MINISTRY OF EDUCATION
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Doctoral School of Energy Engineering

PhD THESIS SUMMARY

CONTRIBUTIONS TO THE CHARACTERIZATION OF RADIOACTIVE WASTE RESULTING FROM NUCLEAR ACTIVITIES

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BUCUREȘTI
2025

MOTIVATION

The doctoral thesis titled *"**Contributions to the Characterization of Radioactive Waste Generated from Nuclear Activities**"* synthesizes original results obtained during the PhD research, in the field of the development and optimization of radiological characterization methods for waste generated from the operation and decommissioning activities of the TRIGA reactor.

This research theme, radiological characterization of radioactive waste, was pursued due to its critical importance in the safe management of radioactive waste and spent nuclear fuel. The need to address challenges in estimating inventory and activity concentrations of radionuclides that are difficult to measure (DTM) across various waste streams was central to the investigative process.

The relevance of this subject at national and international levels, alongside the high applicability of the experimental methodologies developed, strongly supports the selection of this research topic.

Furthermore, the topic aligns with the research directions of RATEN ICN (Institute for Nuclear Research), regarding the development of radiochemical and spectrometric methods for the waste characterization generated following the operation, refurbishment, and decommissioning of nuclear and radiological facilities.

The doctoral thesis provided an opportunity to enhance the author's professional skills in research, data analysis, and interpretation, contributing significantly to the development of expertise in the field of waste radiological characterization. The results obtained contribute to optimizing the characterization process of the radioactive waste generated from TRIGA reactor operation and decommissioning activities, necessary in the development of management solutions for problematic waste in RATEN ICN.

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1 INTRODUCTION

The research topic addressed in this doctoral program fits within a highly relevant field: *"the management of radioactive waste and spent nuclear fuel under safety conditions "*. This field is recognized as a national and international research priority, given the significant progress made in the field of nuclear energy and its strategic integration in the national energy program as a low-carbon energy source.

The thesis presents the research studies undertaken within the doctoral thesis as well as own results, which are structured into six chapters, including an introductory section and a final section dedicated to general conclusions.

In the ***introductory section***, I addressed aspects such as the topicality and importance of the selected topic, the current context of radioactive waste at the international and national levels, and also, I briefly described the objectives and research activities carried out in order to achieve the general objective of the thesis.

Nuclear energy plays a key role in ensuring energy security and achieving climate targets, being the **second-lowest CO_2-emitting source of electricity** after hydropower [1]. However, like any advanced technology, it comes with challenges—radioactive waste generation, accident risk, high costs, and security considerations - all demanding continuous attention and innovation for a sustainable and safe deployment.

The radioactive waste generated from nuclear facility operation represents one of the most important issues associated with nuclear energy, representing a challenge not only from a technological point of view, but also **socio-political** both at national and international levels.

Therefore, **radioactive waste management** must be carried out safely, without significant negative effects on the population and the environment, demonstrating the sustainability of nuclear energy in the global energy mix. Also, it must be constantly updated by developing and optimizing methods and techniques of characterization, treatment, and conditioning for safe storage of radioactive waste in order to limit the impact on human health and the environment.

The implementation of such management is based on the concept of characterization, which must be carried out using validated/certified techniques, technologies, and methodologies. These tools are essential to meet the quality and safety requirements imposed by regulatory authorities in the nuclear field, thus minimizing the impact on the environment and human health [2].

Radioactive waste characterization is an essential component, a multidisciplinary process, of their safe and responsible management and involves the identification of physical, chemical, radiological, and, sometimes, biological properties. Research has shown that the most important component of the characterization process is radiological characterization, based on which the inventory and activity concentration of radionuclides contained in radioactive waste are defined. This information is the basis for the development and implementation of effective

solutions and methods for the safe treatment, conditioning, and final disposal of radioactive waste [2].

The importance of this research topic is given by the need to continuously optimize and develop radiological characterization methods, as well as by the interest that RATEN ICN has in defining the characterization methodology, necessary to establish the inventory of radionuclides contained in the radioactive waste that will result from the decommissioning activity of the TRIGA reactor. These are the considerations that formed the basis for conducting the own experimental research included in this doctoral thesis.

The TRIGA research reactor has been operational since 1980 on the RATEN ICN platform and is used for scientific purposes, for the production of radioisotopes, and for the irradiation testing of structural materials and nuclear fuel. It consists of two cores: a core operating in stationary mode, at a power of 14 MW (SSR), and a core operating in pulsed mode, capable of generating pulses of up to 20,000 MW (ACPR). According to the safety and environmental documentation, the TRIGA reactor is planned to be shut down and put into the decommissioning process in 2035, upon the expiration of the operating permit [3] [4].

Main Objective of the Thesis: To optimize radiological characterization methodologies for liquid waste generated during the TRIGA reactor's operation by implementing scaling factor (SF) methodologies, and to develop new radiological characterization methods for waste resulting from the reactor's decommissioning.

The main objective of this thesis is to optimize the radiological characterization methodology for liquid waste generated during the TRIGA reactor operation by implementing the scaling factors (SF) method, and to develop radiological characterization methodologies for radioactive waste that will result from TRIGA reactor decommissioning activities.

To fulfill the main objective of the doctoral thesis, the research focused on the radiological characterization of three categories of waste (liquids, irradiated aluminum, and boron carbide) from which the following specific objectives resulted:

Specific Objectives:

- **O1:** Implementation of the scaling factor methodology in the radiological characterization process of liquid waste;
- **O2:** Development of the radiological characterization methodology for irradiated aluminum, which will result from the decommissioning activity of the TRIGA reactor;
- **O3:** Development of the radiological characterization methodology for irradiated boron carbide (B_4C), which will result from the decommissioning activity of the TRIGA reactor.

These objectives are closely related to the progress of research and development of radiological characterization methods applied to determine the inventory of radionuclides contained in radioactive waste arising from nuclear facilities operation and decommissioning.

In subchapter 1.1, the results summarized in the latest report of the European Commission, following Directive 2011/70/Euratom, on the inventory of radioactive waste at the EU level,

were presented to emphasize the importance of research in the field of radioactive waste management resulting from nuclear activities [5]. The estimates made for the year 2023 highlight a significant increase for all categories of radioactive waste. This increase is mainly due to decommissioning activities, the operation of existing nuclear power plants, and, to a lesser extent, the generation of waste from medical, industrial, and research activities.

In subchapter 1.2., I briefly presented the national context of radioactive waste, the sources of radioactive waste, and the classification system recommended by the national nuclear authority (CNCAN). Also, within this subchapter, I made a brief presentation of the management of radioactive waste resulting from the operation of the TRIGA reactor and the waste that will result from the decommissioning activity.

2 CURRENT STATUS OF RESEARCH ON CHARACTERIZATION METHODS AND TECHNIQUES APPLIED FOR NUCLEAR WASTE GENERATED BY NUCLEAR ACTIVITIES

Chapter 2 presents the fundamental concepts underlying the characterization process, with an emphasis on the radiological characterization methods and techniques applied at the international level. Also, the main non-destructive and destructive methods used to determine the inventory and activity concentration of easy-to-measure (ETM) and difficult-to-measure (DTM) radionuclides contained in the radioactive waste resulting from nuclear activities were presented and described. Finally, the spectrometric analyses used in different stages of the experimental program of the thesis were briefly described.

The research undertaken has demonstrated the importance of the characterization process at all stages of radioactive waste management to clearly show that the conditioned waste meets the performance requirements established by the acceptance criteria for disposal.

The radiological characterization is the core of the radioactive waste characterization process, determining the radionuclide inventory, activity concentrations, and radiation types. This information is fundamental for waste classification according to regulatory norms, handling and shielding requirements, decisions on treatment and conditioning methods, transport planning, and demonstration of compliance with acceptance criteria for disposal [6].

In general, in the specialized literature, the following characterization methods are applied to estimate the radionuclide inventory: non-destructive, destructive, and methods based on the use of appropriate computational codes, generally those based on the Monte Carlo method and the SF method.

Non-destructive methods involve an analysis based on the spontaneous detection of nuclear radiation, without influencing the physical or chemical form of the waste package. Several passive non-destructive methods have been identified, such as: gamma ray spectrometry (full and partial scanning of the sample), calorimetry, digital autoradiography, passive neutron measurements, gas analysis (tritium - ^{3}H and carbon - ^{14}C) and active non-destructive methods: radiography, tomography, high-energy photon imaging techniques, prompt gamma ray analysis by neutron activation (PGNAA), Bremsstrahlung photon analysis (photo fission) [7], muon tomography and high-resolution laser spectroscopy (Cavity Ring-Down Spectroscopy –

CRDS) [8]. These non-destructive characterization methods and techniques are used in particular for conditioned radioactive waste packages, being mainly intended for determining the inventory of ETM radionuclides.

Regarding the destructive methods, these are applied to determine the inventory of DTM radionuclides and consist mainly of sample dissolution, followed by chemical separation methods specific to each element of interest, as well as radiometric analyses selected according to the chemical and radiometric properties of the studied radionuclides [2]. In this chapter, I presented the radiochemical methodologies studied and applied at an international level for assessing the activity concentration of the radionuclides ^{3}H, ^{90}Sr, ^{63}Ni, and ^{55}Fe, these being the DTM radionuclides of interest for the research carried out in this work.

From the experience of European countries and IAEA member countries, it was identified the scaling factor methodology as one of the most widely applied characterization methodologies used in the evaluation of DTM radionuclides. The SF method is particularly applicable in the situation of characterizing large volumes of radioactive waste in order to meet the acceptance criteria for disposal.

The scaling factor (SF) method is an empirical method that evaluates the activity concentration of DTM radionuclides based on a correlation between key radionuclides (KN) and DTM. Once an SF value corresponding to a radioactive waste stream has been established, it can be applied in the evaluation of the activity concentration of DTM radionuclides (alpha and beta emitters). From the analysis of specialized documents [9], [10], [11], which addressed this topic, the main aspects and stages (documentation, radiological characterization, evaluation and analysis of radiochemical data, and SF determination) that underlie the implementation of the SF methodology were identified and described.

Finally, the principles which are the basis for performing spectrometric analyses (gamma spectrometry, liquid scintillator spectrometry - LSC, and inductively coupled plasma optical emission spectrometry – ICP OES) applied in the different stages of the experimental program implemented within the thesis were briefly described.

3 EXPERIMENTAL RESEARCH ON THE RADIOLOGICAL CHARACTERIZATION OF LIQUID RADIOACTIVE WASTE GENERATED DURING TRIGA REACTOR OPERATION

The experimental research presented in this chapter focused on the development and optimization of the radiological characterization methodology applied to the liquid radioactive waste stream, to determine the inventory and activity concentration of the ETM and DTM radionuclides (^{3}H, ^{63}Ni, and ^{90}Sr) present in the representative samples analyzed. Based on the radiochemical data obtained by performing gamma and LSC spectrometric analyses, the SF method was implemented according to the ISO 21238:2007 standard [12].

At the same time, there were presented the experimental studies carried out for optimizing: the applied spectrometric analyses, by implementing efficiency calibration curves for different measurement geometries, the radiochemical protocol applied in the separation and purification

of ^{63}Ni from beta-gamma interferences, by introducing the AG 1-X8 type ion exchange resin, determining the activity concentration of pure beta radionuclides ^{3}H and ^{90}Sr.

The radiochemical data obtained were used to determine the SF values by applying the linearity relationship that involves estimating the activity concentration of DTM radionuclides by multiplying the scaling factor by the concentration of ETM nuclides. The statistical evaluation of the SF values was performed using statistical parameters.

The reason for which the experimental research was carried out on this category of radioactive waste was that significant quantities of liquid radioactive waste are generated from TRIGA reactor operation, and in this manner, the collection of representative samples does not constitute a limitation in the conduct of the proposed experiments. Also, from the perspective of the storage mode, based on the generating source, this type of waste is considered a homogeneous waste from a radiological point of view. During the experiments, the main challenge was the collection of representative samples, because the TRIGA reactor was shut down for some time for maintenance.

The research studies undertaken regarding the radiological characterization stage involved a series of experimental activities such as:

- Implementation of energy and efficiency calibration curves that are the basis for performing gamma spectrometric analyses of liquid radioactive waste samples in different measurement geometries.
- Performing gamma spectrometric analyses and interpreting the results obtained.
- Development, optimization, and implementation of the protocol for separating ^{3}H from beta-gamma interferences present in liquid radioactive waste samples;
- Development and implementation of the radiochemical protocol for the separation/purification of ^{90}Sr from beta-gamma interferences present in the analyzed samples.
- Development and implementation of the radiochemical protocol for the separation/purification of ^{63}Ni from beta-gamma interferences present in representative liquid radioactive waste samples.
- Evaluation of the activity concentration of ^{3}H, ^{90}Sr, and ^{63}Ni by LSC analyses.
- Evaluation of performance parameters corresponding to the applied characterization methodologies (F.D., E.D, and chemical yield).
- Verification and validation of radiochemical protocols applied in the separation, purification, and quantification of gamma, ^{3}H, and ^{90}Sr radionuclides by participating in intercomparison tests organized by the IAEA.
- Evaluation of radiochemical data and applicability of SF;
- Determination of scaling factors specific to the liquid radioactive waste stream, based on experimental data.

In the framework of the work, for determining the radiochemical data set, experimental research was carried out on establishing the characterization methodology necessary to accurately determine the inventory and activity concentration of gamma radionuclides (ETM) as well as ^{3}H, ^{90}Sr, and ^{63}Ni (DTM) from 22 representative samples of liquid radioactive waste. The samples were taken from the tanks used for the intermediate storage of liquid waste

originating from different generation points such as: floor drainage from the pump room (tanks R3.1 and R3.2), from the regeneration of ion exchange resin filters (tanks R4.2 and R4.1) and the radiochemical laboratories (tanks R2.1 and R2.2).

The initial physico-chemical characterization of the samples revealed conductivity values ranging from 0.1 to 13 mS/cm and the pH ranged from 7 to 11. The high pH and conductivity values, obtained especially in the samples taken from the R4.2 tank, suggest the presence of a significant concentration of dissolved salts in the respective samples and indicate an alkaline environment.

3.1 The assessment of gamma radionuclide inventory (ETM)

In defining the inventory of gamma radionuclides contained in the analyzed samples, I performed gamma ray spectrometry analyses using a GeHP detector with a relative efficiency of 15%. The gamma ray spectrometry involved steps such as: implementation of calibration curves in energy and efficiency according to the experimental geometrical configurations of detector-sample, the acquisition, analysis, and interpretation of the energy spectrum characteristic of the analyzed sample.

The gamma spectrometry measurements were performed at the contact with the detector in detection geometries (TRICARB bottle capacity 10 ml - ET and plastic bottle capacity 250 ml - EF) for which the calibration curves in efficiency and energy are established and verified by participating in the intercomparison tests organized by the IAEA in Vienna.

Tables 3-1 and 3-2 present the activity concentrations and the measurement uncertainties of the radionuclides present in the initial samples taken for analysis.

The main gamma radionuclides identified in significant concentrations in all the samples analyzed are the radionuclides ^{60}Co, ^{54}Mn, and ^{58}Co. While ^{51}Cr, ^{125}Sb, ^{124}Sb, ^{57}Co, and ^{137}Cs radionuclides were presented only in the samples taken from R4.2, R4.1, R2.1, and R2.2 tanks. The activity concentration range of gamma radionuclides is as follows: ^{60}Co is found in the range of $10^2 \div 10^6$ Bq/kg, ^{58}Co in the range of $10 \div 10^4$ Bq/kg, ^{54}Mn in the range of $10 \div 10^3$ Bq/kg, ^{51}Cr is found between 5 10^1 and 10^4 Bq/kg, ^{125}Sb was only detected in sample B4 in a concentration of 10^2 Bq/kg and ^{124}Sb in the activity range of $10^1 \div 10^4$ Bq/kg.

