STUDIES TO ESTABLISH THE SCALING FACTOR METHODOLOGY FOR LIQUID RADIOACTIVE WASTE GENERATED BY TRIGA REACTOR

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Abstract. During TRIGA reactor operation significant amounts of liquid radioactive waste are generated requiring appropriate management to ensure their safe disposal. Radiological characterization is an important activity needed to accomplish the waste acceptance criteria for different management steps including disposal. The purpose of this paper is to assess the activity concentrations of the $^{3}_{1}H$, $^{90}_{38}Sr$, $^{63}_{28}Ni$ (difficult-to-measure), and gamma emitters (easy-to-measure) radionuclides in liquid radioactive waste generated by the TRIGA reactor operation and to establish a correlation among them to determine the scaling factors for this waste category. The radiological protocols applied for $^{63}_{28}Ni$ and $^{90}_{38}Sr$, separation and purification involve extraction chromatography using selective resins, while for $^{3}_{1}H$ separation the distillation technique was applied. The assessment of gamma emitters was carried out using gamma-ray spectrometry and the detection of $^{3}_{1}H$, $^{90}_{38}Sr$, and $^{63}_{28}Ni$ was performed by liquid scintillation counting. The chemical yield of each experiment was determined by measuring the carrier added in each test by inductively coupled plasma optical emission spectrometry. The activity concentrations of $^{90}_{38}Sr$, and $^{63}_{28}Ni$ obtained were correlated with the activity concentration of $^{60}_{27}Co$ for establishing the scaling factor for the liquid radioactive waste stream. There were obtained good correlations but more experimental data are needed to determine the relevant scaling factors for these difficult-to-measure radionuclides. The scaling factors, once established, will improve and optimize the radiological characterization methodology applied for liquid radioactive waste as an easy and rapid method for assessment of concentration activities of difficult-to-measure radionuclides. Until now, no scaling factors data were reported for this liquid radioactive waste generated by TRIGA reactor operated by Institute for Nuclear Research Pitesti. The results obtained in this work represent preliminary data for establishing correlations between difficult-to-measure and easy-to-measure radionuclides and will be used for developing a scaling factor methodology. This will further be used to determine the inventory of difficult-to-measure radionuclides in different waste streams generated by TRIGA operation and decommissioning (foreseen after 2035).

Keywords: Scaling factor methodology, gamma spectrometry; extraction chromatography; liquid scintillation counting.

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1. INTRODUCTION

The TRIGA reactor is an open pool type reactor with two active cores (SSR 14 MW and ACPR) operated by Institute for Nuclear Research Pitesti (RATEN ICN) since 1980. The TRIGA reactor was used for scientific purposes, radioisotope production, and irradiation testing of nuclear fuel and structural materials [1]. During TRIGA reactor operation significant amounts of liquid radioactive waste are generated which require appropriate management for their safe disposal. As an institutional radioactive waste, the conditioned waste resulted from the treatment and conditioning of liquid radioactive waste is disposed of in the National Repository Băița Bihor. According to the waste acceptance criteria (WAC) for disposal, maximum values are imposed for activity concentrations of difficult-to-measure (DTM) radionuclides.

Therefore, the radiological characterization is one of the important aspects in defining the route for radioactive waste management and it has to be accomplished in all steps of the radioactive waste management process. The identification and quantification of the relevant radionuclides must be accomplished systematically using proven methodologies so that the waste acceptance criteria for different management steps, including disposal, can be met [2]. Depending on the type of decay mode and the measurement methods, the radionuclides can be classified as gamma-ray emitters or easy-to-measure radionuclides (ETM) and alpha-beta emitters called difficult-to-measure (DTM) or hard-to-measure (HTM) radionuclides (RN). While ETM RNs can be easily detected by direct non-destructive methods, the DTM RNs need laborious and complex destructive radiochemical methods for their separation and purification [2-6].

The most challenging issue in radiological characterization is the determination of the inventory of long-lived DTM radionuclides. The destructive radiochemical analyses involve the following: the chemical sample preparation to convert the waste matrix and bring the radionuclides into the liquid phase; the radiochemical separation and purification of the elements that are of interest, and the radionuclides measurement. These are time-consuming and intensive laborious activities that are difficult to apply for a large volume of waste. An alternative to these laborious methods is using the scaling factor methodology that estimates the radioactivity of DTM nuclides based on the radioactivity of ETM nuclides and a parameter called scaling factor (SF). The SF is previously derived from the correlation established and demonstrated for a given waste stream between DTM and ETM RNs [3].

To obtain accurate SF values, a representative number of destructive analyses are performed to assess the inventory of DTM nuclides and to correlate them with the ETM RNs. Based on these considerations, the goal of this study is to obtain preliminary data on the inventory and the concentration activity of some DTM radionuclides ($^{3}_{1}$H, $^{90}_{38}$Sr, and $^{63}_{28}$Ni) and gamma RNs in the liquid radioactive waste generated from TRIGA reactor operation. This represents an important step in developing the SF methodology for the radioactive waste streams generated by TRIGA reactor operation. The present study describes the analytical protocol adapted and implemented for the sequential determination of $^{3}_{1}$H, $^{90}_{38}$Sr, $^{63}_{28}$Ni and gamma radionuclides in liquid radioactive waste and some aspects related to their correlation.

Several radiochemical separation methods for $^{90}_{38}$Sr, and $^{63}_{28}$Ni applied for radioactive waste samples are reported in the literature [7-14], including precipitation/co-precipitation, liquid-liquid extraction, ion exchange chromatography, and extraction chromatography. One of the most frequently used methods for $^{90}_{38}$Sr, and $^{63}_{28}$Ni separation and purification is extraction chromatography using columns with a selective resin. This method has many advantages, including using low amounts of reagents, generating less hazardous secondary waste, efficient separation of the radionuclide of interest, and fast exchange kinetics [10].

