Assurance Program of EML (QAP-DOE)

The technique described above was applied to samples from the Quality Assurance Program of EML (DOE), in which the ARN participated from 1995 to 2004, with a frequency of two sets of samples per year. In this QAP program, more than 130 laboratories had participated, and the information was classified in three categories: Class A or Accepted; Class W or Accepted with reservations; and Class C as non-accepted. In table 2 are shown the results obtained by ARN in 15 intercomparison exercises. The EML references values are also shown [3 - 14].

Table 2: Results obtained by ARN in intercomparison exercises performed by EML.

QAP (*)	ARN (Bq / l)	EML (Bq / l)	Evaluation
44	226.0 ± 5.0	251.0 ± 11.4	A
45	500.0 ± 30.0	587.0 ± 58.0	A
47	122.2 ± 5.0	115.0 ± 6.0	A
48	213.8 ± 10.7	218.3 ± 6.5	A
49	76.9 ± 1.5	76.2 ± 2.9	A
50	115.8 ± 1.2	121.1 ± 6.8	A
51	77.1 ± 1.5	80.7 ± 3.7	A
52	85.7 ± 2.2	79.4 ± 2.5	A
52	85.6 ± 2.4	79.4 ± 2.5	A
52	85.3 ± 2.0	79.4 ± 2.5	A
53	84.8 ± 2.0	91.3 ± 0.3	A
53	86.0 ± 2.0	91.3 ± 0.3	A
54	66.6 ± 1.5	79.3 ± 2.0	A
56	283.6 ± 8.6	283.7 ± 3.8	A
57	250.2 ± 5.3	227.3 ± 5.7	A
58	396.6 ± 7.9	390.0 ± 3.4	A
59	458.8 ± 9.2	446.3 ± 2.2	A
60	253.6 ± 10.2	186.6 ± 3.3	W

(*) Quality Assessment Program. Number given by the EML to each intercomparison exercise.

In the last exercise it was obtained a questionable result (W), due to the aging of the scintillation solution. For that reason, and due to the fact that the scintillator was discontinued in its fabrication, it was replaced by another one, Ultima Gold LLT. The results were corrected and validated through the participation in two intercomparisons with the National Institute of Standard and Technology (NIST).

5. Conclusions

From the information reported in table 1, it can be concluded that the method presented in this paper fulfill laboratory requirements as obtained results are optimal. Moreover, this is a simple, quick and economic technique.

In relation with the data presented in Table 2, it can be seen that results obtained by ARN in the past 10 years were very satisfactory. The values were very similar to EML reference values.

The participation in these intercomparison exercises allowed to assure the quality of the determinations performed by the tritium laboratory of ARN.

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