Table 3-1 Activity concentration of ^{54}Mn, ^{58}Co and ^{60}Co radionuclides identified in the analyzed samples

Generating source	**Radionuclide**	**^{54}Mn**		**^{58}Co**		**^{60}Co**	
	ID Sample	Activity Concentration (Bq/kg)	Uncertainty Measurement (Bq/kg)	Activity Concentration (Bq/kg)	Uncertainty Measurement (Bq/kg)	Activity Concentration (Bq/kg)	Uncertainty Measurement (Bq/kg)
R4.2	**B1**	6,84E+03	1,81E+02	1,66E+04	4,24E+02	8,96E+04	1,32E+03
	B2	2,36E+02	1,06E+01	2,20E+02	1,02E+01	5,56E+03	3,28E+01
	B3	1,88E+05	3,90E+03	1,03E+06	1,96E+04	1,90E+06	2,12E+04
	B4	<115		3,95E+03	1,09E+02	9,10E+03	1,47E+02

Generating source	Radionuclide	^{54}Mn		^{58}Co		^{60}Co	
	ID Sample	Activity Concentration (Bq/kg)	Uncertainty Measurement (Bq/kg)	Activity Concentration (Bq/kg)	Uncertainty Measurement (Bq/kg)	Activity Concentration (Bq/kg)	Uncertainty Measurement (Bq/kg)
	B5	1,31E+03	5,03E+01	6,49E+02	4,02E+01	6,82E+04	7,54E+02
	B6	1,15E+03	3,92E+01	1,44E+02	2,45E+01	4,32E+04	4,79E+02
	B7	8,78E+02	2,90E+01	2,81E+02	2,01E+01	4,52E+04	4,94E+02
	B8	3,21E+03	1,30E+02	1,97E+04	4,45E+02	9,99E+04	1,15E+03
	B9	2.18E+03	1.69E+02	2.88E+03	7.16E+01	9.76E+04	1.09E+03
	B10	<1.55E+02		6.11E+02	2.59E+01	2.81E+04	3.38E+02
R3.1	**A**	5,57E+01	3,77	3,79E+02	1,19E+01	8,54E+02	1,54E+01
R2.2	**D1**	3,50E+01	9,01	2,05E+02	1,61E+01	4,19E+02	1,78E+01
	D2	9,54	9,15E-01	1,67E+01	1,07	3,42E+02	4,63E+00
R2.1	**E1**	4,42E+02	3,99E+01	1,47E+03	7,16E+01	4,03E+03	1,01E+02
	E2	7,66	1,67	2,85E+01	2,2	3,40E+02	6,47
	E3	5,33E+01	1,11	4,41E+01	1,60	3,17E+02	4,32
R4.1	**C1**	1,30E+03	4,50E+01	2,76E+03	8,03E+01	1,57E+04	2,42E+02
	C2	6,27E+02	3,49E+01	4,82E+03	1,15E+02	9,10E+03	1,29E+02

Table 3-2 Activity concentration of ^{51}Cr, ^{125}Sb, ^{57}Co, ^{124}Sb and ^{137}Cs radionuclides identified in the analyzed samples

ID Sample	**Activity Concentration ± Uncertainty Measurement (Bq/kg)**				
Radionuclide	**^{51}Cr**	**^{125}Sb**	**^{57}Co**	**^{124}Sb**	**^{137}Cs**
B1	<1320	<562	3,21E+02±21,4	8,80E+02±41,5	<281
B2	<19,6	<82,5	<14,9	<33,6	<42,1
B3	3,17E+04±4,26E+03	<136	6,85E+03±3,78E+02	4,01E+04±1,28E+03	<7E+3
B4	1,68E+03±1,17E+02	4,70E+02±34,18	2,75E+01±5,91E+00	3,71E+03±81	<92
B5	<1090	<460	6,64E+01±1,06E+01	<190	3,17E+02±30,4
B6	<660	<296	3,57E+01±5,91	<128	<160
B7	<690	<321	6,63E+01±5,64	<142	3,12E+02±18,90
B8	<2850	<1110	1,69E+02±28,0	2,41E+03±96,1	<562
B9	<1,03E+03	<442	1,06E+02±45,0	5,34E+02±83	1,11E+02±61,40
B10	<6,02E+02	<257	<4,30E+01	4,32E+02±57	2,06E+02±60
A	2,98E+02±20,6	<37,5	<7,4	1,51E+01±2,26	1,78E+01±2,73

ID Sample	Activity Concentration ± Uncertainty Measurement (Bq/kg)				
Radionuclide	**^{51}Cr**	**^{125}Sb**	**^{57}Co**	**^{124}Sb**	**^{137}Cs**
D1	1,04E+02±38,0	<53	<9	2,82E+01±7,05	<27
D2	2,22E+01±4,15	<12	<2	<4,6	<5,7
E1	<1030	<405	<80	7,85E+01±21,1	<207
E2	5,08E+01±8,94	<26	<4,6	<9,8	<8,24
E3	5,33E+01±4,60	<13	<2,2	<4	<4,2
C1	<565	<245	5,33E+01±6,30E+00	2,11E+02±18,10	1,48E+02±18,5
C2	<724	<310	<48	4.00E+02±26,6	<155

The results obtained revealed higher activity concentrations in the samples taken from the R4.2 storage tank, as expected, given the conductivity and pH values identified, but also because this tank stores liquid radioactive waste resulting from the regeneration of the spent resin used in the water purification system in the TRIGA reactor pool.

Gamma ray spectrometry analyses defined the inventory of gamma radionuclides, respectively, the beta-gamma interferents in the radiochemical procedures applied for the separation and purification of DTM radionuclides (^{3}H, ^{90}Sr, and ^{63}Ni) studied in the doctoral thesis. Also, based on the results obtained, the key radionuclide (KN) necessary for the implementation of the SF method was established as being the ^{60}Co radionuclide. It is present in all analyzed samples in significant concentrations, being the main radionuclide contributing to the total activity of the waste, and at the same time has the longest half-life.

3.2 Assessment of the activity concentration of ^{3}H, ^{63}Ni, ^{90}Sr radionuclides

The assessment of the activity concentration of DTM radionuclides represents an important stage in determining the scaling factors characteristic to the analyzed waste stream. The research in this stage focused on the sequential determination of the ^{3}H, ^{90}Sr, and ^{63}Ni activity concentration present in the waste samples analyzed. The methodology applied for this purpose was developed and optimized through experimental tests performed with inactive solutions (containing stable isotopes of the interest elements) and simulated radioactive solutions (solutions with known content of the interest radionuclides).

The experimental steps carried out to sequentially determine the ^{3}H, ^{90}Sr, and ^{63}Ni activity concentration are presented in Figure 3-1.

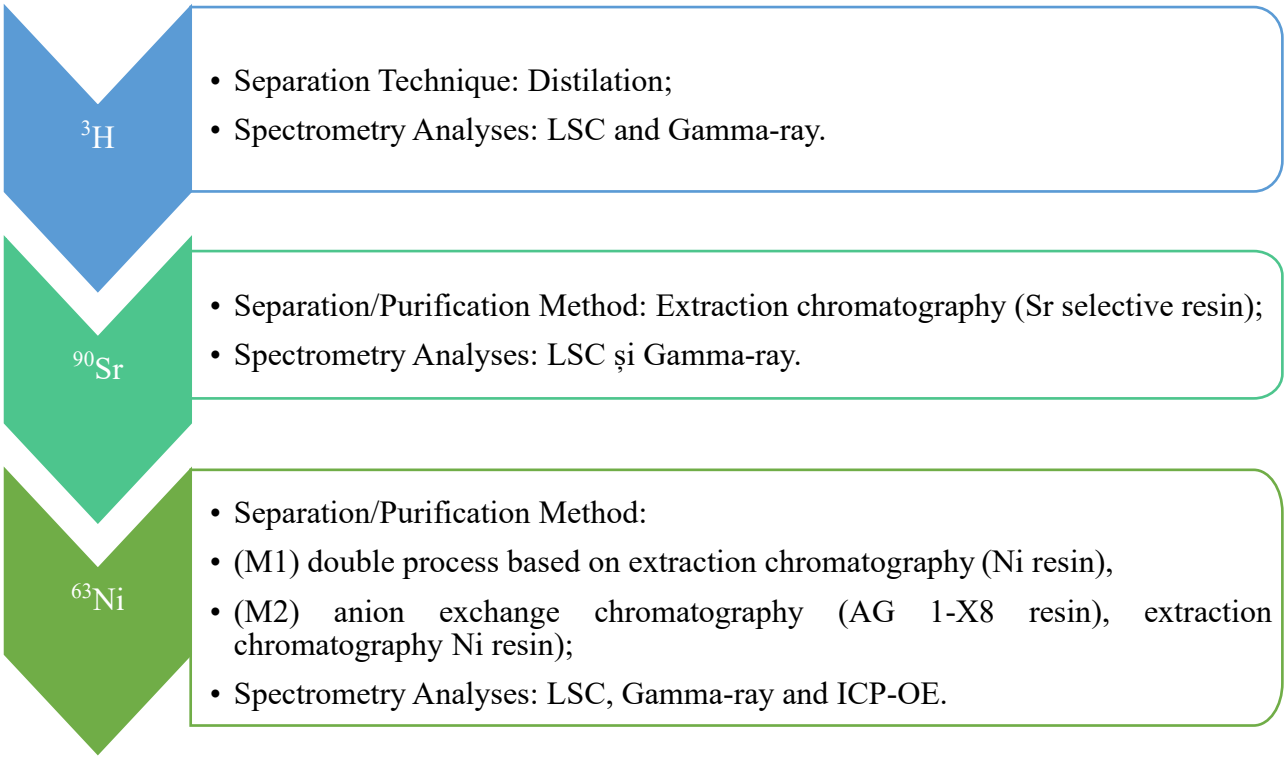


Figure 3-1 Experimental steps carried out to quantify ^{3}H, ^{90}Sr, and ^{63}Ni radionuclides.

The radiochemical separation and purification methods applied for the determination of ^{90}Sr were based on extraction chromatography using Sr selective resin [13], while for the determination of ^{63}Ni, the radiochemical methods applied consisted of: two consecutive separation processes based on extraction chromatography using Ni selective resin (methodology M1) and separation of ^{63}Ni from beta-gamma interfering by ion exchange chromatography using AG 1-X8 resin, followed by purification of ^{63}Ni by extraction chromatography using Ni selective resin (methodology M2) [14] [15] [16]. In order to determine the activity concentration of ^{3}H, the distillation technique was applied as a method for separating tritium from beta-gamma interfering radionuclides [17].

The activity concentration of ^{3}H, ^{90}Sr, and ^{63}Ni radionuclides was determined by performing LSC measurements using a TRICARB model 5110TR analyzer from PerkinElmer (USA). The LSC analyses applied in the quantification of ^{63}Ni and ^{3}H radionuclides involved plotting attenuation curves based on the variation of the measurement efficiency values depending on the attenuation indication parameter values (tSIE, tSIE/AEC). For the quantification of ^{90}(Sr-Y) radionuclides, the Efficiency Tracing technique was applied [18].

Table 3-3 presents the results obtained from LSC analyses related to the activity concentration of ^{3}H, ^{90}Sr, and ^{63}Ni radionuclides contained in the analyzed samples.

The tritium activity concentration (^{3}H) determined in the liquid waste samples falls within the range of $10^{2} \div 10^{4}$ Bq/kg. This variation between the analyzed samples is influenced by a series of parameters such as the operating regime of the reactor, the time of sampling, the date of the analyses, and the volatile nature of tritium. All these aspects have a significant impact on the results obtained, which makes it difficult to correlate with the radionuclide KN corresponding to the liquid radioactive waste stream.

Table 3-3 Activity concentration of ^{3}H, ^{90}Sr and ^{63}Ni obtained in the samples analyzed

ID sample	Activity Concentration± Uncertainty Measurement (Bq/kg)		
	^{63}Ni	^{90}Sr	^{3}H
A	5,54E+02 ± 1,77	<6,604	6,46E+04 ± 0,150
B1	9,27E+04 ± 231,73	2,28E+01±0,33	8,13E+03 ± 0,020
B2	1,09E+04 ± 27,26	<6,604	120 ± 0,002
B3	2,53E+06 ± 5330,03	2,86E+02±1,21	4,64E+04 ± 0,110
B4	1,74E+03 ± 4,78	3,99E+01±0,41	1,42E+04 ± 0,031
B5	1,21E+05 ± 6,07E+02	<9,5	1,05 E+04 ± 0,035
B6	8,27E+04 ± 4,14E+02	<9,4	5,52 E+03 ± 0,026
B7	9,53E+04 ± 4,77E+02	N/A	4,91 E+03 ± 0,034
B8	1,78E+05 ± 8,89E+02	N/A	9,48 E+03 ± 0,024
B9	2,43E+05 ± 7,66E+02	8,75E+01±0,40	1,38 E+04 ± 0,038
B9.1	2,06E+05 ± 5,66E+02	N/A	
B10	1,93E+04 ± 1,04 E+02	3,83E+01±0,24	1,32 E+04 ± 0,036
B10.1	1,89E+04 ± 1,00E+02	N/A	
B10.2	1,94E+04 ± 9,5E+01	N/A	
B10.3	1,92E+04 ± 9,11E+01	N/A	
C1	2,41E+03 ± 6,02	8,24E+01 ± 0,55	1,072E+04 ± 0,025
C2	8,98E+03 ± 21,34	6,51 ± 0,09	1,78E+04 ± 0,041
E1	7,23E+02 ± 2,42	<6,60	8,21E+04 ± 0,191
E2	5,97E+02 ± 2,99	<6,60	1,16 E+04 ± 0,155
E3	5,39E+02 ± 2,70	N/A	3,54 E+04 ± 0,089
D1	1,05E+03 ± 7,90	<6,60	1,71 E+03 ± 0,011
D2	5,33E+02 ± 4,00	<6,60	6,31 E+03 ± 0,075

The ^{90}Sr radionuclide is found in low concentrations and only in samples B1, B3, B4, B9, B10, C1, and C2. The average activity concentration is 1.16×10^{2} Bq/kg for samples taken from R4.2 storage tanks and 4.45×10^{1} Bq/kg for samples from R4.1 storage tanks. In A, B2, D, and E samples ^{90}Sr radionuclide was not identified or was below the MDA (6.604 Bq/kg).

The radionuclide ^{63}Ni is found in all the analyzed samples, and the activity concentration is between 5.33×10^{2} Bq/kg and 2.53×10^{6} Bq/kg. It is observed that in B1-B8 ID samples, ^{63}Ni is found in the highest activity concentration, being representative samples taken from the R4.2 tank, where the liquid waste resulting from the regeneration of the exchange resin bed is stored.

The radiochemical methodologies performance applied in ^{90}Sr and ^{63}Ni activity concentration determination was evaluated based on the decontamination efficiency, the decontamination factor, and the chemical yield.

The chemical yield was determined based on the initial and final concentrations of the stable carriers present in the samples subjected to the separation process, respectively, in the elution samples, values determined by ICP-OES analyses.