The sequential determination of the DTM RNs consists of three radiochemical procedures adapted for tritium, strontium, and nickel separation and purification from the same liquid radioactive waste sample. The distillation technique was applied for the tritium separation from gamma-interfering radionuclides followed by the liquid scintillation counting (LSC) technique. The radiochemical procedures for $^{90}_{38}Sr$ and $^{63}_{28}Ni$ applied in this work are based on one or two separation processes using Sr, respective Ni, selective resin packed in columns. The second separation was applied when the concentration of the interferences in the $^{90}_{38}Sr$ and $^{63}_{28}Ni$ elution samples from the first separation process was significant. $^{3}_{1}H$, $^{90}_{38}Sr$, and $^{63}_{28}Ni$ are β emitters with no gamma-ray emission, and consequently, their detection is achieved by the LSC technique, after adequate separation and purification from other beta-gamma emitting radionuclides [7-8].

This research aims to assess the activity concentration of the DTM ($^{3}_{1}H$, $^{90}_{38}Sr$, $^{63}_{28}Ni$) and ETM (gamma emitters) radionuclides in the liquid radioactive samples generated from the TRIGA reactor operation and to establish a correlation between them to derive the scaling factors for this waste category.

Also, it offers a useful methodology for sequential separation of $^{3}_{1}H$, $^{90}_{38}Sr$, $^{63}_{28}Ni$ radionuclides from the same waste sample. This technique represents an adequate methodology as it requires less work time and human resources and generates less secondary waste. The scaling factors, once established, will improve and optimize the radiological characterization methodology applied for these liquid radioactive wastes being an easy and rapid method for the assessment of activities concentration of DTM radionuclides.

The scaling factor methodology is the most commonly used characterization method at the international level as an efficient solution to avoid the labor-intensive and time-consuming radiochemical analysis needed for the assessment of DTM radionuclides [4]. Until now, no SF data was reported for the liquid radioactive waste generated from TRIGA reactor operation, therefore the results obtained in this work are preliminary data in establishing correlations between DTM and ETM radionuclides. Also, the results will be used for developing a scaling factor methodology to be further used to determine the inventory of DTM radionuclides in different waste streams generated by TRIGA operation and decommissioning (foreseen after 2035).

2. MATERIALS AND METHODS

2.1. MATERIALS

One of the radioactive waste categories generated by the TRIGA reactor operation consists of low and intermediate-level liquid waste that is collected and stored according to the generation sources in eight tanks. After proper characterization, these liquid wastes are transferred to the Radioactive Waste Treatment Department (STDR) for treatment and conditioning in view of disposal to the National Repository Baita Bihor.

In this study, representative samples of liquid waste originating from the floor drainage of the pumps room (R3.1&R3.2), from the regeneration of ion exchange resin filters (R4.2&R4.1), and radiochemical laboratories (R2.1&R2.2) of the TRIGA reactor were sampled and analyzed. Four samples from R4.2, two samples from R4.1, and three samples from R3.1, R2.1, and R2.2 storage tanks were analyzed. For the gamma measurements, an ORTEC HPGe detector GEM15P4 model (46.9 mm diameter and 54.8 mm length made in USA) with Pop Top vertical cryostat configuration was used. A detector interface module (DIM-ORTEC), a DigiDART portable multichannel analyzer, Gamma Vision 32 software for

energetic spectra acquisition, and Genie2000 software for spectra analysis are the main components of the gamma-ray spectrometer. The operational parameters of the detector, measured at a shaping time of 6 μs and a high voltage of 3300V, are a relative efficiency of 15% and 1.80 keV resolution at 1332 keV $^{60}_{27}$Co[15].

A TRICARB 5110TR model, from PerkinElmer (USA) was used for the measurement of $^{3}_{1}$H , $^{90}_{38}$Sr, and $^{63}_{28}$Ni. XR Ultima Gold scintillation cocktail was mixed in an adequate ratio with the liquid samples to be analyzed by LSC. 2 mL columns with Sr Resin (with particle size between 100-150 μm), respectively Ni Resin, were used for $^{90}_{38}$Sr, and $^{63}_{28}$Ni separation and purification. The Sr^{2+} and Ni^{2+} carriers, in the form of 1000 mg/L multi-element standard solution, were added to assess the recovery yields, and their concentrations were measured by inductively coupled plasma optical emission spectrometry (ICP-OES), using an iCAP 6500 model from Thermo Scientific (made in USA). The $^{3}_{1}$H recovery yield was determined based on a certified tritium standard solution.

