„Dunărea de Jos" University from Galaţi
Doctoral School of Mechanical and Industrial Engineering

PhD THESIS

SUMMARY

PERFORMANT ANALYTICAL TECHNIQUES USED FOR THE TOXIC SUBSTANCES MONITORING AND INDUSTRIAL WASTE MANAGEMENT

PhD student,
Eng. Florin SLOATĂ

Scientific coordinator,
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Seria I 4: Inginerie Industrială Nr. 93

GALAŢI
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"Nihil sine Deo" is the motto I read for the first time when I visited Peleș Castle, being curious to learn more about the history of the Romanian Monarchy. Reading this message, sent by the emblematic Founding Monarch of Modern Romania - Carol I, I realized that the social status that any man can have in this world is not enough to make him achieve his goal. I worship the Divinity for giving me: the gift of life, the family that raised me, health, skill, the family I founded, the good people, but also for those that will follow.

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Thank you!
Sincerely yours,

Galați, 2023 Florin SLOATĂ

CONTENT

INTRODUCTION

The environment of our planet, also called the physical environment in short, is represented by all the physical factors such as: solar energy, atmosphere, hydrosphere and geosphere. Without this physical environment life could not exist. In relation to the physical environment, the biological environment is represented by the physical resources, circumstances and events that favor the existence of an organism or several organisms including the relationships between them, it is obvious that the human species also falls into this group. In this sense, the notion of environment is translated and understood as the relationship between the physical and biological environments located in a defined space (the spatial component) in relation to the unit of time (the temporal component), these two components help the reproduction and normal development of a species or a group of species. Any form of human-made modification of the environment that causes negative and irreversible effects that endanger its own survival or the survival of other species can be defined as an environmental problem [Wali et al., 2010].

Environmental science is the scientific study of the interactions and dynamic processes that occur between the physical and biological factors of nature, taking into account their impact on social and economic systems. Environmental science can be said to be a multidisciplinary field of study that addresses one of the oldest and inescapable questions of the contemporary world: what is our relationship with the environment [Botkin, 1992]?

Good and sustainable management of the environment can only be done by applying the sciences that are the basis of environmental science, these being: mathematics, statistics, physics, chemistry, biology, geology, climatology, hydrology, engineering, economics, sociology, etc. [Wali et al., 2010], [Iojă, 2013].

One of the major threats to the integrity of the environment is the generation of large quantities of hazardous industrial waste [Akpan and Olukanni, 2020]. This increase in the generation of hazardous waste can be attributed to the increase in population globally. As the population grows, so do industrial activities, thus generating a larger amount of hazardous waste [Olukanni and Oresanya, 2018].

According to the reports carried out by the United Nations Environment Program (UNEP), approximately 400 million tons of waste containing hazardous substances are generated annually worldwide, i.e. approximately 60 kg per capita [UNEP], [The World Counts].

The classification of hazardous industrial waste is very difficult to apply due to the fact that it does not have a simple chemical composition. Hazardous waste can be treated/recycled to a fairly good extent, but this process is still very slow due to the rules regarding its handling, transport and management in order to reduce the risks to the health of biological species and the environment [Hennebert, 2022].

Due to the advent of high performance analytical techniques such as: Energy Dispersive X-ray Fluorescence (ED-XRF), Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Beam Analysis Techniques of Accelerated Ions (IBA) – Particle Induced X-Ray Emission (PIXE) and Gamma (PIGE), Neutron Activation Analysis (INAA), Gamma Radiation Spectrometry (GRS) and Gas Chromatography (GC) Analysis, can obtain sufficient data on the characterization of hazardous industrial waste, including for their good management.

The motivation for choosing the topic addressed was reinforced by the situation and problems that have arisen in recent decades regarding the pollution of the environment, the management of industrial waste containing dangerous substances and the risk to which the existence of all living organisms is subjected. It is necessary to understand that humanity

needs to think and implement ideas, policies and technologies to stop the poor management of all wastes generated in any industrial field. It is considered that there are very few studies in Romania that provide solid evidence about the negative impact of the non-compliant application of the management of hazardous industrial waste inherited from the communist period or even those generated today.