The chemical yield values depend on aspects such as: the complexity of the radiochemical protocol, human errors in the preparation of the solutions, and how the experiments are conducted. Therefore, it is recommended to determine it for each experimental test performed. The chemical yield values for the separation and purification procedure of Sr were obtained between 70% and 93%, and for Ni, values between 70-87%. The chemical yields obtained were applied in the correction of the ^{90}Sr and ^{63}Ni activity concentration from the analyzed liquid radioactive waste samples.

Regarding the decontamination efficiency values obtained for beta-gamma interferes, they were over 98% after the second purification process, and the decontamination factor values were higher than 10^3 for ^{60}Co radionuclide, the main interfering beta-gamma identified both in the solutions corresponding to the ^{90}Sr elution and in the ^{63}Ni elution.

The radiochemical methodologies applied in the separation, purification and quantification of ^{3}H and ^{90}Sr, as well as the calibrations used in gamma spectrometric analyses, were verified and validated by participating in intercomparison tests organized by the IAEA (IAEA-TERC-2022-01, IAEA-TERC-2023-01, IAEA-TERC-2024-01), in which the accepted qualification was received for both accuracy and precision criteria.

3.3 Implementation of the scaling factor (SF) methodology

The evaluation of radiochemical data, SF applicability and Establishing DTM and KN correlations

Taking into account the physico-chemical behavior, but also the fact that the concentrations identified are of the same order of magnitude for ^{63}Ni and ^{60}Co radionuclides, it can state that there is a correlation between the two radionuclides present in the representative samples of liquid radioactive waste. Another pair of DTM/KN radionuclides studied was ^{90}Sr and ^{137}Cs, based on their similar chemical behavior and mode of production, both being fission products. Unfortunately, the activity concentration of the radionuclide KN: ^{137}Cs, in most representative samples was below the MDA, which is why, based on the recommendations in the specialized literature, I analyzed the correlation between ^{90}Sr and ^{60}Co, although the presence of strontium was not evidenced in all the analyzed samples, and the activity concentrations are low compared to those of ^{60}Co.

The radiochemical data characteristic of the ^{63}Ni/^{60}Co and ^{90}Sr/^{60}Co radionuclide pairs obtained during the radiological characterization stage were evaluated and analyzed to demonstrate the applicability of the methodology and the correlation relationship between the radionuclides studied. For this purpose, statistical indicators such as: Grubbs test, Pearson coefficient, and log-normal data dispersion diagrams were used.

The Grubbs test [19] was applied to identify whether the maximum and minimum values in the data set characteristic of ^{63}Ni activity concentration are outliers. In the analyzed situation, it was identified for the upper value a G_{max}=4.47 value, and for the lower value a G_{min} = - 0.31

value. From the comparison of these values with the critical values derived from the t-Student distribution tables, the maximum value in the analyzed data set (2.53E+06 corresponding to the B3 sample) was identified as an outlier. This value must be eliminated from the calculation of the scaling factors if this calculation algorithm is verified. Since, at this stage of the research, the emphasis was on clarifying the correlation relationship between KN and DTM radionuclides and on how to determine SF, in the data analysis performed to establish the correlation relationship between the $^{63}Ni/^{60}Co$ radionuclides pair, I did not exclude the outlier identified by the Grubbs test.

The Pearson coefficient [20] [21] It was calculated based on equation 3-1 for both sets of radiochemical data corresponding to $^{63}Ni/^{60}Co$ radionuclide pairs (for samples from the same source) and $^{90}Sr/^{60}Co$ (for all samples in which ^{90}Sr was identified).

$$r_{xy} = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 \ \ \sum_{i=1}^{n}(y_i - \bar{y})^2}} \tag{3-1}$$

Where: n is the sample size, x_i *and* y_i are the individual sample points indexed with i, and $\overline{x}$ și $\overline{y}$ are the sample means of the two variables.

Table 3-4 presents the Pearson correlation coefficient values obtained by calculation for the two analyzed situations. The obtained values demonstrate the positive linear relationship between the activity concentrations of the radionuclide pairs: $^{63}Ni/^{60}Co$ (for B1-B10, E1-E3, D1-D2 samples) and $^{90}Sr/^{60}Co$.

Table 3-4 The Pearson correlation coefficient of the $^{63}Ni/^{60}Co$ and $^{90}Sr/^{60}Co$ radionuclides pairs

ID Sample	*Pearson coefficient (r_{xy})*	
	$^{63}Ni/^{60}Co$	$^{90}Sr/^{60}Co$
B1-B10	0,998	0,90
C1-C2	-0,49	
D1-D2	+1	
E1-E3	+1	

Another indicator that highlights the correlation relationship, respectively compatibility between the DTM and KN radionuclides, is the logarithmic normal distribution of the radiochemical data. The distribution of the radiochemical data regarding the ^{63}Ni, ^{90}Sr, and ^{60}Co activity concentrations was graphically represented on a linear (Figure 3-2) and logarithmic (Figure 3-3) scale.

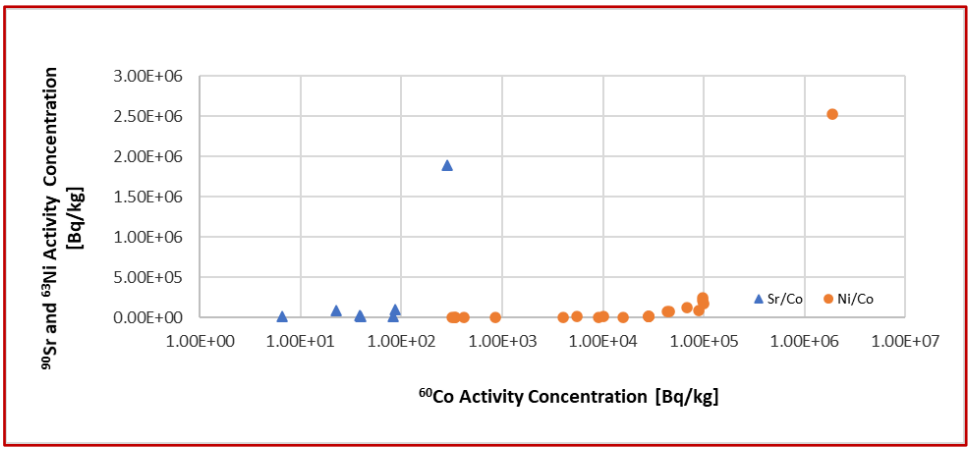


Figure 3-2 Radiochemical data distribution on a linear scale

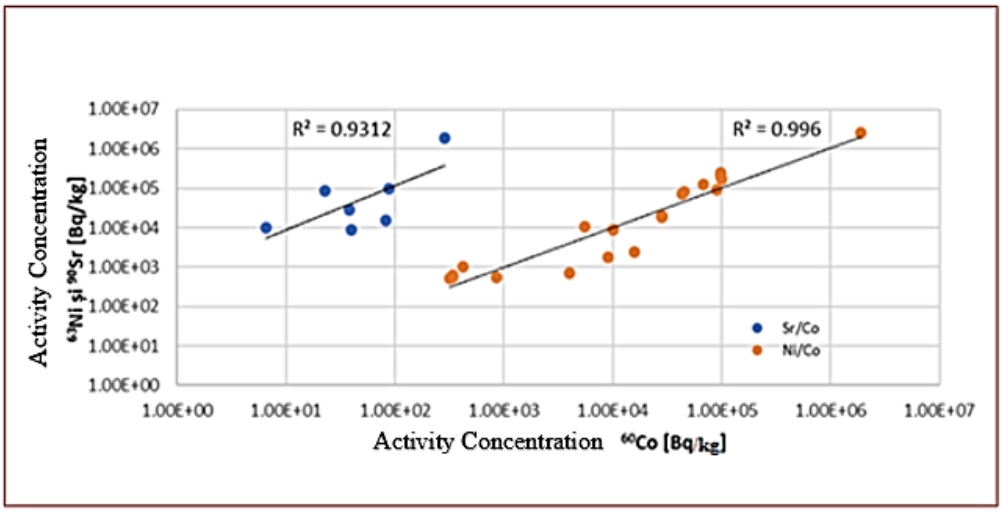


Figure 3-3 Radiochemical data distribution on a logarithmic scale

The analysis of the values distribution corresponding to the ratios between $^{63}Ni/^{60}Co$ and $^{90}Sr/^{60}Co$ depending on ^{60}Co activity concentration highlights a strong positive correlation between ^{63}Ni and ^{60}Co radionuclides, most likely due to similar chemical and production characteristics. While for ^{90}Sr and ^{60}Co radionuclides the correlation is much weaker, the values being more dispersed, most likely due to the different chemical behavior of strontium, but also to the small number of data points.

Regarding the way of representing the radiochemical data distribution, it can be observed that Figure 3.2 (arithmetic scale scatter diagram) is not an optimal representation to understand the distribution characteristics of the radionuclides studied. On the other hand, the scatter diagram on a logarithmic scale allows a clear understanding of the correlation between radionuclides. Both the concentration ranges and the SF ratios present log-normal distributions, an important aspect in applying the SF methodology to the radioactive waste stream studied.

The improvement of the correlation coefficient obtained in the logarithmic data scatter diagram (R2= 0.9962 for $^{63}Ni/^{60}Co$, respectively R2= 0.91 for $^{90}Sr/^{60}Co$) can be achieved by analyzing a large number of representative samples. Consequently, based on the results obtained, it is observed that there is a positive correlation for the studied radionuclide pairs ($^{63}Ni/^{60}Co$ and $^{90}Sr/^{60}Co$) for which the SF methodology can be successfully applied.

Scaling Factor Determination

Once the existence of the correlation relationship between the radionuclides studied was demonstrated, the SF determination was performed based on linearity relationships that involve estimating the activity concentration of the DTM radionuclides by multiplying the scaling factor by the concentration of the key nuclides (equation 3-2). The scaling factor values are determined as the geometric mean of the analyzed values according to equation 3-3 [10] [22].

$$C_{A,DTM} = SF \times C_{A,KN} \quad \text{or} \quad SF = \frac{C_{A,DTM}}{C_{A,KN}} \tag{3-2}$$

$$SF = \sqrt[n]{\frac{C_{A\ DTM(1)}}{C_{A,KN(1)}} \times \ldots \times \frac{C_{A\ DTM(i)}}{C_{A,KN(i)}} \times \ldots \times \frac{C_{A\ DTM(n)}}{C_{A,KN(n)}}}. \tag{3-3}$$

Where:$C_{A,KN}$= *key radionuclide activity concentration (Bq);*$C_{A,DTM}$= *difficult-to-measure radionuclide activity concentration (Bq); SF=factor de scalare; KN=key radionuclid; DTM=difficult-to-mesure; n= sample number.*

For obtaining the most accurate and useful information in the study, the evaluation of the data obtained was carried out using statistical indicators such as central tendency indicators (mean, median), dispersion indicators (standard deviation), asymmetry indicators, position indicators (score-z) [23].

Table 3-5 presents the SF values obtained by calculation for each analyzed sample corresponding to the $^{63}Ni/^{60}Co$ and $^{90}Sr/^{60}Co$ radionuclide pairs, the geometric mean (Mg), respectively, the arithmetic mean (Ma), the standard deviation from the arithmetic mean, and the median SF value.

The corresponding SF data for the $^{63}Ni/^{60}Co$ radionuclide pair were evaluated from three perspectives as follows:

- Analysis 1: involves a general assessment of the entire data set (SD1) specific to the determined SF values, without excluding possible outliers;

The data were evaluated by considering their distribution with respect to the mean, median and frequency. The score-z (Figure 3.6) was also calculated to indicate in terms of standard deviation how far an individual value (SF) is from the SF values mean.

From Figure 3-4, an asymmetric distribution to the left of the data is observed, given that the median value (1.47) is higher than the mean value (1.28) of the data. The dispersion of the data seems to be moderate, the related standard deviation (0.73) is relatively small compared to the data mean, which suggests that the data are not extremely spread out, but there is significant variability with respect to the mean value, which means that the values are not concentrated around the mean, but they are not very dispersed either.

Table 3-5 The SF values corresponding to the radiochemical data

Radionuclide	$^{63}Ni/^{60}Co$					$^{90}Sr/^{60}Co$			
ID Sample	SF	SF_Mg	SF_Ma	Standard Deviation	Median	SF	SF_Mg	SF_Ma	Standard Deviation
A	0.649	1,002	1,285	0,748	1,285	N/A	0,000952	0,001852	0.002
B1	1.042					0.000256			
B2	1.960					N/A			
B3	1.332					0.000151			
B4	0.191					0.004385			
B5	1.799					N/A			
B6	1.629								
B7	1.752								
B8	1.726								
B9	2.491					0.000896			
B9.1	2.109					N/A			
B10	0.685					0.001362			
B10.1	0.673					N/A			
B10.2	0.690								
B10.3	0.684								
C1	0.154					0.005261			
C2	0.899					0.000652			
D1	0.179					N/A			
D2	1.619								
E1	2.506								
E2	1.859								
E3	1.633								

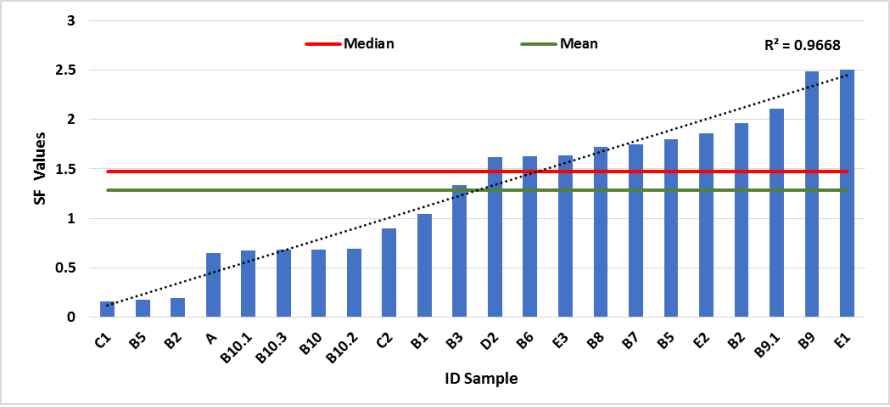


Figure 3-4 Data distribution (SF) compared to the mean and median of the analyzed dataset

The data distribution according to frequency in the form of a histogram (Figure 3-5) highlights that most of the data are found in the range 0.5-0.8 and 1.6-2 respectively and the distribution seems to be asymmetric to the left, with the possibility of the presence of outliers at low values of SF.

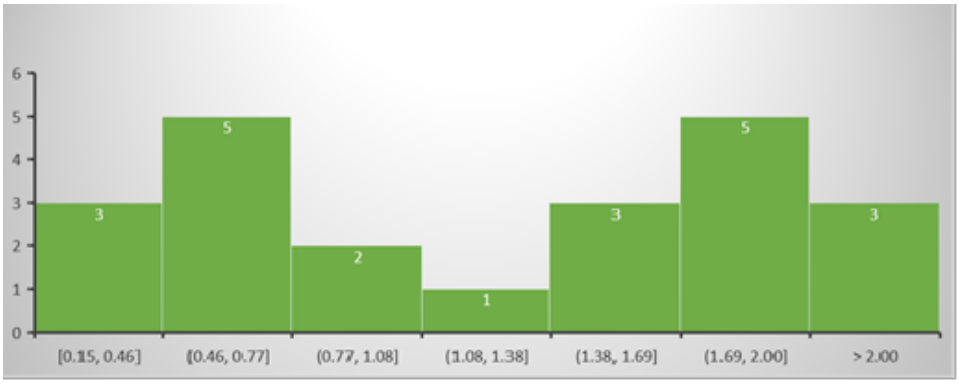


Figure 3-5 Histogram of the SF dataset

The score-z indicates in terms of standard deviation how far an individual value (SF) is from the mean of SF values and identifies possible outliers in the data set. From the analysis of the distribution of score-z values (Figure 3-6), it is found that for E1 and B 9.1 samples, the score-z values are very close to 2, which means that they are two standard deviations above the mean, so they have a higher performance than the other values [23], while for C1, D1 and B4 samples, the score-z values are negative values, indicating performance below the mean. The rest of the values are close to 0, being representative values of the general behavior of data close to the mean value.