2.2. METHODS AND EXPERIMENTAL SETUP

The main steps of the radiochemical protocol applied for the separation and purification of the RN of interest are graphically presented in Fig. 1.
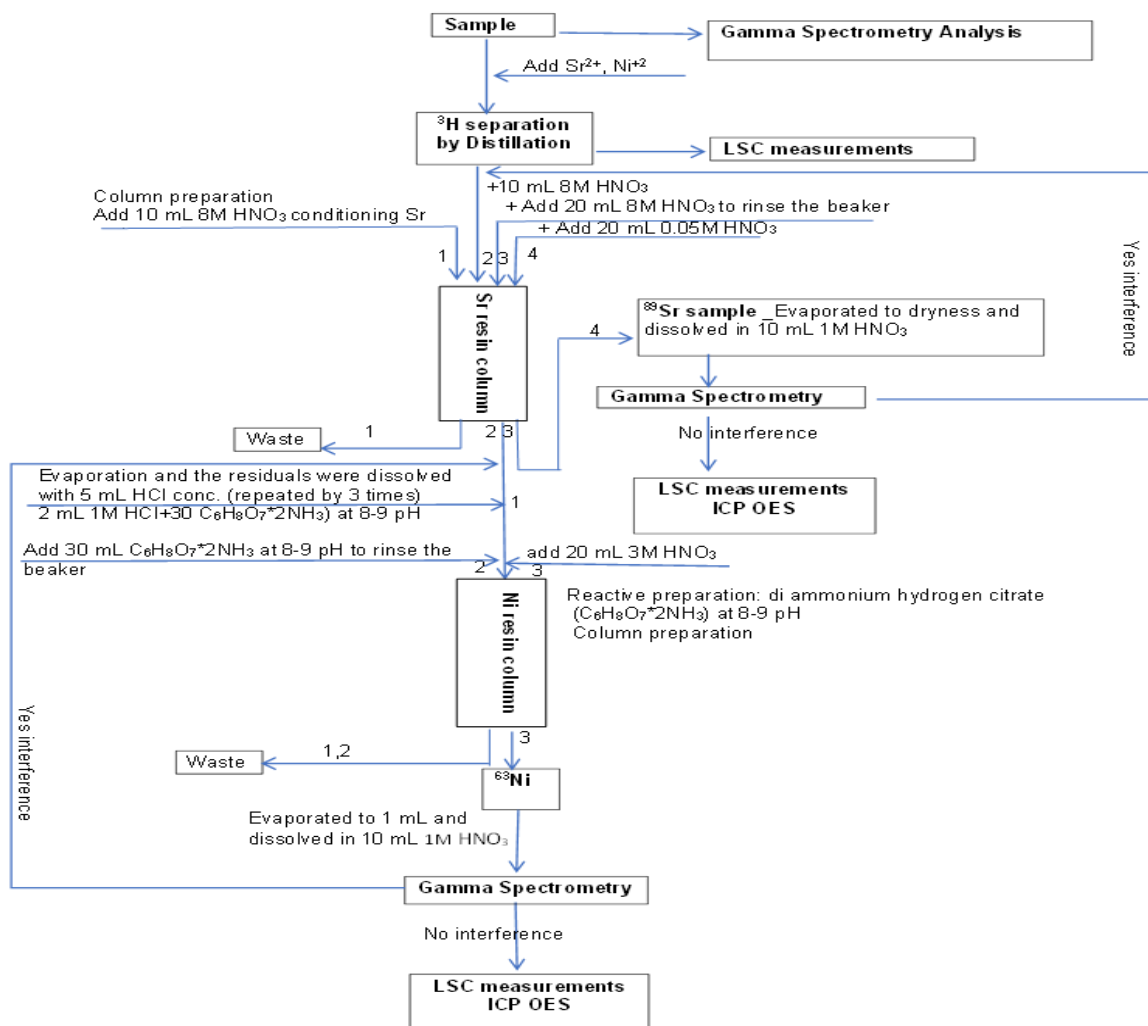

Figure 1. The flow diagram of sequential determination of $^{3}_{1}$H , $^{90}_{38}$Sr, and $^{63}_{28}$Ni in liquid radioactive waste.

2.2.1. Gamma spectrometry method

All the radioactive samples were first measured by gamma spectrometry to identify and quantify the gamma-ray emitters. The characteristic spectra of each sample were acquired with Gamma Vision software and the interpretation was carried out using Genie2000 software.

The gamma measurements were performed at contact with the HPGe detector, in a configuration (100 mL sample in 250 mL cylindrical vial or 10 mL sample in TRICARB vial) for which the efficiency calibration curve was previously established and verified by the participation in the IAEA intercomparison proficiency test.

2.2.2. Radiochemical protocol for $^3_1$H separation

Tritium ($^3_1$H) is a radioactive isotope of hydrogen with a half-life of 12.3 years that emits only low-energy beta-particles ($E_{beta\ max} = 0.0186$ MeV); it is produced by fission in the nuclear fuel and also by neutron activation of the boron contained in the control rods as B_4C and lithium-6 contained as impurities in the coolant water [16].

After the initial measurement by gamma spectrometry, an aliquot of 90 g of liquid sample was transferred to the reaction flask of the distillation set-up and weighed. 1 mL of Ni^{2+} and 2.5 mL of Sr^{2+} stable carriers were added and then the sample was distilled using a laboratory set-up to separate the $^3_1$H from the analyzed sample. The distillation technique was performed at a temperature of around 100 ^{0}C. By heating, tritium is evaporated and condensed in the distillation fractions, while other beta-gamma emitters, characterized by significantly higher evaporation temperatures, remain as wet salts in the reaction flask. When the distillation was completed, the wet salts were dissolved in 10 mL of HNO_3 (concentration 8M) and the solution was used to separate and purify first the $^{90}_{38}$Sr , and then the $^{63}_{28}$Ni.

After each distillation test, the experimental set-up was cleaned using nitric acid and distilled water to recover the tritium that might have remained on the installation components. The background samples, the distillation fractions, and representative samples from the cleaning solution were analyzed by LSC in the energetic range of 0-18.6 keV characteristic for tritium.

To determine the tritium recovery yield, two tritiated water solutions with known activities were prepared and distilled. The distillation fractions were measured by LSC. The tritium recovery yield was calculated based on the tritium activities in the initial solutions and in the distillation fractions. The tritium concentration activity obtained for the liquid radioactive waste samples was corrected with the recovery yield.

2.2.3. Radiochemical protocol for $^{90}_{38}$Sr separation

$^{90}_{38}$Sr is a pure beta emitter with a half-life of about 29 years (the reported half-life varies from 27.7 to 29.1 years), that decays to $^{90}_{39}$Y ($T_{1/2} \approx 64$ hours) with the emission of a 546 keV maximum energy beta particle [16]. Based on a research survey [9-11] the separation of $^{90}_{38}$Sr was carried out by using one or two chromatographic extraction processes (Eichrom$^®$ Sr Resin in 2 mL columns), depending on the activity of the interferences in the elution samples after the first separation process. The purpose was to obtain high decontamination efficiency values.

The wet salts obtained after sample distillation were dissolved in 10 mL of HNO_3 concentration 8M and the resulted solution was loaded in the Sr resin column previously conditioned with 10 mL of nitric acid concentration 8 M. $^{90}_{38}$Sr isotope is retained in the Sr resin forming complexes with high stability constant [18].

The reaction vessel was rinsed with another 20 mL of HNO$_3$ concentration 8M that was also loaded into the strontium column and after it passed through the strontium resin column it was collected and evaporated to dryness together with an initial volume of 10 mL HNO$_3$ concentration 8M. The solution resulting after $^{90}_{38}$Sr separation was prepared according to the radiochemical method proposed for $^{63}_{28}$Ni separation and purification and detailed below.