The doctoral thesis, entitled: "***Performant analytical techniques used for the toxic substances monitoring and industrial waste management***", has as its general objective the determination of the amounts of toxic chemicals (heavy metals, chlorinated organic compounds and radioactive elements) in waste samples from various industries heavy, respectively in soil samples located around industrial facilities that have ceased their activity or that are still active today.

The research subject discussed in this paper, through the results obtained and compared with the European norms transposed into the national ones regarding hazardous industrial waste and the protection of environmental factors, could influence the change in the way of thinking for the correct application of waste management, environmental protection and of the health of living organisms.

The most important original aspect of this work is represented by the application of varied multi-elemental analysis for the characterization of hazardous waste samples and contaminated soils, using high-performance and sensitive atomic and nuclear analytical techniques that revealed trace concentrations of toxic chemicals.

The unique aspect encountered in the composition of this doctoral thesis is represented by the results of the project of the total management of radioactive waste that contain nuclear materials pertinent to the proliferation of nuclear weapons. This project was applied within the SetCar S.A. company from Brăila, Romania, the implementation period was 2 years and aimed at the transfer of all radioactive waste of nuclear interest to an authorized operator in the nuclear field, respecting international and national norms regarding radiological protection, temporary storage, application of physical protection, application of control of guarantees, safe transport (transfer), removal from the temporary authorization regime, etc.

The experimental results obtained as a result of the research were presented in the form of communiques (37) within the national and international conferences mentioned in the section Dissemination of research results. Also, the results were published in full in scientific journals, out of a total of 8 articles, 2 articles being published in ISI indexed journals. The entire research program carried out within the Doctoral School was supported by a number of 10 international projects and 1 national project (INTERVENT), the author being part of the research team as a member or volunteer.

This doctoral thesis written under the title "***Performant analytical techniques used for the toxic substances monitoring and industrial waste management***" was built with the careful coordination of the scientific guidance committee made up of the following members: Mrs. Prof. univ. habil. dr. Antoaneta ENE (scientific coordinator), Mr. Prof. univ. dr. eng. Puiu-Lucian GEORGESCU, Mrs. Prof. univ. dr. phys. eng. Luminița MORARU, respectively Mrs. Prof. univ. dr. Mirela PRAISLER. The content of the thesis is structured in 4 chapters, spread over a number of 233 pages, a number of 32 tables, 91 figures and 15 annexes are included.

Chapter I presents aspects related to the impact of industrial pollution worldwide, exemplifying certain sites contaminated with dangerous substances and human settlements that are exposed to industrial emissions harmful to their health, but also measures that the great economic powers of the world take to reducing pollution. At the same time, cases of excessive industrial pollution of ecosystems at the national level are exposed, such as: contamination of the Olt river watershed and soil pollution around the active areas of the extractive industry or the metallurgical industry. Also in this chapter, aspects relating to the

implementation of legislative frameworks, at the level of the European Union, with the aim of regulating the transfer of hazardous waste between member states, the method of final storage of industrial waste, their recycling strategy, etc. can be noted.

In ***Chapter II***, the high-performance analytical techniques used for the elementary physical and radiological characterization of hazardous industrial waste matrices and soil samples located around inactive or active industrial units in the Brăila-Galați region are described. The analytical techniques used in this research are: Energy Dispersive X-ray Fluorescence (ED-XRF), Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Ion Beam Analysis Techniques (IBA) – Particle Induced X-ray Emission (PIXE) and Gamma-ray Emission (PIGE), Neutron Activation Analysis (INAA), Gamma Ray Spectrometry (GRS), including in-situ applied and Gas Chromatography (GC).

Chapter III consists in the presentation of the results obtained following the application of the experimental program. These results refer to the determination of the content of PCBs, major elements, heavy metals, trace elements, natural and artificial radionuclides in hazardous industrial waste samples and industrial soil samples. Following the results obtained, ecological and radiological risk assessments related to the health status of the population living near active and inactive industrial units in Galati and Brăila were drawn up. Aspects regarding the adoption of best practices regarding the total management of interest nuclear materials and radioactive waste represented by solid materials contaminated with ^{238}U and ^{232}Th are also presented.

In ***Chapter IV***, the general conclusions drawn up based on the analyses, the experimental results obtained and the ecological and radiological risk analyzes are presented. The author's original contributions to this PhD thesis and his intentions for future research can be noted.