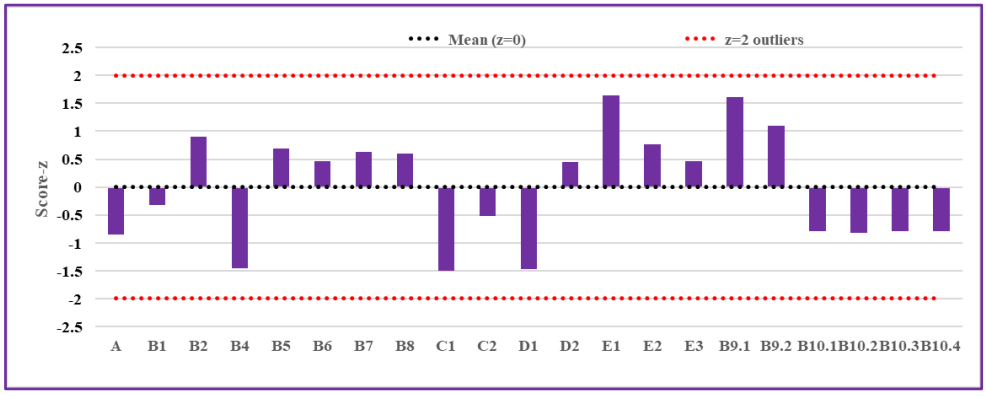


Figure 3-6 Distribution of score-z values compared to the mean value (z=0)

- **Analysis 2:** involves the restricted evaluation of the data set (SD2) related to SF values for samples resulted from the same generating source (R4.2) without excluding possible outliers;

The scaling factor values determined for this data set are found in the range 0.6÷2.5 with one exception, the SF value (0.191) determined for B4 sample.

To observe the influence of the SF_Mg and SF_Ma values in estimating the activity concentration of ^{63}Ni in the waste samples, the equation 3 - 2 was applied based ^{60}Co concentration and the SF value determined as geometric and arithmetic mean.

The estimated values of the activity concentration of ^{63}Ni based on the two SF values (Mg=1.13 and Ma=1.34) behave as follows:

- For initial SF values within the range 1≤SF ≤ 1.5, the ^{63}Ni activity concentration values estimated with the SF_Mg value are close to the ^{63}Ni activity concentration value experimentally determined, while the activity concentration values estimated using SF_Ma overestimate the ^{63}Ni activity concentration experimental.
- For initial SF ≥ 1.5, it is found that the estimated values with SF_Ma are much closer to the ^{63}Ni activity concentration values determined experimentally.

From the graphic representation (Figure 3-7), it can be seen that the values are in the same order of magnitude and follow the same trend, with small differences due to the inherent uncertainties associated with the applied methodology.

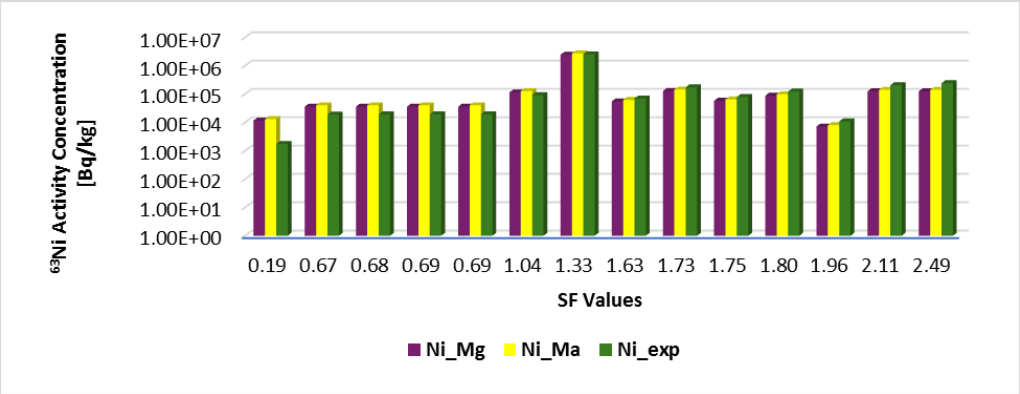


Figure 3-7 ^{63}Ni activity concentration values obtained experimentally and by calculation for SD2

The standard deviation from the geometric and arithmetic mean is 0.660, indicating a data distribution in the range of 0.47-1.79 (Mg) and 0.674 -2.006 (Ma), respectively. In this context, the value 0.19 (B4) is a suspicious value, with a score-z of -1.46, located at the lower edge of the distribution, and can be considered an outlier.

- **Analysis 3:** involves the evaluation of the data set (SD3) excluding outliers.

According to the Grubbs test and score-z analysis, the SF values corresponding to the B3 and B4 samples may be outliers that influence the mean of the SF values, especially at low values. Analyzing the SF data without these two values, it was obtained the geometric mean of the SD3 set equal to 1.29 and the arithmetic mean was 1.43. Although an increase in the Mg and Ma values is observed compared to those obtained in the SD2 analysis, the ^{63}Ni activity concentration estimated values behave approximately the same as in the SD2 analysis. The initial SF values interval of [1.1÷2] presents activity concentration values, estimated with Mg and Ma, close to the experimental values.

Figure 3-8 shows the ^{63}Ni activity estimated values compared to those determined experimentally.



Figure3-8 The ^{63}Ni activity concentration values for SD 3 analysis

From the analysis of the results related to SD_2, respectively SD_3 it can be conclude that the exclusion of values considered outliers did not lead to significant differences in the ^{63}Ni activity concentration estimates compared to the experimental values. Their distribution according to the SF initial value confirms that at SF <1 initial values there is an overestimation of the ^{63}Ni activity, at SF values within the interval [1.1÷2] the ^{63}Ni activity tends towards the experimental one, while at SF> 2 values the activity seems to be underestimated.

The results obtained led to the conclusion that the SF value corresponding to the liquid radioactive waste flow for the ^{63}Ni/^{60}Co radionuclide pair is found in the interval [1÷1.44] according to the initial SF mean values (geometric, respectively, arithmetic). Of course, this interval may change as the radiochemical data set is completed.

The results obtained regarding the determination of the SF value corresponding to the ^{63}Ni/^{60}Co and ^{90}Sr/^{60}Co radionuclide pairs are preliminary information that will be completed with experimental data, in order to finalize the implementation of the SF method in the characterization of liquid radioactive waste generated from TRIGA reactor operation.

The research results will be used to optimize the radiological characterization methods currently applied in RATEN ICN. The data obtained regarding the implementation of the SF methodology in the process of liquid waste characterization resulting from TRIGA reactor operation are preliminary and constitute **the novelty of this study**; to date, no studies have been conducted regarding the determination of SF based on experimental data for waste generated from TRIGA reactor operation at ICN Pitesti.

4 EXPERIMENTAL RESEARCH ON THE RADIOLOGICAL CHARACTERIZATION OF IRRADIATED ALUMINUM

From TRIGA reactor decommissioning it is expected to result significant quantities of solid waste, consisting in particular of the structural materials used in the construction of the two cores SSR and ACPR. The following categories of radioactive waste have been identified: cement, reinforced concrete, sheet metal, cables, process pipes, metals (sheet metal and profiles) made of aluminum, stainless steel, carbon steel, boron carbide, beryllium, irradiated nuclear graphite and ventilation filters [24].

Ensuring the safe management of radioactive waste resulting from the reactor decommissioning activity is an important issue for the licensee, which requires research studies

to develop and validate characterization, treatment and conditioning methods. The implementation of the decommissioning plan also requires knowledge of the inventory of radionuclides contained in each structural material considered radioactive waste after decommissioning, especially for high-energy gamma emitters that contribute significantly to the radiation dose to which personnel performing the dismantling activities may be exposed.

In this context, the research carried out on the aluminum alloy matrix ($AlMg_3$) aimed to develop a methodology for characterizing the aluminum resulting from TRIGA reactor decommissioning, a methodology that will be applied in estimating the inventory and activity concentration of radionuclides contained in irradiated aluminum. This category of radioactive waste is considered problematic, due to its high reactivity in the hyperalkaline environment characteristic of the cement matrices commonly used for waste conditioning.

The decommissioning activities of the TRIGA reactor are expected to result in significant quantities of several tons of irradiated aluminum consisting of technological pipes, metal sheet and profiles.

The research activities carried out to develop the methodology for radiological characterization of controlled irradiated aluminum in the reactor consisted of:

- Experimental tests to determine the chemical composition and the inventory of impurities contained in the analyzed matrix;
- Mathematical modeling using MCNP6 and ORIGEN-S computational codes to estimate the activity concentration of radionuclides, based on the irradiation history and aluminum composition;
- Experimental tests, using samples of irradiated aluminum controlled in the TRIGA reactor, to test and optimize the radiological and radiochemical methods that will be applied in the characterization of irradiated aluminum resulting from decommissioning.

Taking representative samples of aluminum from the core is an impossible activity, given that the TRIGA reactor is still in operation. Therefore, to achieve the proposed objectives, a cylindrical bar with dimensions of 250x10x6 mm and density of 2.7 g/cm^3 was manufactured from an $AlMg_3$ alloy plate, which was irradiated in the reactor using an appropriate irradiation device; this did not allow the aluminum to come into contact with the reactor pool water to become contaminated. The mathematical modeling and experimental tests carried out in order to develop the methodology for characterizing this type of waste were performed on representative samples taken from the irradiated $AlMg_3$ bar.

The aluminum bar, after irradiation was transferred to the post-irradiation examination laboratory (PIEL) for a 180-days cool-down period. After this period, two representative samples (ID: A1 and A2) were taken by cutting in the hot cells and transferred to the radiometric analysis laboratory from Radioactive Waste Treatment Plant in order to conduct experimental tests regarding their radiological characterization.

4.1 Experimental tests carried out to establish the chemical composition of the $AlMg_3$ alloy

The chemical composition and the inventory of impurities present in the analyzed matrix represent an important aspect, especially in the realization of mathematical modeling, more precisely in the creation of the input characteristic to the studied configurations. The accuracy of the results obtained through mathematical modeling depends on the precision of the chemical composition and irradiation data.

Characterization techniques such as SEM-EDS, EDXRF, and ICP-OES were used to determine the chemical composition and implicitly the distribution of impurities in the analyzed $AlMg_3$ sample.

Characterization tests were performed on inactive aluminum alloy ($AlMg_3$) samples. SEM-EDS measurements were performed using a HITACHI SU5000 scanning electron microscope combined with an energy dispersive detector (EDS), and EDXRF analyses were performed using a SPECTRO MIDEX M spectrometer that allows rapid point-by-point analysis of unidentified samples.

The following chemical elements were identified in the investigated sample: Al, Fe, Mn, Mg, Cr, Ni, Ti, Si, Zn, and Ca. Significant differences were observed between the two sets of values obtained from SEM-EDS and EDXRF analyses for the elements: Mn, Zn, Ti, and Cr. These discrepancies can be attributed to both the volume and the inherent inhomogeneity of the investigated AlMg3 alloy sample.

Since SEM-EDS and EDXRF characterization techniques are surface techniques, which limit the accuracy of the results, ICP-OES measurements were performed for a precise analysis of impurities.

ICP - OES analyses were performed using the iCAP 6500 spectrometer model produced by ThermoScientific, with dual plasma visualization (axial and radial). In order to perform ICP - OES analyses, experimental activities were carried out regarding the dissolution of the aluminum alloy and the implementation of the calibration curve necessary for quantitative analysis. Experimental tests carried out with the aim of establishing the $AlMg_3$ dissolution procedure determined the combination of HNO_3 and HCl acids (mixture called aqua regia) as the most efficient and fastest method for cold dissolution of the studied matrix.

Calibration curves were plotted in the concentration range between 3 and 15 mg/L for Al, Fe, Zn, Si, Mg, Mn, Cr, and Cu, between 0.1 ÷ 1 mg/L for Co, Ni, Zr, Nb, Eu, Sc, and 0.1 ÷ 0.3 mg/L for Li. ICP-OES analyses were performed on solutions resulting from the dissolution of four representative aluminum alloy samples.

ICP – OES analyses defined the inventory of chemical elements present in the tested matrix (Figure 4-1). The main elements identified were Al (95÷99%), Fe (≈2%), Zn (≈ 0.3%), and Si (≈ 0.4%), and the impurity elements were Li, Co, Sc, Zr, Nb, Ti, Mn, Cu, Cr, Mg, and Ni.

The average impurity concentration in the four analyzed solutions is found in the range 10^{-1} ÷ 10^{-5} mg/g as follows: Co ($4{,}21\times10^{-4} \pm 7{,}59\times10^{-6}$) mg/g, Li ($6{,}28\times10^{-3} \pm 5{,}12\times10^{-4}$) mg/g, Sc

($4{,}75\times10^{-5} \pm 3{,}70\times10^{-6}$) mg/g, Mn ($2{,}81\times10^{-1} \pm 1{,}03\times10^{-2}$) mg/g, Ti ($1{,}94\times10^{-1} \pm 1{,}37\times10^{-2}$) mg/g and Eu ($1{,}74\times10^{-7}$) mg/g.

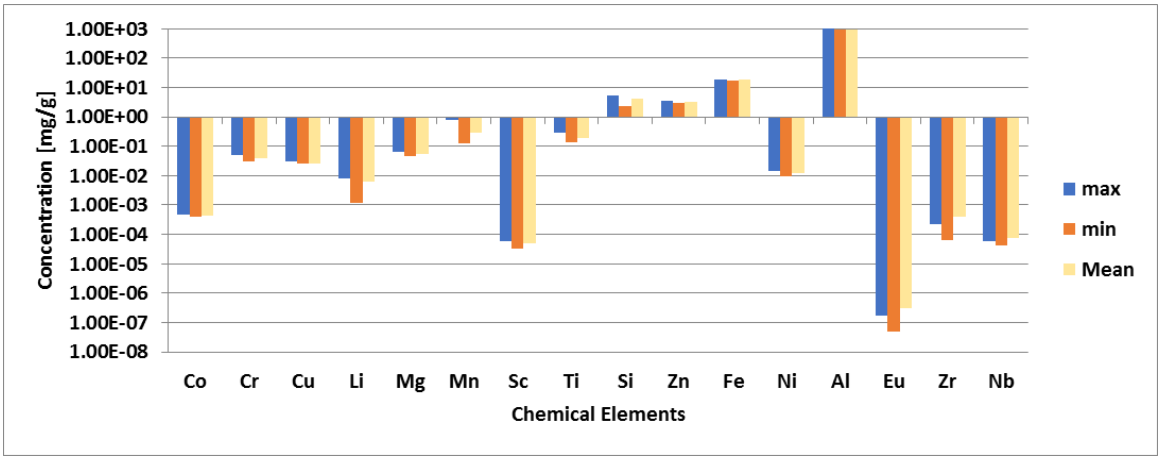


Figure 4-1 Chemical composition determined by ICP-OES measurements

The presence of elements such as Li and Co in the aluminum matrix, even in low concentrations, can generate, through neutron activation, a significant amount of tritium and cobalt radioisotopes (^{58}Co and ^{60}Co).