The $^{90}_{38}$Sr retained in the resin was eluted with 20 mL of HNO$_3$ concentration 0.05 M. The eluted solution was evaporated to dryness and the dry salts were dissolved in 10 mL of HNO$_3$ concentration 1M and measured by gamma spectrometry. If the activity of gamma RNs in this solution is high enough to influence the LSC results, a second separation is performed before $^{90}_{38}$Sr measurement by LSC. The characterization methodology applied for the assessment of $^{90}_{38}$Sr and $^{3}_{1}$H from liquid radioactive waste was tested and verified by annually participating in intercomparison proficiency tests organized by IAEA.

2.2.4. Radiochemical protocol for $^{63}_{28}$Ni separation

$^{63}_{28}$Ni is the result of two neutron reactions involving Ni and Cu: $^{62}_{28}$Ni(n, γ)$^{63}_{28}$Ni, and $^{63}_{29}$Cu(n, p) $^{63}_{28}$Ni. It is a long-lived radionuclide with a half-life of 100.1 years, emitting pure beta particles with a maximum energy of 66.95 keV. $^{63}_{28}$Ni is found mainly in the structural materials of the reactor and in the water coolant [14, 17]. The radiochemical protocol applied for $^{63}_{28}$Ni measurement in liquid radioactive samples was adapted based on the methods developed by the Nordic countries in the NKS-B RadWaste project [12-14] for the radioactive waste generated from decommissioning activities.

Using Eichrom Ni Resin columns, $^{63}_{28}$Ni separation from other beta-gamma interfering radionuclides was achieved based on the creation of a complex between Ni and dimethylglyoxime (DMG), and the precipitation or organic extraction of the Ni- DMG complex. 0.5 g of Ni Resin (100 - 150 μm) was left to swell in 0.2 M alkalinized ammonium citrate solution (25% HN$_3$ solution was added over C$_6$H$_{14}$N$_2$O$_7$ to obtain a pH between 8 and 9). After swelling, the Ni Resin was loaded in a column of 2 mL capacity and 0.7 cm diameter, to obtain, according to the manufacturer's recommendations [19], a resin height above 4 cm.

The effluent resulted from $^{90}_{38}$Sr separation was evaporated to wet salts and dissolved with 5 mL of concentrated HCl. The complete conversion of the solution to the chloride form was achieved by three repeated evaporations of 5 mL of concentrated HCl. The resulted salts were dissolved in 2 mL of HCl concentration 1M and transferred to a centrifuge tube. 30 mL of alkalinized ammonium citrate solution was used to rinse the vessel. Then this was added to the same centrifuge tube and the resulting solution was alkalinized to 8-9 pH with NH$_3$ concentration 25%.

The solution obtained was then loaded in the Ni resin column, where nickel-dimethylglyoxime (Ni(DMG)$_2$) complex is formed by precipitation of nickel with dimethylglyoxime (DMG), which is highlighted by a red precipitate. To remove any potential interfering radionuclides still present in the resin, 30 mL of ammonium citrate (pH=8) concentration 0.2 M was used as a washing solution.

The elution of Ni(DMG)$_2$ complex from the resin was performed with 20 mL of HNO$_3$ concentration 3M. The eluate was evaporated to 1 mL on a hotplate and diluted with 10 mL distilled water to be analyzed by gamma spectrometry and check the presence or absence of the inferences that can influence the accuracy of $^{63}_{28}$Ni measurement by LSC. The elution samples are analyzed by LSC for $^{63}_{28}$Ni quantification and by ICP-OES for Ni carrier assessment if the gamma spectrometry results indicate that there aren't gamma interferences or if the identified radioactivity is insignificant.

For some of our samples, especially those that had a $^{60}_{27}Co$ concentration higher than 10^3 Bq/g, gamma interference was highlighted in the Ni eluate samples and a second extraction was performed in the same conditions as the first one described above. $^{60}_{27}Co$ is the most problematic interference in nickel analysis due to the similar chemical behavior of these two metals and therefore the cobalt 60 is retained in the material of extraction of the Ni resin and also present in the elution samples of $^{63}_{28}Ni$.

2.2.5. Liquid scintillation counting measurements

^3_1H, $^{90}_{38}Sr$, and $^{63}_{28}Ni$ radionuclides were measured with the liquid scintillation counting spectrometer model TRICARB 5100 TR. $^{63}_{28}Ni$ and ^3_1H activities were measured by using appropriate quench curves generated based on quenched standards ($^{63}_{28}Ni$ and respectively ^3_1H). Because the $^{90}_{38}Sr$ low activities are expected, the samples containing $^{90}_{38}Sr$ were counted after three weeks from the separation moment to accomplish the condition of equal activities between $^{90}_{38}Sr$ and $^{90}_{39}Y$ (secular equilibrium). $^{90}_{38}Sr$ activity was evaluated by using the efficiency trancing (ET) technique with a single unquenched ^{14}C standard. Ultima Gold AB scintillation cocktail was mixed with an appropriate volume of strontium and nickel elution samples (3mL of Ni elution sample and respectively 5 mL of Sr elution sample) and let to stabilize at least overnight before measurement by LSC for a 0.5 value of 2 sigma%. For tritium measurements, the Ultima Gold XR scintillation cocktail was mixed with a 5 mL distillation fraction.

2.2.6. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

ICP-OES measurements were performed to monitor the chemical yield of $^{90}_{38}Sr$ and respectively $^{63}_{28}Ni$ from the separation processes, based on the measurement of Sr and Ni stable isotopes. 0.5 mL of an aliquot sample from the strontium and nickel elution samples were diluted into ultrapure HNO_3 concentration 2% for ICP OES measurements. The calibration curve was realized in the concentration range of 1 ppm -3 ppm.

3. RESULTS AND DISCUSSION

3.1. GAMMA RESULTS

The inventory of gamma radionuclides and the activity concentration of each radionuclide were determined by gamma spectrometry performed on representative radioactive waste samples. This represents an important input in applying the radiochemical protocol for strontium and nickel measurements. The results obtained from gamma spectrometry are reported in Tables 1 and 2.

The initial concentration activities for $^{60}_{27}Co$, $^{58}_{27}Co$, and $^{54}_{25}Mn$, in the samples from R4.2 (B1-B4) and R4.1 (C1-C2) storage tanks are higher than 10^4 Bq/kg, therefore adequate protection must be taken when handling this waste. The most significant gamma emitter to the total activity concentration is $^{60}_{27}Co$, (47%-92% of the total gamma radioactivity), followed by $^{58}_{27}Co$ (4%-32%), $^{54}_{25}Mn$ (4%-9%), and $^{124}_{51}Sb$ (1%-19%).