Original contributions

The PhD thesis "***Performant analytical techniques used for the toxic substances monitoring and industrial waste management*** " focused on the adaptation and optimization of some high-performance analytical techniques (ED-XRF, AAS, ICP-MS, PIXE, PIGE, INAA, GRS and GC) for the compositional characterization and radiological evaluation of hazardous industrial waste and industrial soils. The main original contributions are:

- optimizing the application of the ED-XRF method to reduce the analysis error values by improving the peak-background ratio in the energy spectra. This optimization was put into practice by increasing the irradiation time of hazardous industrial waste samples;

- characterization of trace elements composition of industrial waste containing hazardous substances from the decommissioning of some industrial facilities or resulting from the industrial activities of some economic operators on the territory of Romania in order to establish the best criteria for managing this waste. The characterization of hazardous industrial waste was carried out with the help of ED-XRF, PIXE and PIGE analytical techniques;

- adoption of the best practices related to the total management of materials of nuclear interest and radioactive waste represented by solid materials contaminated with ^{238}U and ^{232}Th. Compliance with national and international norms in the nuclear field, the application of analytical gamma spectrometry methods for the identification of ^{238}U and ^{232}Th from unknown samples and the use of radiometric equipment to determine the gamma radiation flow to which the operating personnel were subjected during the physical inventory of nuclear materials, were at basis for carrying out the operation of the total management of all nuclear and radioactive materials. By obtaining these experimental results, a contribution was made to the updating of national and international databases regarding holders or former holders of interest nuclear materials and radioactive waste;

- establishing the degree of PCB contamination of oils from high-voltage industrial electrical equipment to make a parallel between the concentrations obtained in this research and the results obtained in other scientific contributions from abroad, respectively to establish the technological parameters of the installation, property of SetCar S.A. Braila, for the dehydration, dechlorination and reuse of these oils. The determination of the PCB content in industrial transformer oils contributed to the updating of the inventory regarding the quantities of hazardous waste with PCB content located on the territory of Romania;

- determining the elemental composition of the soils and performing the ecological and toxicological risk assessment related to the health of the population that agriculturally exploits the soils polluted with heavy metals located around the former chemical plant in Brăila county. This ecotoxicological risk assessment was carried out based on the results obtained following the application of complementary analytical methods ED-XRF, AAS, ICP-MS and PIGE for the analysis of industrial soil samples and a set of soil pollution/contamination indices;

- determining the compositional scheme of the soils and performing the ecological and toxicological risk assessment related to the health status of the population living in the vicinity of the Galati metallurgical complex using the experimental data resulting from the application of INAA and ED-XRF instrumental and non-destructive analytical techniques for the analysis of soil samples industrial and simple pollution and ecotoxicological indices;

- the assessment of the mobility and the risk of migration in the depth of the soil of a large number (42) of chemical elements (metals, rare earths, actinides, lithogenic elements, trace elements) detected in the industrial area of the Galati metallurgical complex;

- radiological risk assessment, related to the health of the population living near the Galati metallurgical complex, based on the results obtained following the application of the analytical technique of high-resolution and low-background gamma spectrometry on industrial soil samples. The results of this study will contribute to the updating of national databases on the content of natural and artificial radionuclides in industrial soils and international databases on the radioactivity of soils around steel enterprises.

I. DOCUMENTARY STUDY

1.1. The impact of industrial pollution

Due to the advent of the Industrial Revolution in the United Kingdom of Great Britain [Mohajan, 2019 people have been able to advance more quickly into the 21st century. At that time, the industries were represented by small factories that generated mainly gaseous pollutants (fine particles in suspension, smoke), their number was limited and they operated only a certain number of hours a day, and the level of pollution did not increase significantly [Elsharkawy, 2020]. When these factories became large-scale industrial production units, the problem of industrial pollution began to become a very important one [Kabir et al., 2020], [Elsharkawy, 2020].

Technology developed rapidly, science advanced, and thus the age of manufacturing emerged. At the same time, another phenomenon called industrial pollution developed [Elsharkawy, 2020], [Shah et al., 2021] which induces a significant degradation of environmental factors [Kabir et al., 2020]. This environmental degradation is the irresponsible response of human activities [Kabir et al., 2020], however, humanity has begun to pay more attention to environmental pollution and implement certain measures in recent years, but many problems remain to be solved [Xiong et al., 2021]. From an economic point of view, the industrial production sector represents the pillar of a nation's development, but from an ecological point of view, it accounts for approximately half of the pollution produced worldwide [Shah et al., 2021].