The chemical concentration values determined by ICP-OES analyses were used to provide the data inputs necessary for mathematical modeling with the MCNP6 computational code.

4.2 Mathematical modeling with MCNP6 and ORIGEN-S codes

The specific objective of the mathematical modeling study was to obtain theoretical data on DTM radionuclides that can be generated by activating impurities in the aluminum alloy and their activity level, to develop and optimize radiochemical methods for separation and purification of DTM radionuclides that will be applied in the radiological characterization process of irradiated aluminum.

In the evaluation of the theoretical activity concentration and the inventory of radionuclides accumulated in the irradiated aluminum bar, the combination of MCNP6 calculation codes, CSAS1X, COUPLE, and ORIGEN-S modules was used. Figure 4-2 shows the calculation procedure applied in the mathematical simulations.

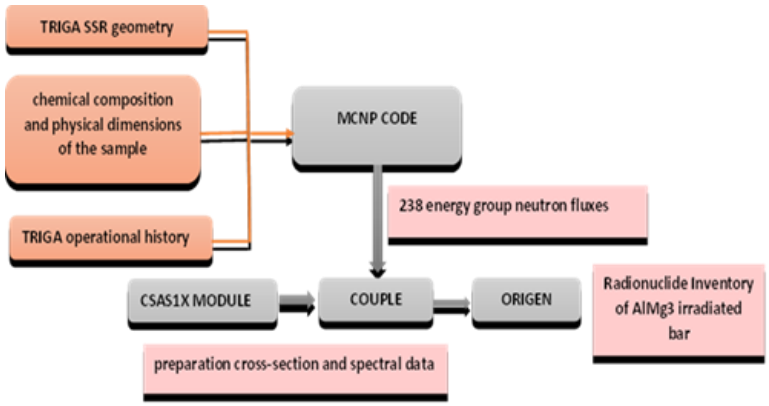


Figure 4-2 Graphical scheme applied in the calculation of theoretical activity inventory [25]

The mathematical simulations had as input data the chemical composition determined by ICP-OES analyses, the physical data, and the irradiation history of the $AlMg_3$ bar, the data relating to the geometry of the TRIGA SSR reactor core. Inputs were created for three sets of data characteristic to the chemical composition (minimum, average, and maximum values). Although the discrepancies between the three sets of values are insignificant, in terms of radioactivity, they can significantly influence the activity concentration of the radionuclides. In Figure 4-3, the activity concentrations of the radionuclides with long half-lives, after the cooling period, obtained by modeling, for the three sets of data characteristic of the chemical composition of the material, are presented in comparison.

From the analysis of the data obtained for the three sets of values, significant differences are found for ^{3}H, ^{51}Cr, ^{152}Eu, and ^{95}Nb radionuclides, up to an order of magnitude. For the other radionuclides such as ^{60}Co, ^{65}Zn, ^{54}Mn, and ^{46}Sc, the activity concentration remains in the same order of magnitude.

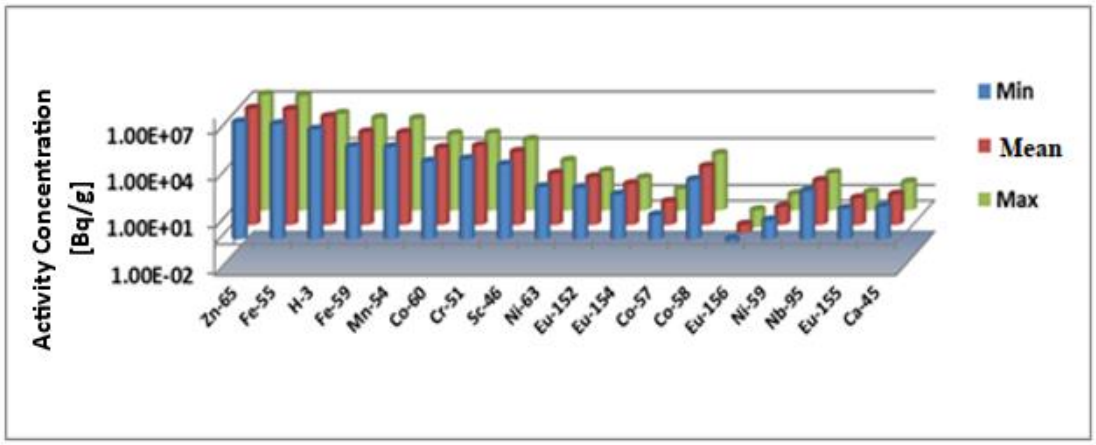


Figure 4-3 Activity concentration of radionuclides determined by mathematical modeling

The activity concentration of radionuclides in the $AlMg_3$ matrix after the 6-month cooling period of the $AlMg_3$ sample is as follows: 43% ^{65}Zn, 41% ^{55}Fe, 13 ^{3}H, 1,3% ^{59}Fe, 1,2 % ^{54}Mn, 0,13% ^{60}Co, 0,17% ^{51}Cr, 0,07% ^{46}Sc and in a percentage of 0.01% other radionuclides (^{63}Ni, radioactive isotopes of Eu, ^{57}Co, ^{58}Co, ^{59}Ni, ^{95}Nb. The DTM radionuclides present in irradiated aluminum are ^{55}Fe, ^{3}H, and ^{63}Ni, the other identified radionuclides being beta-gamma ETM radionuclides.

The resulting theoretical data contributed to the selection of radiochemical methods applied in experimental tests on representative samples of the alloy $AlMg_3$ irradiated, also, for the efficient and safe conduct of laboratory experiments.

4.3 Experimental tests carried out to determine the DTM and ETM radionuclide inventory in the irradiated $AlMg_3$ alloy

The experimental tests were carried out with the aim of validating the results obtained from modeling by comparing theoretical data with experimental ones, but also to develop the radiochemical methods applied in the separation and purification of DTM radionuclides determined by modeling from irradiated aluminum.

The determination of the activity concentration of gamma radionuclides (ETM) was performed by gamma spectrometric analyses on solid $AlMg_3$ samples (ID sample: A1, A2). The spectrometric analyses were performed with a GeHP detector with a relative efficiency of 15%, at a distance of 7 cm from the detector. The calibration curves in efficiency necessary for the quantitative evaluation of the two samples were established based on the detection efficiency values determined by mathematical modeling with the MCNPX code. To accurately estimate the activity of radionuclides in the aluminum samples and to establish the relative deviation due to the efficiency curve obtained with MCNPX, the aluminum sample A2 after the acquisition of the energy spectrum was dissolved (HNO_3: HCl ratio 1:3), the solution being measured by gamma spectrometry using an efficiency calibration curve verified with calibration solutions and by participating in intercomparison tests organized by the IAEA.

The results obtained from gamma spectrometric analyses of $AlMg_3$ samples are presented in Table 4-1.

Table 4-1 Inventory and activity concentration of gamma radionuclides in the analyzed $AlMg_3$ samples

ID sample	**A1**		**A2**		**A2 Solution**	
Radionuclide	**Activity Concentration (Bq/g)**	**Uncertainty Measurement (Bq/g)**	**Activity Concentration (Bq/g)**	**Uncertainty Measurement (Bq/g)**	**Activity Concentration (Bq/g)**	**Uncertainty Measurement (Bq/g)**
^{46}Sc	1,08E+05	1,83E+03	1,10E+05	1,86E+03	1,50E+05	2,42E+03
^{51}Cr	2,40E+04	2,06E+03	3,00E+04	2,26E+03	3,52E+04	4,00E+03
^{54}Mn	1,10E+05	3,06E+03	1,15E+05	3,17E+03	1,83E+05	4,73E+03
^{58}Co	1,56E+04	5,96E+02	1,63E+04	6,41E+02	2,34E+04	1,04E+03
^{59}Fe	8,90E+04	1,98E+03	8,89E+04	2,03E+03	1,08E+05	2,48E+03
^{60}Co	2,02E+05	4,06E+03	2,05E+05	4,14E+03	3,21E+05	4,94E+03
^{65}Zn	1,92E+06	4,10E+04	1,92E+06	4,11E+04	3,09E+06	5,81E+04
^{95}Nb	4,21E+03	3,46E+02	5,38E+03	4,05E+02	7,61E+03	7,83E+02
^{97}Nb	2,06E+03	3,98E+02	<2,50E+3		<2,40E+3	
^{141}Ce	1,65E+03	2,42E+02	8,99E+02	2,08E+02	<1,0E+3	
^{144}Ce	4,50E+04	3,85E+03	4,40E+04	3,78E+03	4,34E+04	4,07E+03
^{152}Eu	<1,60E+03		<1,70E+03		2,18E+03	5,57E+01

From the analysis of the results obtained, the following conclusions are highlighted:

- Similar values of the gamma radionuclides activity concentration were obtained in the two analyzed samples of irradiated aluminum A1 and A2, which suggests a homogeneity of the chemical composition;
- Zinc 56 is found in the largest proportion, with an activity of the order of 10^6 Bq/g, followed by the activity of ^{60}Co, ^{46}Sc, ^{54}Mn, și ^{59}Fe (10^5 Bq/g), ^{144}Ce,^{51}Cr, and ^{58}Co (10^3Bq/g). The beta-gamma radionuclide with the longest half-life is ^{60}Co ($T_{1/2}$ = 5.274 years), being one of the radionuclides with a significant contribution to the total activity of irradiated aluminum.
- The radionuclides identified in the samples at the time of spectral analysis are: ^{65}Zn, ^{60}Co, ^{46}Sc, ^{54}Mn, ^{51}Cr, ^{58}Co, ^{59}Fe, ^{95}Nb, ^{144}Ce, and ^{152}Eu, accounting for 76-78%, 8%, 4%, 4.5%, 1%, 0.64%, ≈4%, 0.19, 1.8%, and 0.06% of the total radioactive activity of the samples.

Determination of the activity concentration of DTM radionuclides

Based on the research conducted, the potential DTM radionuclides generated by activating impurities with neutrons are ^{3}H, ^{63}Ni, ^{55}Fe, and ^{36}Cl in very low concentrations. The research undertaken for this purpose focused on establishing and applying radiochemical methods for separating and purifying DTM radionuclides from other beta-gamma interferents present in the studied matrix.

The experimental program (Figure 4-4) applied in the sequential evaluation of DTM radionuclides involved the following experimental activities:

- Dissolution of the irradiated AlMg3 solid sample in the distillation installation;
- Distillation of the solution obtained to recover ^{3}H in the distillate fraction;
- Implementation of radiochemical procedures for the separation and purification of ^{55}Fe and ^{63}Ni;
- Performance of gamma, LSC, and ICP-OES analyses.

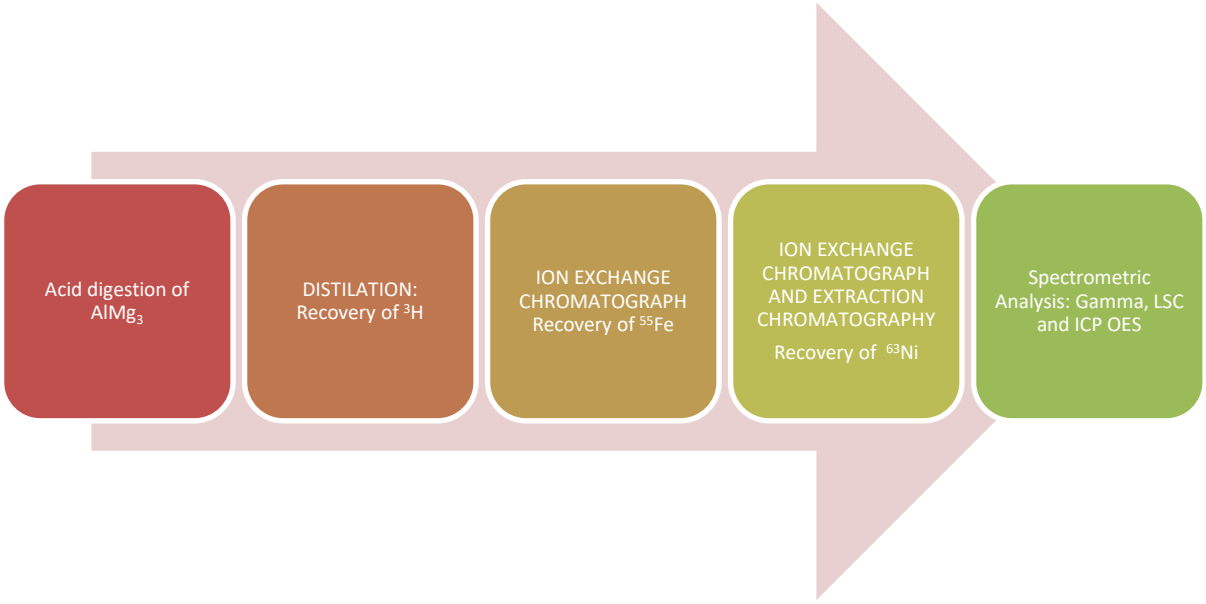


Figure 4-4 Experimental Program applied in DTM radionuclides assessment

The quantification of the DTM radionuclides studied was achieved by performing LSC analyses based on the acquisition of the spectra characteristic of beta radiation and the application of standard attenuation curves.

Gamma spectrometric analyses were performed to establish the beta-gamma radionuclides inventory present in the solutions resulting from the separation and purification stages of the DTM radionuclides studied. While ICP-OES analyses were performed to determine the recovery yields of stable carriers following the separation and purification procedures applied.

Experimental tests performed for the determination of ^{3}H

In the determination of tritium from the $AlMg_3$ matrix, it is important to take into account the fact that tritium is a volatile radionuclide; therefore, the dissolution step of the material was performed under safe conditions both to avoid possible losses through volatilization of the element but also to limit personnel exposure. The distillation installation was adapted by

replacing the reaction vessel with a three-necked flask and a separating funnel, which allowed the introduction of reagents during the digestion process.

The distillation tests were performed on two representative samples of $AlMg_3$ taken from the irradiated aluminum bar (P1, P2) and on the solution resulting from the dissolution of the solid aluminum sample A2 (A2=13.86 g). The determination of the activity concentration of ^{3}H was performed by performing LSC measurements on representative distillate samples.

Table 4-2 presents the tritium activity concentration values measured in the analyzed samples, corrected with the recovery yield (91%) determined by applying the distillation procedure for a solution with known tritium concentration.

Table 4-2 The activity concentration of ^{3}H in $AlMg_3$ irradiated samples

ID Sample	***Activity Concentration (Bq/g)***
P1	1,17E+05 ± 2,92E+02
P2	2,86E+05 ± 7,15E+02
P3	1,13E+05 ± 2,82E+02
Mean	1,72E+05 ± 4,30E+02

The ^{3}H activity concentration obtained through experimental tests is an order of magnitude lower than the concentration determined through mathematical modeling (10^{6} Bq/g). In order to validate the obtained results and to accurately quantify the radioactive concentration of tritium, it is necessary to perform several experimental tests on representative aluminum samples to determine the distribution (homogeneous or inhomogeneous) of tritium in the aluminum bar.