Table 1. Gamma spectrometry results for the samples from R4.2 (B1÷B4 sample code) and R4.1 storage tanks (C1, C2 sample code).

Radionuclide	Activity Concentration ± Uncertainty counting [kBq/kg]					
	B1	B2	B3	B4	C1	C2
$^{54}_{25}$Mn	6.84±0.18	0.24±0.01	187.79±3.90	<0.12	1.30±0.5	0.63±0.34
$^{57}_{27}$Co	0.32±0.02	<0.015	6.85±0.38	0.03±0.01	0.05±0.06	<0.05
$^{58}_{27}$Co	16.64±0.42	0.22±0.01	1033.70±19.58	3.95±0.11	2.76±0.8	4.82±0.11
$^{60}_{27}$Co	89.56±1.32	5.56±0.03	1898.20±21.24	9.09±0.15	15.66±0.2	9.10±0.1
$^{124}_{51}$Sb	0.88±0.04	<0.03	40.12±1.28	3.71±0.08	0.21±0.02	0.40±0.03
$^{137}_{55}$Cs	<0.28	<0.04	<7.23	<0.09	0.15±0.2	<0.2
$^{51}_{24}$Cr	<1.32	<0.2	31.70±4.26	1.68±0.12	<0.6	<0.7
$^{125}_{51}$Sb	<0.56	<0.08	<0.14	0.47±0.03	<0.3	<0.3

As expected, the highest gamma radioactivity has been found in samples taken from the R4.2 storage tank, as here the liquid radioactive waste resulting from the regeneration of spent ion exchange resins are stored.

Table 2. Gamma spectrometry results for the samples from R3.1 (A), R2.2 (D), and R2.1(E) storage tanks.

Radionuclide	Activity Concentration ± Uncertainty counting [Bq/kg]		
	A	D	E
$^{54}_{25}$Mn	55.68 ± 3.77	35.02 ± 9.01	441.88 ± 39.90
$^{57}_{27}$Co	<7.4	<9	<80
$^{58}_{27}$Co	379.18 ± 11.91	205.34 ± 16.05	1472.46 ± 71.65
$^{60}_{27}$Co	853.88 ± 15.42	419.22 ± 17.84	4029.24 ± 100.62
$^{124}_{51}$Sb	15.14 ± 2.26	28.22 ± 7.05	78.52 ± 21.14
$^{137}_{55}$Cs	17.78 ± 2.73	<27	<207
$^{51}_{24}$Cr	297.62 ± 20.60	103.98 ± 37.99	<1030
$^{125}_{51}$Sb	<37.5	<53	<405

Also, it can be observed that some radionuclides such as $^{137}_{55}$Cs, $^{51}_{24}$Cr, $^{125}_{51}$Sb, and $^{57}_{27}$Co are not present in all the analyzed samples and for this reason, for these radionuclides, the minimum detectable activity was reported. Based on the gamma results, the inventory of interfering radionuclides that can influence the LSC measurements was established and $^{60}_{27}$Co was identified as a key nuclide.

All the elution samples resulted from the radiochemical protocols applied for $^{90}_{38}$Sr and $^{63}_{28}$Ni measurements were analyzed by gamma spectrometry, to identify the potential gamma interfering radionuclides in the elution samples before performing the LSC measurements for $^{90}_{38}$Sr and $^{63}_{28}$Ni. The minimum detectable activity (MDA) is a measure of how small an activity could be present and not be detected. The MDA is calculated based on the background value of the peak and can be influenced by the calibration geometry, the detector resolution, the background, and by the spectrum acquisition time [20].

The MDA values presented are generated with the Genie software algorithm, which is based on the Curries method, the most widely accepted and used method for MDA calculation in gamma spectrometry. The MDA is indicative that the elution samples resulted from the separation and purification of strontium and nickel can be measured by LSC without any influence of other beta-gamma radionuclides. The values obtained by gamma measurements of elution samples resulted from the first and/or the second separation processes of strontium and nickel are reported in Tables 3 and 4.

Table 3. The activity of gamma-interfering radionuclides for the strontium elution samples from the first and the second separation process.

ID ^{90}Sr elution samples	Activity Concentration ± Uncertainty counting [Bq/kg]							
	$^{54}_{25}$Mn	$^{57}_{27}$Co	$^{58}_{27}$Co	$^{60}_{27}$Co	$^{124}_{51}$Sb	$^{51}_{24}$Cr	$^{137}_{55}$Cs	$^{125}_{51}$Sb
B3_P1	$2\times10^3\pm60$	76.60 ± 9	$1.4\times10^4\pm286$	$26\times10^3\pm305$	$3.7\times10^3\pm76$	$<10^3$	<211	<438
B4_P1	<92	<34	$4.7\times10^2\pm28$	$1.4\times10^3\pm38$	$6.3\times10^2\pm29$	<498	<99	<208
C2_P1	<23	<10	54 ± 4.2	$1\times10^2\pm4.6$	<17.7	<134	<27	<53
E_P1	<23	<9	<23	<26	<19.6	<127	<21	<51
D_P1	<22	<9	<22	<24	<19	<120	<25	<48
B1_P1	<62	<25	<61	<75	<54	<365	<72	<135
B2_P1	<23	<10	<23	<26	<20	<129	<28	<54
C1_P1	<22	<9	<22	<24	<19	<125	<20	<49
A_P1	<57	<23	<57	<63	<49	<321	<43	<127
B4_P2	<53	<21	<52	<57	<31	<287	<59	<124
B3_P2	<39	<16	<38	<46	<324	<216	<37	<91
C2_P2	<25	<10	<23	<45	<18	<135	<30	<50

Table 4. The gamma-interfering radionuclide results for the nickel elution samples from the first and the second separation process.