According to [Mahmood and Saeed, 2023] industrial pollution is one of the most dangerous types of pollution known because it has toxic side effects on living organisms. There is no doubt that industrial pollutants, especially chemical ones, have a strong physico-chemical stability and do not decompose naturally, and for this reason their effects remain for very long periods. Even though living organisms possess the ability to self-regenerate, they cannot withstand exposure to high doses of chemical pollutants. The amount of chemical pollutant required to kill 50% of members of a given species is called the lethal dose 50, symbolized by LD 50 [Zubcov and Ene, 2021].

Industrial pollution and the degradation of environmental factors represent one of the most serious problems that the large, highly industrialized countries are trying to manage correctly. However, the reduction of pollution and waste generation on an industrial scale is a topic of debate avoided by large producers because it involves high costs and affects production if it will be implemented [Khan and Tarique, 2015].

Gao et al., 2019 highlight the adsorption potential of additives added to the coal used by combustion in metallurgical processes in order to prevent and reduce the emissions of fine particles carrying heavy metals such as: arsenic, cadmium, chromium, copper, nickel, lead, titanium, zinc, etc. These can be embedded in fine particles such as PM2.5 and PM10 and can enter the human body through inhalation. The researchers of this study observed that the additive reacted with heavy metals, including some alkali metals (sodium and potassium).

Marlow et al., 2022 combined flood risk predictions with historical data on former manufacturing plants in 6 US cities. They have identified more than 6000 industrial sites contaminated with hazardous substances. These hazardous substances can seep into the soil contaminating groundwater or be carried by flood waters to populated areas. The calamity could endanger the health of more than 560,000 inhabitants and the integrity of more than 229,000 housing units. Based on the results obtained, the authors of this study draw attention to the potential calamities that may occur in the near future and request an action to prevent a humanitarian and environmental disaster.

Rahman et al., 2021 used the annual data of the World Development Indicator, published by the World Bank, during the years 1960-2019, to make the connection between industrial pollution and the state of health of the population. The study was applied to data from the twenty most industrialized countries in the world. The authors of this theoretical study demonstrated that industrial pollution significantly increases the mortality rate. Adopting sustainable socio-economic and environmental development lowers the mortality rate.

Sidor et al., 2021 identified an anomaly in the growth and vitality of spruces and silver firs, caused by atmospheric pollution in the town of Tarnița, Romania, between 1978 and 1990. The atmospheric pollution was induced by mining operations and the primary processing activity of non-ferrous ores with content of complex sulfides of several heavy metals. The revival of the studied trees appeared after 1990 when there was a sudden slowdown in mining activities in the area. This revival phenomenon intensified after the cessation of industrial activities starting in 1998.

Bravo et al., 2009 assessed mercury pollution in the sediments of the Babeni reservoir, on the Olt River, Romania. This location was chosen because it is downstream of an electrolysis plant that uses an elemental mercury electrode. The concentration of mercury in the sediments sampled from a depth of 50 cm was 45 ppm. Mercury concentration ranged from 1.3–2.4 ppm in surface sediments.

Iordache et al., 2022 carried out a study to determine the concentrations of mercury and other heavy metals in the sediments of the Olt River, Romania. Mercury pollution was caused by the discharge into the river of some contaminated effluents from the industrial activity of obtaining chlorosodium products through electrochemical processes. Mercury concentrations ranged from 0 to 1.11 ppm.

Using INAA and ED-XRF analytical techniques Ene et al., 2011a characterized certain soil samples taken from the immediate vicinity of the metallurgical plant in Galați, Romania. Following the characterization of industrial soil samples, 44 chemical elements were identified. The results of the research show that the high concentrations values of nickel, chromium and arsenic significantly exceed the normal limit specified in the Romanian regulations. In some of the soil samples analyzed, the mercury concentrations exceed the alert levels and the intervention threshold in the regulation. Cadmium and selenium concentrations exceed the alert level. The concentration values of 23 determined elements represented by heavy metals, alkali metals, major elements and rare earths, are approximately similar to average values in surface soils in Europe and/or worldwide.