Experimental tests performed for ^{55}Fe radionuclide estimation

The specific objective of this subchapter consisted in the development and implementation of the radiochemical protocol applied for the quantification of ^{55}Fe from the aluminum matrix and the implementation of the attenuation curve necessary for the quantitative evaluation of the radionuclide ^{55}Fe by LSC analyses. The most widely applied methods at the international level for ^{55}Fe separation from other interferents are ion exchange chromatography and precipitation with NH_4OH [16] [26] [27] [28]. In this context, I tested the two methods for the iron separation from the interferents existing in the studied matrix. To achieve the proposed objective, experimental tests were performed in inactive conditions, using simulated solutions, and experimental tests using solutions with known concentrations for the interest radionuclides (active tests). These tests were performed to observe the behavior and degree of retention of ^{55}Fe and ^{60}Co in the stages of the separation and purification protocol studied, testing the reagents and the quantities necessary to perform the elution of the elements of interest.

For the inactive tests, solutions of different concentrations were prepared gravimetrically from multielement ICP-OES standards (Zn, Mn, Co, Ni, Fe, Sc, Cr, Eu, Ce, Cu, Ni), taking into account the estimated value by modeling corresponding to the concentration of radionuclides present in the aluminum alloy, shortly after irradiation and after approximately 1 year. The

concentration of stable elements in the solutions resulting from the separation experiments was determined by ICP-OES analyses.

From the analysis of the results obtained in the experimental tests, the following conclusions were drawn:

(1) It is confirmed that the elements: Mn, Cr, Ce, Eu, Ni are not fixed on the anionic ion exchange resin at any concentration of HCl, which demonstrates the efficient separation of iron from these elements;

(2) elements, such as Zn, Co, Cu, and Fe, are fixed on the resin with a retention rate between 76% and 100%. The recovery yield in inactive for Fe was 87% in both tests, and for Co, over 90%, which confirms the efficiency of separating Ni from the two interferents (Co and Fe).

(3) in the 6M HCl solution, elements such as Co and Cu were highlighted in significant concentrations, approximately 80% and respectively 50%, while Mn is found almost entirely in the effluent sample; for the experimental tests that will be carried out on real waste samples, the elution of cobalt and copper will be performed with HCl solutions of 6M and 5M concentrations.

(4) in the precipitation step with NH_4OH, along with Fe (92%) precipitated in the form of hydroxides and elements such as: Co (56%), Eu (91%), Mn (84%), Ni (6.9%), and Zn (11%), and cobalt precipitates together with iron in a percentage of 56%, the remaining 34% remains in the supernatant, the difference of 10% being considered a loss related to the applied protocol.

The data obtained defined two radiochemical procedures that can be applied in the determination of Fe from the $AlMg_3$ matrix:

Protocol 1: Fe separation by precipitation with NH_4OH, followed by purification by ion exchange chromatography using AG 1-X8 resin.

Protocol 2: Two separation processes based on ion exchange chromatography using AG 1-X8 resin.

The simulated active experiments were performed to test the two radiochemical procedures using radioactive solutions with known concentrations of ^{55}Fe and ^{60}Co. The results obtained validated the applicability of the two proposed radiochemical procedures. The ^{55}Fe radionuclide recovery yield values obtained from testing protocol 1 and protocol 2 were 82% and respectively 90%.

Taking into account the results obtained in the simulated inactive and active tests, especially the iron recovery yields, but also the fact that I am pursuing the application of a sequential protocol for the estimation of ^{55}Fe, respectively ^{63}Ni from the irradiated $AlMg_3$ matrix, I applied the radiochemical protocol consisting of a double process of ^{55}Fe separation and purification based on ion exchange chromatography using the AG 1-X8 ion exchange resin.

Regarding the ^{63}Ni separation and purification protocol, I adapted the M2 procedure, developed in the radiological characterization of liquid radioactive waste. The radiochemical methods were based on ion exchange chromatography, using the AG 1-X8 resin, and extraction chromatography, using the Ni resin.

The radiochemical procedures corresponding to the separation and purification of ^{55}Fe and ^{63}Ni from beta-gamma interferences in the irradiated aluminum matrix were applied both to the residue obtained from the distillation step of the solutions resulting from the dissolution of samples P2 and P3, and to two other representative samples (P3.1=1.1 g, P3.2=1.178 g) from the solution resulting from the dissolution of solid sample A2.

Table 4-3 presents the activity concentration values of the ^{55}Fe and ^{63}Ni radionuclides determined by LSC measurements from the studied $AlMg_3$ matrix. The activity concentration values were corrected with the recovery yields determined based on the concentration of stable elements.

Table 4-3 The LSC results obtained for ^{55}Fe and ^{63}Ni radionuclides

ID Sample	**^{55}Fe Activity Concentration [Bq/g]**	**^{63}Ni Activity Concentration [Bq/g]**
P2	3,66E+06 ± 8,43E+03	8,12E+03 ± 20,30
P3	1,65+06 ± 2,96E+03	3,56E+03 ± 9,00
P3.1	2,07E+06 ±5,07E+03	5,26E+03 ± 26,31
P3.2	2,15E+06 ± 5,27E+03	5,03E+03 ± 31,20
Mean	2,63E+06 ± 6,57E+03	5,49E+03 ± 13,70

The DTM radionuclides accumulated in the aluminum alloy bar during the controlled irradiation period were identified in concentrations on the order of 10^3 Bq/g for ^{63}Ni, 10^6 Bq/g for ^{55}Fe, and 10^5 Bq/g for ^{3}H.

The recovery yields corresponding to the Ni and Fe stable carriers, determined based on ICP – OES analyses, were in the range of 90-99%. The performance parameters of the applied radiochemical methods demonstrated, through the decontamination efficiency values (83 – 100 %) and the decontamination factors (greater than 10^4), an efficient separation of the ^{63}Ni and ^{55}Fe radionuclides.

From the experience of the countries involved in the decommissioning process of nuclear facilities, the dismantling activity is carried out approximately 10 years after the reactor shutdown. In this context, the activity inventory of the radionuclides obtained both through experimental tests and mathematical modeling was evaluated, by calculation, taking into account the decay time of the radionuclides, for 10 years. Figures 4-5, 4-6 and 4-7 show the evolution of the long-lived radionuclides activity inventory.

The results obtained highlight the fact that after 10 years, the radionuclides found in significant concentrations are ^{3}H (in the case of the controlled irradiated bar, the activity of this radionuclide represents 25% of the total activity), ^{55}Fe (in a percentage of 52%), ^{60}Co (in a percentage of 22%), ^{65}Zn (in a percentage of 1%), as well as very small quantities of ^{63}Ni, ^{152}Eu. From the analysis of the activity concentration evolution graphs, a significant decrease in the activity inventory of the radionuclides ^{54}Mn and ^{65}Zn is observed, an aspect due to the half-life (312.3 days and 244.26 days), as a result, they will not represent a problem in terms of radiological safety and security during the storage stage.

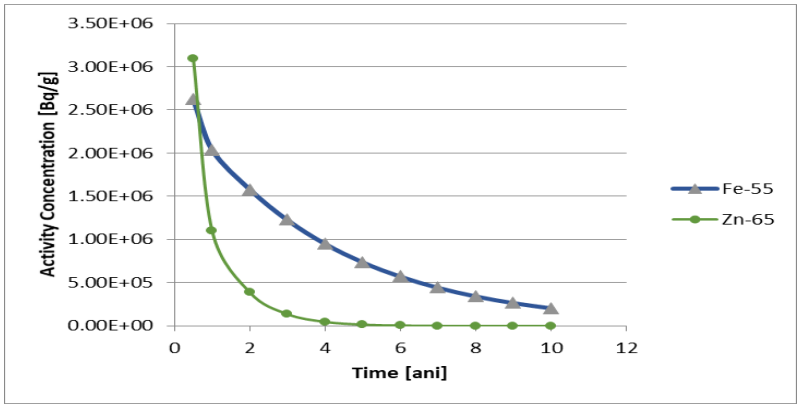


Figure 4-5 Activity concentration evolution of ^{65}Zn and ^{55}Fe radionuclides

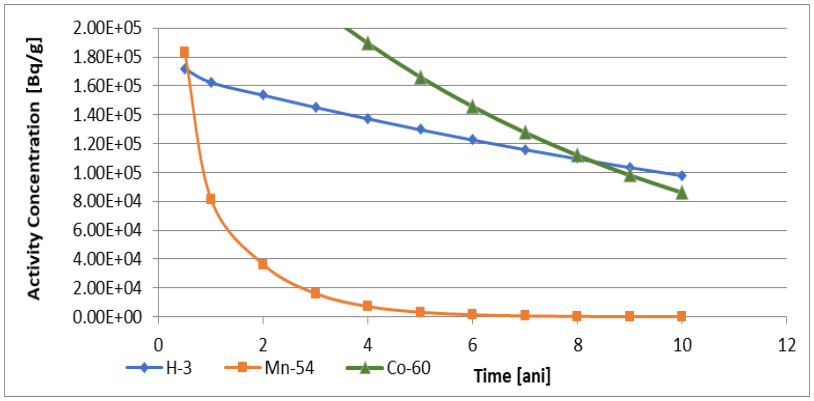


Figure 4-6 Activity concentration evolution of ^{54}Mn, ^{3}H, ^{60}Co radionuclides

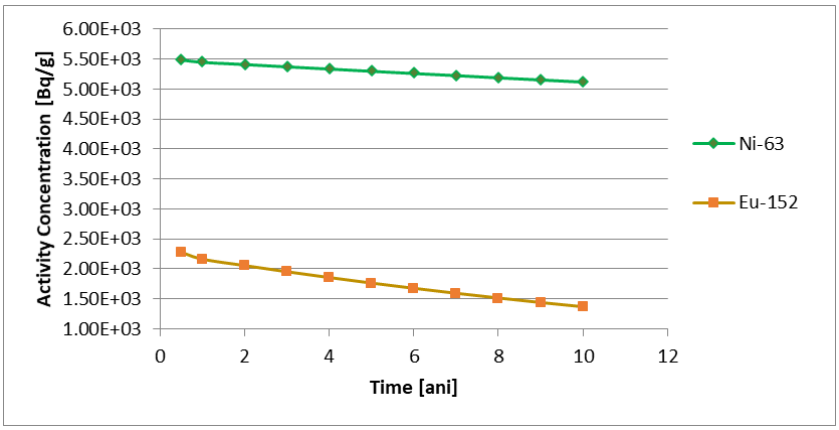


Figure 4-7 Activity concentration evolution of ^{152}Eu and ^{63}Ni radionuclides

From the comparative analysis of theoretical and experimental data, it can be conclude that the values of total radioactivity of radionuclides in one gram of aluminum differ by almost an order of magnitude, a difference that can be attributed to: the uncertainties in determining the chemical composition of the aluminum alloy, the uncertainties associated with the radiochemical analyses performed to measure the DTM radionuclides, as well as the uncertainties associated with the irradiation data used in the modeling.

This difference is observed for radionuclides such as ^{3}H, ^{152}Eu, ^{55}Fe, and ^{65}Zn, while for radionuclides such as ^{60}Co and ^{63}Ni, the activity inventory values remain in the same order of

magnitude. To accurately establish the activity range of the interest radionuclides, I compared the experimental data with all the data obtained from the modeling (Set max, Set Min, Set Average), which are closely related to the values of the chemical composition of the studied material (Figure 4-8).

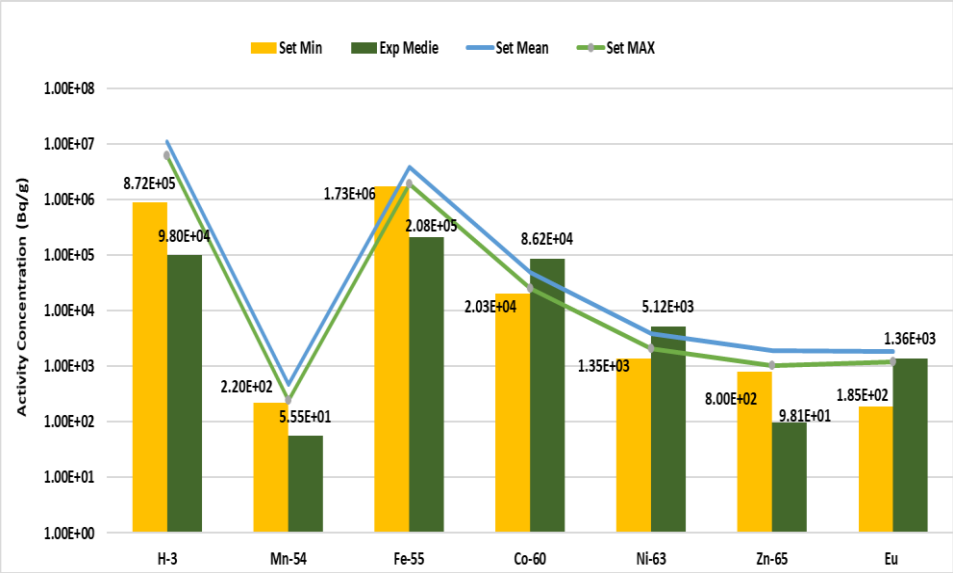


Figure 4-8 Comparative analysis of experimental and theoretical data

Although differences persist between the data sets, it is observed a slight approximation of the experimental data with those obtained from the minimum value modeling of the ^{3}H and ^{55}Fe activity concentration, an aspect that can be attributed to the inhomogeneous distribution of Li and Fe impurities in the studied $AlMg_3$ alloy.

The data obtained in this research study are preliminary data that will be used in establishing the characterization methodology of irradiated aluminum in order to define the effective dismantling program of the TRIGA reactor core components.

5 EXPERIMENTAL RESEARCH ON THE RADIOLOGICAL CHARACTERIZATION OF IRRADIATED BORON CARBIDE (B_4C)

Boron carbide, used as a neutron absorber in the control rods of the TRIGA reactor, is one of the problematic waste categories that will result from the reactor decommissioning activity. It is expected that only a few tens of kilograms of activated boron carbide will be generated, for which a characterization methodology must be developed in order to determine the radionuclide inventory based on which the appropriate management option will be developed.

In this context, the research studies presented in this chapter aim to determine the inventory and activity concentration of the radionuclides present in B_4C, as well as to identify the challenges that may arise in carrying out the experimental tests necessary to perform the radiological characterization of this category of radioactive waste.

The experiments conducted for this type of material are in the early stages, and in this first stage, I focused on determining the gamma radionuclide inventory and establishing the steps preceding destructive analyses in order to determine the DTM radionuclide inventory.

The characterization methodology applied in this study involved performing experimental tests with the following objectives:

- Mechanical processing of the boron carbide pellet;
- Development of efficiency calibration curves using computational codes such as MCNP and EFFTRAN, necessary in gamma spectrometric analyses;
- Establishment of the dissolution method of the B_4C samples taken for analysis;
- Determination of the impurity inventory and chemical composition of B_4C by ICP-OES analyses;
- Performance of spectrometric analyses;
- Determination of the ^3H activity concentration in the B_4C matrix.

The experimental tests were performed on representative samples of radioactive boron carbide resulting from the replacement of the initial control rods. Due to its hardness, the processing of the B_4C pellet was one of the challenges of this study. The processing of the samples consisted of cutting the square-shaped ring using a diamond disc, which resulted in pieces of various sizes, which were brought into a stainless-steel mortar and ground into a powder state.

The dissolution step represented another challenge of this study, due to the hardness of the material and to the fact that it is inert in the presence of chemical reagents under normal conditions. The dissolution step of the B_4C matrix represents an important intermediate step in establishing the DTM radionuclide inventory, as well as in verifying gamma spectrometric analyses based on the efficiency calibration curves determined with computational codes.