ID ^{63}Ni Elution Samples	Activity Concentration ± Uncertainty counting [Bq/kg]							
	$^{54}_{25}$Mn	$^{57}_{27}$Co	$^{58}_{27}$Co	$^{60}_{27}$Co	$^{51}_{24}$Cr	$^{124}_{51}$Sb	$^{125}_{51}$Sb	$^{137}_{55}$Cs
A	<24	<10	139 ± 6	249 ± 6	<134	<21	<53	<23
B1_P1	<88	85 ± 4	$3.8\times10^3\pm75$	$2.6\times10^4\pm292$	<343	<65	<143	51 ± 10
B2_P1	<112	<31	231 ± 20	$6.7\times10^3\pm95$	<464	<80	<186	<100
C1_P1	<44	11 ± 2	535 ± 14	452 ± 54	<190	17.9 ± 4	<79	58 ± 6
B1_P2	<38	7 ± 1	187 ± 8	$3.4\times10^3\pm42$	<169	<29	<157	<37
B2_P2	<72	<26	<70	$1\times10^3\pm29$	<360	<49	<157	<75
C1_P2	<75	<29	<73	183 ± 16	<410	<42	<153	<81
2.1_E	<58	<9	156 ± 6	485 ± 9	<133	<23	<54	<29
B4_	<48	<19	85 ± 9	203 ± 10	<257	206 ± 11	<109	<53
B3_P1	$2.5\times10^3\pm143$	<150	$7.7\times10^3\pm260$	$2.2\times10^4\pm383$	<2.300	<450	<930	<490
B3_P2	$1.8\times10^3\pm57$	<32	223 ± 20	757 ± 27	<489	<86	<188	<103
C2	<56	<27	<60	83 ± 9	<327	<50	<126	<65
2.2_D	<61	<63	<79	<26	<357	<53	<145	<73

From Table 3 it can be observed that for the B3, B4, and C2 samples a single $^{90}_{38}$Sr separation process was not enough, and therefore, the strontium elution samples were passed through another Sr resins column to eliminate all the beta-gamma radionuclides. The P1 and P2 indicatives symbolize how many separations processes were performed to eliminate the interfering radionuclides from the elution samples. Also, a $^{63}_{28}$Ni double separation process was needed to be performed for B1, B2, B3, and C1 samples due to the high activity concentration of gamma emitters presented in the nickel elution samples (especially for cobalt-60). Also, after the second separation process, $^{60}_{27}$Co, $^{58}_{27}$Co, and $^{54}_{25}$Mn are still present in the elution samples but it was considered that their activity concentrations would not influence the LSC measurements for nickel-63, considering that the amount of sample measured at LSC is 3 mL that correspond to a maximum activity of 10 Bq for cobalt-60 in B1 elution sample. As a performance parameter of the separation process, it was calculated the decontamination efficiency (D.E in %). Based on the activities of all gamma-emitting radionuclides in the initial waste samples and in the elution samples, the decontamination efficiency was calculated using the following equation:

$$D.E = 100 - \left(\left(\frac{A_{sample\ elution}}{A_{sample\ initial}}\right) \cdot 100\right)$$ (1)

The decontamination efficiency was calculated only for the interferences present in the strontium and nickel elution samples, considering that the other initial interferences with activity under MDA are characterized by a D. E of around 100%. The D.E values obtained for the first and second separation processes of $^{63}_{28}Ni$ are presented in Figs. 2 and 3.
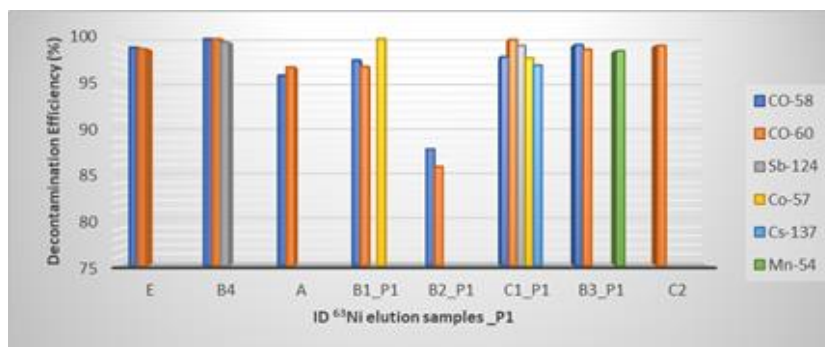

Figure 2. The decontamination efficiency for gamma interferences identified in the Ni elution samples after the first separation process.
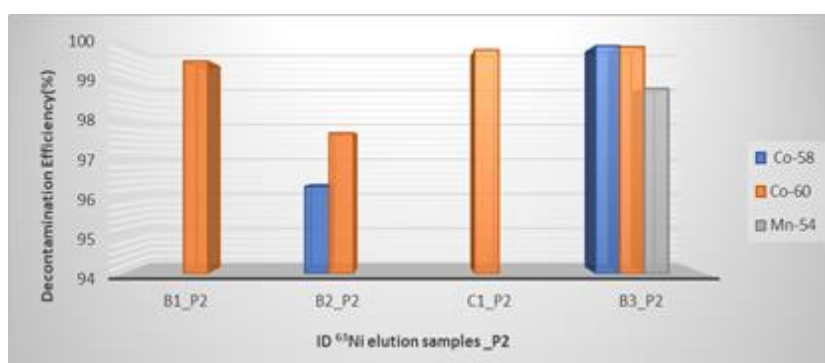

Figure 3. The decontamination efficiency for gamma interference was identified in the Ni elution samples after the second separation process.