Pantelică et al., 2013 used the INAA analytical method to determine the concentrations of 42 elements in surface soil samples collected from seven industrial sites in Romania and a control site in a relatively unpolluted area. According to the results obtained, it was observed that the highest degree of soil pollution with antimony and cadmium is found in Copșa Mică, where there is a non-ferrous metallurgical industrial activity. An appreciable degree of soil contamination with arsenic, cadmium and antimony was identified in Baia Mare where there is non-ferrous and metallurgical mining activity. Due to the activity of a coal-fired thermal power plant and a cement factory, respectively construction materials, the soils of Deva are significantly contaminated with arsenic, cadmium and nickel. The light chemical industry in Oradea was the cause of the considerable contamination of the soil with staium. Agricultural and industrial soils in Afumați and Măgurele were significantly polluted with zinc and cadmium. The soil considered to be unpolluted was taken from the Fundata locality [Ene, 2015a].

Stihi et al., 2017 conducted a nationwide survey of heavy metal air pollution, analyzing 330 moss samples using INAA and AAS (graphite oven method) analytical techniques. The results of this research indicate the presence of heavy metals in very high concentrations such as: zinc, copper, cadmium and lead. This excessive heavy metal pollution is found in the

northern and northwestern part of the country, caused by mining and metallurgical activities in the area.

1.2. Aspects of hazardous industrial waste management at European and national level

The accelerated industrialization of nations during the 21st century has led to an increase in the generation of industrial waste quantities that have a negative impact on environmental factors and people's health. With the development and implementation of industrial technologies worldwide, the economy, the standard of living and the provision of all services have improved, but the industrial sector has generated a very large amount of hazardous waste [Ogunwumi and Salami, 2023].

The constant increase in the generation of hazardous industrial waste at the European level leads to the adoption of measures regarding the protection of environmental factors and natural resources. In Europe, approximately three billion tons of waste are produced annually. In this context, the European Union promotes several industrial waste management strategies with the aim of reducing the negative impact on environmental factors [Pini et al., 2018].

According to [Fazzo et al., 2023] at the European level, 38% of the contaminated areas are represented by the final deposits for household waste and hazardous industrial waste. The faulty management of hazardous industrial waste, together with their non-compliant and illegal storage in unauthorized landfills, lead to the release of potentially dangerous substances into the environment, affecting the health of the population living in the bordering area of these landfills.

Fazzo et al., 2017 argue that the term hazardous waste is adopted differently in many countries, being generally defined as non-household waste containing hazardous chemicals. [Ekvall, 2008] defines hazardous waste as those wastes produced as a result of an industrial process (mining activities, waste incineration and recycling processes, medical and public services etc. [Ogunwumi and Salami, 2023]), in any physical form (solid, semi-solid, sludge , liquid, semi-liquid etc. [Ogunwumi and Salami, 2023]), which have an infectious, toxic, corrosive, explosive or radioactive character [Ogunwumi and Salami, 2023], [Pinzon Zurita et al., 2022], which induce a negative effect directly on ecosystems and human beings and that require mandatory control in their use and management.

According to [Latorre et al., 2021] at the European level, there are different legislative frameworks on the management of hazardous waste that must be respected by all member states of the community block. The member states are forced to comply with the recovery objectives established in the European legislation on hazardous waste, having options to choose from: adopting appropriate material recycling facilities in the country of origin of the hazardous waste or exporting this waste.

From the analysis of Latorre et al., 2021 it appears that the European states that are in the top of the largest hazardous waste generators (Germany – 21812 Mtone, Bulgaria – 12206 Mtone, France – 10783 Mtone and Estonia – 10410 Mtone) are not in the top among the states exporting such waste to be recovered (Norway – 887 Mton, the Netherlands – 574 Mton and Belgium – 524 Mton), the states that exported the largest amounts of hazardous waste expressed as a percentage of the total amount generated are: Liechtenstein - 66, 76%, Norway - 64.87% and Iceland - 33.85%.

Grzegorz et al., 2022 report that the management of hazardous waste is still a problem at the level of the European Union today and that it is essential to perfect the mechanisms of record management and recognition.