Taking into account the information presented in the specialized literature [29], but also the available equipment, I studied and applied the acid digestion of boron carbide in a microwave field, using the BERGHOF Speedwave XPERT digestion system. The optimal protocol for the dissolution of B_4C consisted of applying two consecutive digestion processes at 240 ^0C temperature, without opening the digestion vessels, followed by a complexation process with H_3BO_3. The digestion reagents used were HNO_3 (67%), H_2SO_4 (98%), and HF (40%).

ICP-OES analyses performed on the solutions resulting from the digestion of B_4C samples defined the chemical composition (Ni, Co, Eu, B, Sr, Ca) of the studied material. This information will be used in creating the input for the mathematical modeling with the MCNP computational code and in estimating a first possible radionuclides theoretical inventory, taking into account the neutron activation reactions of the identified elements. Consequently, a theoretical inventory composed of radioactive isotopes of cobalt, iron, europium, and nickel is estimated. Also, it is expected the presence of tritium due to the activation of boron impurities existing in the B_4C matrix.

5.1 Gamma spectrometric analyses

Non-destructive analyses applied to boron carbide samples consisted of performing gamma spectral measurements using the HPGe detector for all analyzed geometric configurations of B_4C (powdered B_4C sample, B_4C ring, and solutions resulting from the dissolution of representative samples).

In performing spectral analyses, the emphasis was placed on implementing efficiency calibration curves, based on the detection efficiency values determined with the MCNP computational codes, for the boron carbide ring sample, and EFFTRAN, for the B_4C powder sample. EFFTRAN is an efficiency transfer code based on the Monte Carlo method, being used in particular for different cylindrical detector-sample geometries and axially symmetric configurations [30]. This is a relatively easy-to-use code for determining efficiency calibration curves, having as reference values being the efficiency values determined with standard calibration solutions.

In performing the modeling with the EFFTRAN code, I varied the B_4C sample height parameter in the measurement geometry, since the geometry of the vial, at the bottom, has a thickness of approximately 1.5 mm, thus influencing the total height of the geometric configuration. Thus, there were obtained two data sets corresponding to the analyzed configurations (B_4C powder h=8 mm and B_4C powder h=9 mm) were obtained. In Figures 5-1 and 5-2, the curves obtained with MCNP and EFFTRAN are presented.

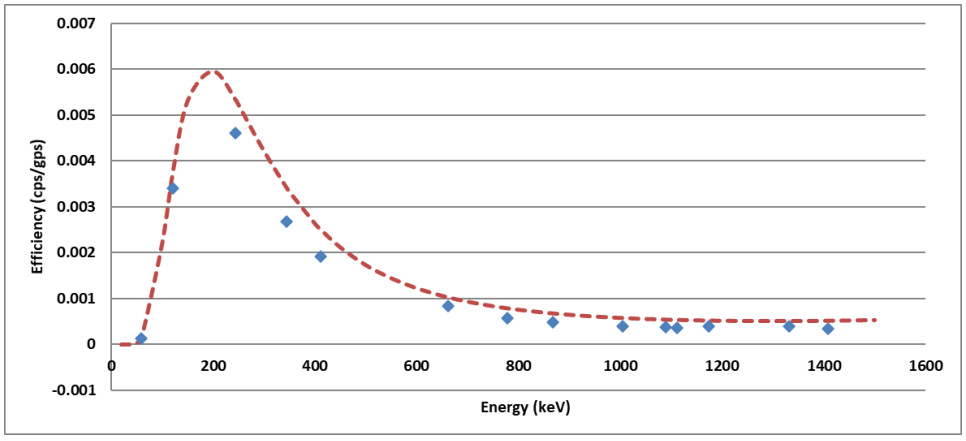


Figure 5-1 The efficiency calibration curve obtained with the MCNP code

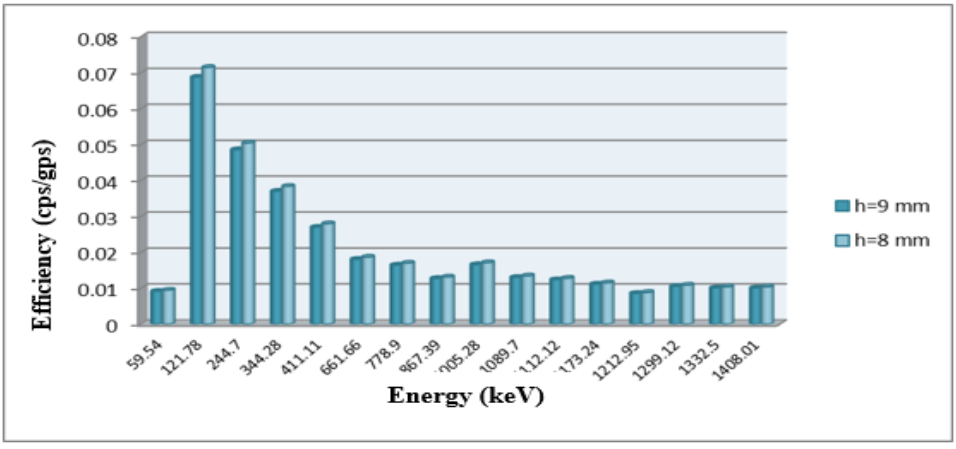


Figure 5-2 The detection efficiency values obtained with EFFTRAN for the studied configurations analysis

Based on the energy spectra acquired with the Gamma Vision software and the efficiency calibration curves specific to the analyzed configurations of the B_4C samples, the data analysis and interpretation were performed with the GENIE2000 software.

The results obtained from the gamma spectrometric analyses are presented in Tables 5-1 and 5-2.

Table 5-1 The activity concentration identified in the B_4C configuration analyzed

Analyzed configuration	ID Sample	Activity Concentration (Bq/g)	
		^{60}Co	^{152}Eu
The solution resulted from acid digestion of B_4C.	S1	4,29±0,25	63,63±1,03
	S2	6,24±0,51	76,86±1,39
Dust of B_4C _EFFRAN m=6,22 g	h = 9 mm	2,39±0,06	54,88±0,55
	h = 8 mm	2,47±0,06	56,18±0,56

Table 5-2 Concentration of activity identified in the ring configuration of B_4C

Radionuclide	Total Activity [Bq]	Activity Concentration [Bq/g]
^{58}Co	83,54 ± 12,26	0,21 ± 0,03
^{60}Co	2142,89 ± 40,60	5,51 ± 0,10
^{95}Nb	64,99 ± 13,47	0,17 ± 0,03
^{95}Zr	531,86 ± 28,02	1,37 ± 0,07
^{109}Cd	4602,63 ± 573,81	11,84 ± 1,48
^{122}Sb	196,93 ± 15,07	0,51 ± 0,04
^{152}Eu	21064,82 ± 254,33	54,17 ± 0,65

The results obtained from the gamma spectrometric analysis of the B_4C sample (square ring shape) revealed, in addition to the radionuclides ^{60}Co and ^{152}Eu, also radionuclides such as ^{58}Co, ^{95}Nb, ^{95}Zr, ^{109}Cd, and ^{122}Sb.

Regarding the results obtained using the efficacy curves determined with the MCNPX calculation code, values very close to the values obtained with the EFFRAN code for ^{152}Eu are found, while for the activity concentration of ^{60}Co, a difference of approximately 2 Bq/g is found between the two values obtained from the modeling. In contrast, very close values are found between the results obtained with the MCNPX code and those obtained from the analysis of the solutions resulting from the digestion of representative B_4C samples.

5.2 Determination of tritium in the B_4C matrix

The experimental tests carried out to evaluate the activity concentration of tritium in the B_4C matrix (powder) consisted of applying the distillation method to separate tritium from other beta–gamma interferents. It should be noted that, by this method of distillation of the solid matrix without dissolving the sample, most likely only the tritium formed at the surface of the sample will be released, while the tritium formed in depth will probably require complete dissolution of the matrix. Based on the results obtained, a minimum activity concentration of tritium of the order of 10^5 Bq/kg of boron carbide was estimated, without the B_4C matrix being completely dissolved.

Experimental tests will continue applying methods such as thermal decomposition of boron carbide at temperatures above 1000 ^{0}C, with the ^{3}H and ^{14}C capture in bubblers with absorption solutions specific to these radionuclides, to accurately establish the activity concentration of tritium in the boron carbide matrix. It is also proposed to apply radiochemical procedures for ^{63}Ni separation, purification, and quantification from the B_4C matrix.

6 GENERAL CONCLUSIONS

The experimental studies carried out within the doctoral thesis contribute to the optimization of the characterization process of radioactive waste generated following the operation and decommissioning of the TRIGA ICN reactor. The results obtained from the experimental tests constitute a database on the radionuclide inventory and the total radioactivity of the studied radioactive waste. The results obtained will be used in the establishment and development of methods for the treatment, conditioning, and safe storage of liquid radioactive waste, as well as irradiated aluminum and boron carbide that will result from the decommissioning activity of the TRIGA reactor.

The documentation and research undertaken during the elaboration of the doctoral thesis contributed to the establishment of the characterization methods that were applied within the research carried out, allowing the identification of the most developed and applied non-destructive and radiochemical methods in defining the inventory of ETM and DTM radionuclides. The most widely used characterization method at the international level is the SF method, which involves combining non-destructive and destructive methods to establish an accuracy scaling factor value that can subsequently be applied in the DTM radionuclides evaluation.

Gamma spectrometric analyses performed on representative samples of liquid radioactive waste defined the inventory and activity concentration of gamma radionuclides. The main gamma radionuclides present in the analyzed samples were ^{60}Co, ^{58}Co, ^{54}Mn and ^{124}Sb, and among them, the ^{60}Co radionuclide is found in the highest concentration in the analyzed samples, being the main contributor to the total radioactivity, therefore, it can be considered the KN radionuclide corresponding to this waste stream.

The radiochemical methods necessary for the sequential determinations of ^{3}H, ^{63}Ni, and ^{90}Sr radionuclides were developed within the thesis through experimental tests using solutions with known concentrations for the interest elements, to adapt, respectively, optimize the separation/purification methods of the interest radionuclides identified in the specialized literature.

The experimental tests performed defined and established the radiochemical methods necessary for the accurate evaluation of ^{3}H, ^{63}Ni, and 90Sr radionuclides from the analyzed liquid radioactive waste.

For the **^{3}H evaluation,** the distillation method was optimized and implemented for the efficient separation of tritium from beta-gamma interferences. The recovery yield determined through experimental tests under controlled conditions was 91%. The ^{3}H activity concentration measured in the analyzed liquid waste samples was found in the activity range of 10^{2} - 10^{4}

Bq/kg. Discrepancies between the analyzed samples may be due to the volatile nature of tritium, but also to parameters such as the reactor operating regime, the time of sampling, and the date of analysis.

For the **^{90}Sr evaluation,** the radiochemical protocol for the ^{90}Sr separation/purification from beta-gamma interferents based on extraction chromatography, using Sr selective resin, was adapted and implemented. Depending on the concentration of beta-gamma interferents in the initial sample, one or two ^{90}Sr separation/purification processes were applied for concentrations higher than 10^1 Bq/mL, two separation processes are required.

The ^{90}Sr radionuclide was not identified in all the analyzed liquid waste samples, and in the samples in which it was identified, the activity concentration value is a maximum of 10^2 Bq/kg.

For the evaluation of ^{63}Ni, two methodologies for its separation/purification from beta-gamma interferences were developed, optimized, and implemented. Methodology M1 involves the application of two separation/purification processes based on extraction chromatography using selective Ni resin, while methodology M2 involves a separation process based on ion exchange chromatography using anionic resin AG 1-X8 and a purification process based on extraction chromatography using selective Ni resin.

The results obtained in the experimental tests carried out to test the two methodologies related to the ^{63}Ni separation and purification, recommended the M2 methodology for samples with a ^{60}Co content greater than 10 Bq/mL, cobalt being retained on the selective Ni resin together with nickel 63, and at high concentrations cobalt affects the accuracy of ^{63}Ni measurements by LSC. In the liquid radioactive waste samples, an activity concentration of ^{63}Ni was identified in the range of 10^2-10^6 Bq/kg.

Regarding the performance parameters of the studied and implemented radiochemical methods, recovery yield values for Sr and Ni were determined to be between 70%-93% and respectively 60%-98%, the decontamination efficiency values obtained for beta-gamma interferents are over 98% after the second purification process, and the decontamination factor values are higher than 10^3 for the ^{60}Co interferent.

Spectrometric analyses performed on the solutions of the ^{90}Sr and ^{63}Ni elution samples revealed that ^{60}Co radionuclide is the main beta-gamma interferent, which is also the main contributor to the total activity of the liquid radioactive waste samples.

The radiochemical methodologies applied in the separation, purification, and quantification of gamma, ^{3}H, and ^{90}Sr radionuclides were verified and validated by participating in intercomparison tests organized by the IAEA (2022, 2023, and 2024), in which the declared results received the accepted qualification for both the accuracy and precision criteria.

The radiochemical data characteristic of the analyzed samples was evaluated by applying the Pearson coefficient, the Grubbs test, and data distribution diagrams, demonstrating the correlation relationship between the ^{63}Ni/^{60}Co and ^{90}Sr/^{60}Co radionuclide pairs. The distribution of radiochemical data in the logarithmic scatter plots shows a good correlation of the data related to the ratio between ^{63}Ni/^{60}Co (R2 = 0.996) and ^{90}Sr/^{60}Co (R2 = 0.9312). The characteristic SF values for each analyzed sample were calculated taking into account the linearity relationship between the radionuclide KN and DTM, as a ratio of the specific activity

concentrations of the two radionuclides. The evaluation of the obtained data was carried out by applying statistical indicators (score-z, arithmetic and geometric mean, median). Since one of the limitations of this research study was the lack of waste samples, at this stage of the research, it cannot accurately determine an SF value for the studied radionuclide pairs, a value that can be directly applied in the estimation of DTM radionuclides in liquid radioactive waste. From the analysis of the results obtained for the $^{63}Ni/^{60}Co$ pair, the range of values [1÷1.44] was estimated for SF, an interval for which the estimated activity concentration of the DTM radionuclide approaches that determined experimentally.

Experimental tests will continue to determine the activity concentration of nickel and strontium, to obtain a significant number of radiochemical data necessary to accurately determine the scaling factor specific to the liquid radioactive waste stream.

Accurately establishing an optimal SF value for this type of waste will considerably optimize the characterization process carried out in RATEN ICN, once the correlations between DTM radionuclides and KN nuclides have been established, the SF methodology being the most efficient solution to avoid the laborious and time-consuming radiochemical analyses required for the direct measurement of DTM radionuclides. The evaluation and testing of the SF methodology in the characterization process of liquid waste generated from TRIGA reactor operation constitutes the novelty of this study. The research conducted within this doctoral thesis is the first study in this field carried out in Romania.

From the analysis of the results obtained in the research study on the radiological characterization of irradiated aluminum and boron carbide, waste categories considered problematic that will result from TRIGA reactor decommissioning, the following conclusions were drawn:

SEM-EDS, EDXRF, and ICP-OES analyses defined the chemical composition of the $AlMg_3$ alloy sample as well as the inventory of existing impurities that, upon activation, can generate radionuclides in significant concentrations in the aluminum used as a structural material in TRIGA reactor construction. The main elements identified are Al (95÷99%), Fe, Zn, and Si, and the elements at the impurity level are Li, Co, Sc, Zr, Nb, Ti, Mn, Cu, Cr, Mg, and Ni. The average impurity concentration is found in the range $1.94 \cdot 10^{-1} \div 4.75 \cdot 10^{-7}$ mg/g, as follows: 10^{-4} mg/g Co, 10^{-3} mg/g Li, 10^{-5} mg/g Sc, 10^{-1} mg/g Mn, 10^{-1} mg/g Ti, and 10^{-7} mg/g Eu.