The decontamination efficiencies achieved by performing two separation processes are higher than the values obtained from one separation process for B1, B2, C1, and B3 samples. It is observed that for the B2 sample, the decontamination efficiency values achieved after two separation processes remain under 100% (98% for $^{60}_{27}Co$ and 96% for $^{58}_{27}Co$) but these values are accepted, and the very low gamma radioactivity still present in the elution samples does not influence the nickel measurements by LSC. The decontamination efficiencies achieved for gamma interferences in strontium separation are represented in Fig. 4.
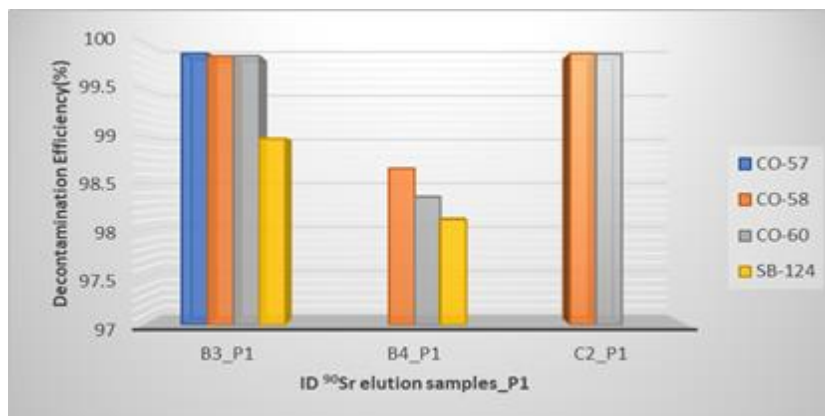

Figure 4. The decontamination efficiency for gamma interferences identified in the Sr elution samples from the first separation process.

High decontamination efficiencies were obtained after the first strontium separation process (98% for cobalt in the B4 and 99% for all other gamma-interfering radionuclides in the B3 and C1). After the second separation process, the decontamination efficiencies are around 100% as all the gamma interfering radionuclides were below the MDA.

4.2 CHEMICAL YIELD RESULTS

The results of the $^3_1$H activity concentration obtained for the simulated solutions and the recovery yields are presented in Table 5.

Table 5 The recovery yield for tritium.

ID experiments	$^3_1$H in initial solutions [kBq/g]	$^3_1$H in distillation fractions [kBq/g]	Yield [%]
Exp 1	9.55 ± 0.024	8.77 ± 0.022	91.8
Exp 2	3.11 ± 0.008	2.80 ± 0.007	90.1
Average			90.98

The average recovery yield was applied to correct the tritium activities measured in the liquid radioactive waste samples.

The chemical yield for Ni and Sr was calculated based on the initial amount of the carriers introduced at the beginning of the experiments and the amount measured at the end of each separation process performed for strontium and nickel measurement (Table 6).

Table 6 Chemical yield values for strontium and nickel monitoring in the radiochemical protocol.

ID samples	Chemical yield for Sr [%]	Chemical yield for Ni [%]
A	70.55	94.87
B1	90.61	78.94
B2	85.71	74.34
B3	80.45	84.13
B4	87.68	59.95
C1	87.52	81.84
C2	87.78	74.29
E	93.37	90.43
D	91.85	98.82

The chemical yield depends on many aspects such as the complexity of the radiochemical protocol, the human errors in the preparation of the solutions, and the accuracy of performing the experiments. The strontium chemical yield is between 70% and 93% and the nickel chemical yield is between 60% and 98%. For samples where two separation processes were performed, the nickel chemical yield is between 70-87%.

4.3. LIQUID SCINTILLATION COUNTING RESULTS

The results obtained by LSC measurements for $^3_1$H, $^{90}_{38}$Sr, and $^{63}_{28}$Ni were corrected with the chemical yields determined for each sample analyzed and presented in Table 7. The $^3_1$H activity is around 10^2 and 10^4 Bq/kg. The $^{90}_{38}$Sr is found in low concentrations only in B1, B3, B4, C1, and C2 samples. The average activity by generation source is around 1.16×10^2 Bq/kg for the liquid waste sampled from the R4.2 storage tank and around 4.45×10^1 Bq/kg for an R4.1 storage tank.

Table 7 The activity concentration of $^{3}_{1}$H, $^{90}_{38}$Sr and $^{63}_{28}$Ni in all the samples analyzed.

ID sample	Activity Concentration [Bq/kg]		
	$^{63}_{28}$Ni	$^{3}_{1}$H	$^{90}_{38}$Sr
A	$5.54 \times 10^2 \pm 2$	$6.46 \times 10^4 \pm 146.97$	<6.60
B1	$9.27 \times 10^4 \pm 231.73$	$8.12 \times 10^3 \pm 19.59$	$2.28 \times 10^1 \pm 0.33$
B2	$1.09 \times 10^4 \pm 27.26$	$1.18 \times 10^2 \pm 1.72$	<6.60
B3	$2.53 \times 10^6 \pm 5330.03$	$4.64 \times 10^4 \pm 105.47$	$2.86 \times 10^2 \pm 1.21$
B4	$1.74 \times 10^3 \pm 4.78$	$1.42 \times 10^4 \pm 32.40$	$3.99 \times 10^1 \pm 0.41$
C1	$2.41 \times 10^3 \pm 6.02$	$1.07 \times 10^4 \pm 24.38$	$8.24 \times 10^1 \pm 0.55$
C2	$8.98 \times 10^3 \pm 21.34$	$1.78 \times 10^4 \pm 40.48$	6.51 ± 0.09
E	$7.23 \times 10^2 \pm 2.42$	$8.21 \times 10^4 \pm 186.73$	<6.60
D	$1.05 \times 10^3 \pm 7.90$	$1.71 \times 10^3 \pm 11.44$	<6.60

In A, B2, D, and E samples $^{90}_{38}$Sr radionuclide was not identified or it is below the MDA (6.604 Bq/kg). $^{63}_{28}$Ni is found in all the analyzed samples and the activity concentration is between 5.54×10^2 Bq/kg and 2.53×10^6 Bq/kg; it is observed that the highest activity concentrations of $^{63}_{28}$Ni are in the B1÷B4 samples.

4.4. EVALUATION OF RADIOCHEMICAL OBTAINED DATA AND THE SCALING FACTOR APPLICABILITY

The evaluation of the radiochemical data obtained for DTM and key radionuclides should be carefully evaluated and a large number of representative samples from the same waste have to be analyzed to derive representative scaling factors to be further applied in the radioactive waste characterization. Correlations are affected by a variety of parameters, including reactor type, reactor component materials, fuel history, the process by which nuclides are produced, differences in reactor coolant chemistry, and waste management [4].

The data obtained for DTM radionuclides ($^{90}_{38}$Sr and $^{63}_{28}$Ni) and key nuclide ($^{60}_{27}$Co) were evaluated according to the ISO standards [3, 5] to obtain correlation relationships. Based on the results obtained, $^{63}_{28}$Ni is very well correlated with $^{60}_{27}$Co, correlation also indicated in the literature [2- 5].