1.3. Description of high performance analytical techniques used to characterize industrial hazardous waste and contaminated soils

X-ray fluorescence (XRF) analysis technique

X-rays arise when electrons are instantaneously decelerated, these radiations are called bremsstrahlung or bremsstrahlung X-rays. The characteristic X-rays arise when electrons switch from a higher electronic layer to a lower one, thus occupying the vacant place left by the dislocated electron from that layer [Clapera, 2006], [Barbooti, 2015], [Schramm, 2015]. The two phenomena of producing X-rays are represented in Figures 1.4 and 1.5.

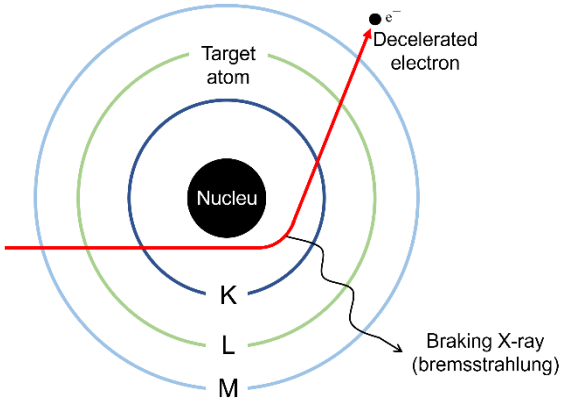


Figure 1.4. The phenomenon of producing braking X-ray (bremsstrahlung) (source: adapted according to [Roque, 2018])

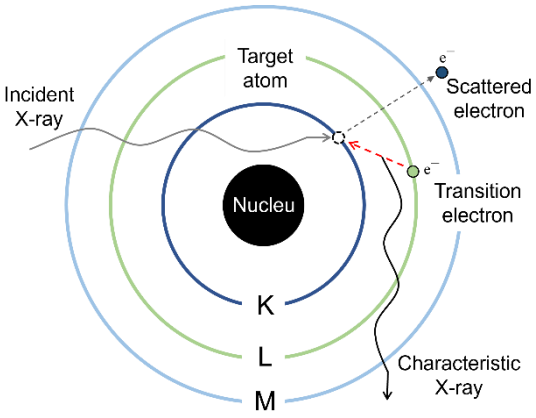


Figure 1.5. The phenomenon of producing characteristic X-rays (source: adapted according to [Ene and Pantelică, 2011a])

The generation of X-rays is done using a device called an X-ray tube or fluorescent tube, illustrated in figure 1.6 [Xing et al., 2022], [Lee Drake and Shannon, 2022]. This vacuum tube consists of an electron source consisting of two metal electrodes. A high voltage, usually 50 kV, is applied and maintained on the two electrodes (anode and cathode), thus producing a flow of electrons that moves rapidly from the cathode to the anode (the target element). By rapidly striking the anode with the accelerated electrons and decelerating them, X-rays are produced which are radiated in all directions. To obtain a guided beam at the exit from the fluorescent tube, certain windows are used.

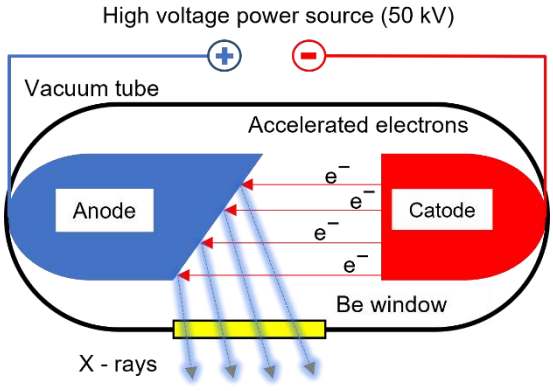


Figure 1.6. X-ray tube generator (source: adapted according to [Beckhoff et al., 2006], [Roque, 2018])

ED-XRF analyzers can be configured to work in two modes. The first method refers to the direct irradiation of the target sample using or a filter for screening the low energy photons. The second method refers to the use of a secondary target, irradiated directly by the X-ray source, and which in turn irradiates the sample of interest in order to intensify its excitation. The characteristic X-ray emitted by the target sample falls on a detector. The signal given by the detector is processed by a preamplifier, an amplifier and an analog-to-digital converter, and finally the multichannel analyzer assigns an energy value to each pulse. The function between the impulse and the energy value is transposed into the energy spectrum by means of a computer-assisted program [Clapera, 2006]. The schematic diagram of an ED-XRF spectrometer, which uses direct irradiation of the target sample, is represented in figure 1.7.