Mathematical modeling performed with the MCNP6 and ORIGEN-S computational codes defined the inventory and theoretical activity concentration of the radionuclides contained in the $AlMg_3$ alloy irradiated under controlled conditions. The simulations were performed for the three data sets related to the chemical composition established by ICP-OES analyses. The percentage activity concentration, obtained by modeling, of the radionuclides in the $AlMg_3$ matrix after the 6 months is as follows: 45,42% ^{65}Zn, 38,18% ^{55}Fe, 13,34 ^{3}H, 1,38% ^{59}Fe, 1,27% ^{54}Mn, 0,14% ^{60}Co, 0,18% ^{51}Cr, 0,08% ^{46}Sc and in a percentage of 0.01% the other radionuclides (^{63}Ni, radioactive isotopes of Eu, ^{57}Co, ^{58}Co, ^{59}Ni, ^{95}Nb). Based on the results obtained through mathematical modeling, the radiological characterization methodologies necessary for defining the inventory of radionuclides in irradiated aluminum through experimental tests were established and implemented.

Spectrometric analyses performed on representative samples of controlled irradiated aluminum in TRIGA reactor revealed the following gamma radionuclides: ^{65}Zn at a concentration of 10^6 Bq/g, ^{60}Co, ^{46}Sc, ^{59}Fe, ^{54}Mn, at a concentration of 10^5 Bq/g, ^{58}Co,^{144}Ce, ^{51}Cr at a concentration of 10^4 Bq/g and ^{95}Nb at a concentration of 10^3 Bq/g. In order to perform spectrometric analyses of solid aluminum samples, calibration curves were implemented in efficiency using the MCNP6 calculation code.

The DTM radionuclides inventory in the $AlMg_3$ matrix was determined through experimental tests that consisted of the sequential application of separation/purification radiochemical methods specific to DTM radionuclides: ^{3}H, ^{55}Fe, ^{63}Ni.

The radiochemical protocol applied in the experimental tests on representative samples of irradiated aluminum consisted of dissolving the solid sample in the distillation installation, in a sealed environment, followed by the distillation of the actual solution obtained, with the recovery of tritium in the distillate fraction, the resulting residue then being subjected to the procedure of simultaneous separation of the two radionuclides of interest ^{63}Ni and ^{55}Fe. The purification of ^{63}Ni was carried out by extraction chromatography using the selective Ni resin, while the purification of ^{55}Fe was carried out by a second process based on ion exchange chromatography using the AG 1-X8 resin.

The recovery yields ranged between 90 - 99% for the stable Ni and Fe carriers, the E.D. values ranging between 83 - 100%, respectively, F.D values greater than 10^4, demonstrated the performance of the radiochemical methods applied in the evaluation of DTM radionuclides.

LSC analyses revealed an activity concentration of ^{63}Ni of the order of 10^3 Bq/g of aluminum, a concentration of ^{55}Fe of 10^6 Bq/g of aluminum, and an activity concentration of tritium of the order of 10^5 Bq/g of aluminum.

The gamma radionuclides inventory obtained both through mathematical modeling and through gamma spectrometric analyses (on solid $AlMg_3$ samples and on solutions) highlighted the presence of the following gamma radionuclides: ^{65}Zn, ^{60}Co, ^{46}Sc, ^{54}Mn, ^{51}Cr, ^{58}Co, ^{59}Fe, ^{95}Nb, ^{144}Ce. Also, the destructive methods studied and implemented in the experimental tests confirmed the inventory of DTM radionuclides (^{3}H, ^{55}Fe, and ^{63}Ni) established by mathematical modeling.

Regarding the activity inventory obtained through experimental tests after 10 years, it is presented as follows: ^{3}H in a percentage of 24%, ^{55}Fe in a percentage of 52%, ^{60}Co in a percentage of 22%, ^{63}Ni in a percentage of 1%, the difference being due to the radionuclides ^{65}Zn, ^{152}Eu and ^{54}Mn present in extremely small percentages. **The novel elements** of this study are: the sequential application of radiochemical procedures related to the DTM radionuclides evaluation, the radiochemical protocol for the ^{55}Fe separation/purification from other beta-gamma interferents, as well as the experimental tests performed on the $AlMg_3$ alloy matrix.

The data obtained in this research study will be used to establish the methodology for characterizing irradiated aluminum, based on which the TRIGA reactor decommissioning plan will be finalized. Also, the date will be used for components dismantling activities, as well as in developing treatment and conditioning methods for the safe disposal of this waste category,

considered problematic due to its reactivity in the hyperalkaline environment characteristic of cement-based materials currently used for radioactive waste conditioning.

Experimental tests carried out on boron carbide samples established the gamma radionuclide inventory by performing gamma spectrometric analyses on solid samples (powder and B_4C ring) and solutions resulting from the microwave acid digestion of B_4C samples. The gamma radionuclides detected in the analyzed samples are ^{60}Co (10^3 Bq/kg), ^{152}Eu (10^4 Bq/kg), ^{58}Co (10^2 Bq/kg), ^{95}Nb (10^3 Bq/kg), ^{95}Zr (10^4 Bq/kg), ^{109}Cd (10^4 Bq/kg), ^{122}Sb (10^2 Bq/kg).

The results obtained from the acid digestion tests in the microwave field established the optimal digestion procedure for a complete dissolution of B_4C in a mixture of concentrated acids (HNO_3, H_2SO_4, and HF) at a temperature of 240 ^{0}C. Also, the ICP-OES analyses established the chemical composition of B_4C required in the mathematical modeling to estimate the accumulation of radionuclides in boron carbide during irradiation. Distillation tests established a tritium activity concentration fixed to the surface of the B_4C matrix of 10^5 Bq/kg. The inventory and activity concentration of the identified gamma radionuclides, respectively, of tritium, represent another novelty of this study. The results obtained in this study are preliminary results, which at this stage define the gamma radionuclide inventory in the boron carbide samples.

Experimental tests on B_4C samples will continue in order to determine the activity inventory of the DTM radionuclides (^{63}Ni, ^{36}Cl, and ^{14}C) both through experimental tests and mathematical simulations. It is also proposed to apply the thermal decomposition of boron carbide in furnaces reaching temperatures above 1000 ^{0}C, to capture ^3H and ^{14}C in solutions suitable for the absorption of these radionuclides (weakly acidic solutions with high tritium absorption capacity and, respectively, alkaline solutions with high ^{14}C absorption capacity)

The results obtained have met the objectives established in the doctoral thesis and will contribute to the development of radiological characterization methods of waste resulting from the operation and decommissioning of the TRIGA reactor, an important stage in the development and implementation of safe management of radioactive waste in RATEN ICN.

6.1 Personal contributions

- **Developed, optimized, and implemented** a comprehensive radiochemical protocol for the **sequential separation and purification** of difficult-to-measure radionuclides (^3H, ^{90}Sr, and ^{63}Ni) from liquid radioactive waste produced by TRIGA reactor operations, **protocol described in chapter III.**
- **Implemented the efficiency calibration** curves for gamma measurements, using computational codes based on the Monte Carlo method, such as MCNP and EFFTRAN, curves used in gamma analyses of solid $AlMg_3$ samples and B_4C samples (described in chapters IV and V);
- **Implemented the SF methodology on the liquid radioactive waste stream,** determined and evaluated the corresponding SF data, establishing the optimal range of the SF value that can be applied in estimating the activity concentration of ^{63}Ni from the analyzed waste stream (described in chapter III);

- **Implemented the attenuation curve required for ^{55}Fe analysis by LSC (chapter IV);**
- **Developed the specific radiochemical protocol** for the sequential separation and purification of ^{3}H, ^{55}Fe and ^{63}Ni radionuclides from the $AlMg_3$ alloy matrix; I also, estimated the activity inventory of gamma and beta radionuclides (^{3}H, ^{55}Fe, ^{63}Ni) from the $AlMg_3$ alloy matrix, through mathematical modeling, using the MCNP6 and ORIGEN-S computational codes, and through experimental tests (chapter IV);
- I compared the data obtained through modeling with those obtained through experimental tests, thus contributing to the validation of the methods applied in the numerical estimation of the activity inventory of radionuclides accumulated in the $AlMg_3$ matrix.
- I determined through experimental tests the inventory and activity concentration of gamma and ^{3}H radionuclides in irradiated boron carbide (chapter V);

6.2 Perspectives

Considering the results obtained within the Research Program carried out for the realization of this doctoral thesis, as well as the importance of the characterization process of radioactive waste resulting from the TRIGA reactor operation and decommissioning, the perspectives of the application and continuation of the initiated experimental and modeling activities can be structured as follows:

Continuation of research studies on SF determination for the liquid waste stream resulted from TRIGA reactor operation, by completing it with radiochemical data on the activity concentration of the DTM and KN radionuclides resulting from destructive experimental measurements. Extension of research study on the SF methodology for the radioactive waste categories that will result from the TRIGA reactor decommissioning activity. Continuation of experimental research to establish the activity inventory of the DTM radionuclides in the boron carbide used in the control rods of the TRIGA reactor.

Analysis of the uncertainties associated with the radiochemical experiments carried out within the research program related to this doctoral thesis to evaluate the activity concentration of the studied radionuclides, both from the liquid radioactive waste stream and from the irradiated aluminum and boron carbide matrix.

Verification and validation of the model created to estimate the radioactivity inventory accumulated in the $AlMg_3$ matrix by performing experimental tests on real irradiated aluminum samples and by refining and developing the mathematical model used in the mathematical modeling with the MCNP6 and ORIGEN-S computational codes.

Verification and validation of the radiochemical methods applied in the separation, purification, and measurement of the ^{63}Ni and ^{55}Fe radionuclides by participating in intercomparison tests.

6.3 List of Published /Presented Papers

Articles in WOS indexed journals

C. E. Diaconescu, S.D. Dulugeac, A. D. Negrea, I. C. Florea, D. Dupleac, "*Preliminary Assessment Of The Radionuclides Inventory In Irradiated $AlMg_3$ Alloy*", U.P.B Scientific Bulletin Series B, Vol. 87, Iss. 1, ISSN 1454-2331, pp. 147-162, 2025. ISI THOMSON REUTERS; Indexed in EMERGING SOURCES CITATION.

C. E. Diaconescu, M. Dianu, C. Bucur, I. C. Florea, V. Neculae, "*Studies to Establish the Scaling Factor Methodology for Liquid Radioactive Waste Generated by TRIGA Reactor",* Journal of Science and Arts Volume 24, Issue 1, pp. 185-198, 2024. Indexed in EMERGING SOURCES CITATION, Clarivate Analytics.

I. C. Florea, C. M. Bucur, E. A. Florea, **C. E. Diaconescu**, D. Dupleac „*The effect of curing temperature on the hydration process of CEM II cement type*", U.P.B Scientific Bulletin Series B, Vol. 87, Issues 1, ISSN 1454-2331, pp. 69-80, 2025.

I. C. Florea, C. M. Bucur, **C. E. Diaconescu**, E. A. Florea, C. E. Ichim, „*Analysis of the hydration process of CEM II/B-M composite cement*", Journal of Science and Arts, Vol. 24, Issue 3, ISSN 1844-9581, pp. 735-746, 2024. Indexed in EMERGING SOURCES CITATION, Clarivate Analytics.

Article submitted for publication: V. Neculae, C. Dulama, **C. Diaconescu**, D. Dupleac, „ *Optimization of a passive sampling method for tritium measurement in indoor air of nuclear facilities",* U.P.B Scientific Bulletin Series B.

Articles in BDI indexed journals

C.E. Diaconescu, M. Dianu, I.C. Florea, „*Influence of ^{60}Co in Separation, Purification, and Quantification of ^{63}Ni from Radioactive Waste Samples*", Nuclear Research and Development (JNRD), No. 29, pp. 43-47, 2025, ISSM 2247-191X, Index Copernicus International Journal Master List database.

C.E. Diaconescu, *I.C. Florea*, C. Bucur, și A.R. Budu Stănilă, *„Assessment of Gamma Dose Rate for Waste Packages with Radioactive Concentrate using Microshield Software",* Journal of Nuclear Research and Development (JNRD), ISSM 2247-191X, No. 24, pp. 38-42, 2022; Index Copernicus International Journal Master List database.

I. Florea, **C. Diaconescu,** C. Bucur, A. Budu Stănilă, „*Modelling of cement hydration using PHREEQC code*", Journal of Nuclear Research and Development (JNRD), December 2022. ISSM 2247-191X, Index Copernicus International Journal Master List database.

C. M. Bucur, C. Ichim, I. Florea și **C. Diaconescu**, „*Cementitious Materials Characterisation by Inductively Coupled Plasma Emission Spectroscopy,"* Journal of Nuclear Research and Development, nr. 26, pp. 48-54, 2023. ISSM 2247-191X, Index Copernicus International Journal Master List database.

International/National Conference

C. E. Diaconescu, I. C. Florea, V. Neculae, „*Studiul privind aplicarea codului de calcul MicroShield în evaluarea debitului de doză al coletelor cu deșeuri condiționate din RATEN*

ICN", Conferința Națională a Societății Române de Radioprotecție "Utilizarea Radiațiilor în Beneficiul Dezvoltării Durabile a Societății Românești", oral presentation session, 2024;

C.E. Diaconescu, M. Dianu, I.C. Florea, „*Influence of Co-60 in Separation, Purification, and Quantification of Ni-63 from Radioactive Waste Samples"*, The 15th Biennial International Conference on Sustainable Development through Nuclear Research and Education, May 2024, oral presentation session.

Crina Bucur, C. Ichim, M. Dianu, ***C. Diaconescu***, A. Stafie, V. Toboşaru *"Measurement of C-14 in Spent Molecular Sieve and Metallic Waste",* The 15th Annual International Conference on Sustainable Development through Nuclear Research and Education, may 2024, oral presentation session – Radioactive Waste Management.

Valentina Neculae, Cristian Dulama, Rodica Magereanu, ***C. Diaconescu,*** *"Experimental Tests for the Optimization of the Tritium Determination Method in Air Using Passive Collectors"*, The 24th International Conference New Cryogenic and Isotope Technologies for Energy and Environment, 2023 (poster session).

C.E. Diaconescu, *I.C. Florea*, C. Bucur, și A.R. Budu Stănilă, *„Assessment of Gamma Dose Rate for Waste Packages with Radioactive Concentrate using Microshield Software",* The 14th Annual International Conference on Sustainable Development through Nuclear Research and Education, May 2022, (poster session).

Mihai Eduard Pavel, Monica Valeca, **Cristina Diaconescu,** "*Determination of HPGe Detector Efficiency Calibration Curve for Liquid Radioactive Waste Measurements",* The 14th Annual International Conference on Sustainable Development through Nuclear Research and Education, poster session, May 2022.

C. Diaconescu, L. Bujoreanu, I. Florea, Ilie Prisecaru, „*Assessment of the Tritium and Gamma Ray Emitters Activities in Liquid Radioactive Waste Generated by TRIGA Reactor",* XXIII rd International Conference "New Cryogenic and Isotope Technologies for Energy and Environment" EnergEn 2021, ISSN:2810-3203, ISSN-L:2810-3203, book of abstract, poster session, 2021.

C. Diaconescu, M. Mihalache, I. Florea, C. Ichim, "*Efficiency Calibration Methods of GeHP Detector for Gamma Ray Measurements from Solid Radioactive Waste",* The 13th Annual International Conference on Sustainable Development through Nuclear Research and Education, Nuclear, poster session, 2021.

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