For the development of the scaling factor methodology, $^{90}_{38}$Sr is correlated with $^{137}_{55}$Cs, as both radionuclides are generated by fission reactions, but from the results obtained in our work, $^{137}_{55}$Cs is present in small concentrations only in A and C1 samples, and it was impossible to make a correlation between $^{137}_{55}$Cs and $^{90}_{38}$Sr. ISO 21238:2007 and various research studies related to the scaling factor methodologies applied in Japanese, European, and United States practice [4], have demonstrated that $^{60}_{27}$Co provides comparable correlations for fission-product nuclides and alpha-emitting nuclides, which could be the case of the waste we analyzed. There are some criteria to demonstrate the correlation of $^{63}_{28}$Ni and $^{90}_{38}$Sr with $^{60}_{27}$Co, respectively the applicability of the SF method. One of them is the sample Pearson correlation coefficient ($r_{xy)}$) given by the following formula:

$$r_{xy} = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 \sum_{i=1}^{n}(y_i - \bar{y})^2}} \qquad (2)$$

where n is the sample size, x_i and y_i are the individual sample points indexed with i, and $\bar{x}$ and $\bar{y}$ are the sample means. According to the Cauchy-Schwarz inequality, the Pearson correlation coefficient has a value between +1 and -1 and measures the strength of a linear relationship between two variables [4].

For $^{63}_{28}$Ni and $^{60}_{27}$Co correlation the Pearson correlation coefficient was calculated for the samples from the same generation source and +1 was obtained for the B1÷B4 samples and -1 for C1-C2 samples. To verify the correlation of $^{90}_{38}$Sr and $^{60}_{27}$Co, the Pearson correlation coefficient was calculated for all the samples where strontium was identified and 0.97 was obtained, indicating that such a correlation can be valid.

The values obtained for the Pearson correlation coefficient demonstrate the linear relationship between nickel and cobalt activity and strontium and cobalt activity. Fig. 5 shows the distribution of the radiochemical data obtained in all the analyzed samples for $^{63}_{28}$Ni, $^{90}_{38}$Sr, and $^{60}_{27}$Co.
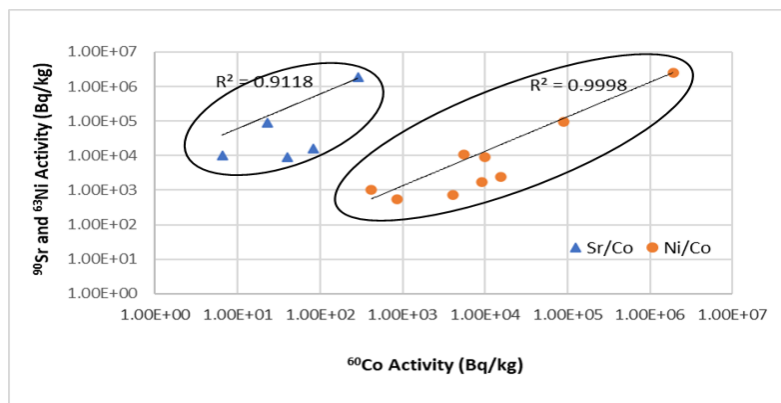

Figure 5. Correlation between $^{90}_{38}$Sr and $^{60}_{27}$Co respectively $^{63}_{28}$Ni and $^{60}_{27}$Co.

Linear correlations were obtained for both sets of data, with correlation coefficients above 0.9 indicating that based on a larger number of waste samples analyzed, representative scaling factors can be determined for $^{63}_{28}$Ni/$^{60}_{27}$Co and $^{90}_{38}$Sr /$^{60}_{27}$Co. Usually, the correlation factors above 0.95 are considered relevant and at least twenty samples are recommended to be analyzed from the same waste stream [4].

4. CONCLUSIONS

The results obtained in this work are preliminary data in establishing correlations between DTM and ETM radionuclides and will be used for developing a scaling factor methodology to be further employed to determine the inventory of DTM radionuclides in different waste streams generated by the TRIGA reactor operation and decommissioning (foreseen after 2035). The obtained results indicated a good correlation of $^{63}_{28}$Ni with $^{60}_{27}$Co in the liquid radioactive waste from the TRIGA reactor operation. Also, a potential correlation of ^{90}Sr and $^{60}_{27}$Co was highlighted, but supplementary tests are needed to derive representative scaling factors both for $^{63}_{28}$Ni and for $^{90}_{38}$Sr. Tritium is difficult to be correlated with a key radionuclide and it is recommended to be directly measured. All the analyzed samples contain tritium in a concentration between 0.10 kBq/kg and ~ 80 kBq/kg. The radiochemical protocol tested and adapted for sequential determinations of the concentrations of $^{3}_{1}$H, $^{90}_{38}$Sr, and $^{63}_{28}$Ni proved to be efficient and led to achieving good decontamination efficiencies both in the Sr and Ni separations. The chemical yield determined for each experiment was between 70%-93% and the values were used for the correction of radioactivities measured for the interest radionuclides. At this stage of our research work, it is difficult to establish the relevant scaling factors between $^{63}_{28}$Ni and $^{60}_{27}$Co or between $^{90}_{38}$Sr and $^{60}_{27}$Co, as the number of analyzed samples was low, but further tests will be performed for the same waste stream in order to derive representative scaling factors.

To improve these preliminary results, the following will be performed: (1) the concentration of the initial samples before gamma measurement or a cesium separation process to establish with good accuracy the activity concentration of $^{137}_{55}$Cs in the initial samples to test the correlation of $^{90}_{38}$Sr with $^{137}_{55}$Cs ; (2) supplementary tests for nickel and strontium measurements; (3) an additional separation method using AG1X8 ion exchange resin before extraction chromatography with Niresin will be tested for improving the radiochemical protocol applied for $^{63}_{28}$Ni measurement. The AG1x8 ion exchange resin is a selective resin for Co, Fe, and Cu and could be useful for $^{60}_{27}$Co separation from the initial samples.

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