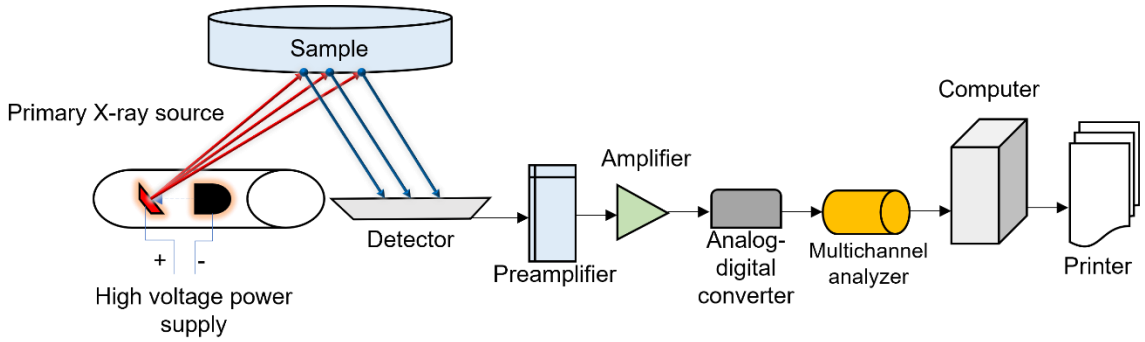


Figure 1.7. Schematic diagram of an energy dispersive X-ray fluorescence spectrometer – ED-XRF (source: adapted according to [Ene and Pantelică, 2011a])

Analytical Atomic Absorption Technique (AAS)

Every chemical element consists of a nucleus and a specific number of electrons orbiting around the nucleus. A chemical element is in its ground state when it has a specific and stable electronic configuration. The same chemical element goes into an excited state when an external energy is applied to it, and one or more electrons absorb this energy and move to another higher electronic layer. Due to the fact that the chemical element in the excited state is unstable, it will promptly return to its ground state, the electrons will return to their original orbits and release energy in the light form. This phenomenon is represented in figure 1.8 [The Perkin Elmer Corporation, 1996].

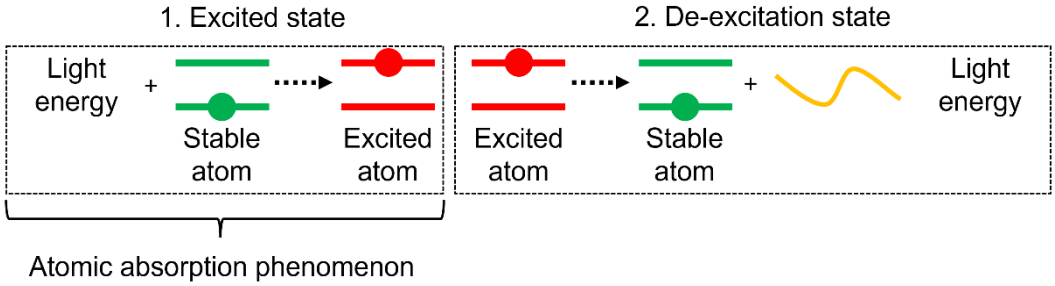


Figure 1.8. Atomic excitation and deexcitation phenomenon (source: adapted according to [Beaty and Kerber, 1993])

The analytical technique of atomic absorption involves transforming the sample into a vapor state and measuring the absorption of the vaporized atoms at a well-established wavelength. The most commonly used sample vaporization equipment are electric burners and ovens. The flame atomic absorption method is rapid, accurate, does not require the use

of sophisticated equipment, and can assist in the determination of sixty-four chemical elements [Walsh et al., 1982], [Farrukh, 2012]. This technique measures the concentration of chemical elements based on the intensity of the detected light emitted by the de-excitation of a number of the same type elements. It can be mentioned that this analytical technique has high sensitivity and that it can measure concentrations of the order of $1x10^{-9}$ grams/liter [Barbooti, 2015], [Levinson, 2002].

The atomic absorption spectrophotometer contains the following components: light source (hollow cathode lamp), optical separator, vaporization equipment equipped with a burner or furnace, equipment for sorting light by wavelength (monochromator), detector represented by a photomultiplier, a signal processor and a data reader. The schematic diagram of an atomic absorption spectrophotometer is represented in figure 1.9 [Barbooti, 2015].

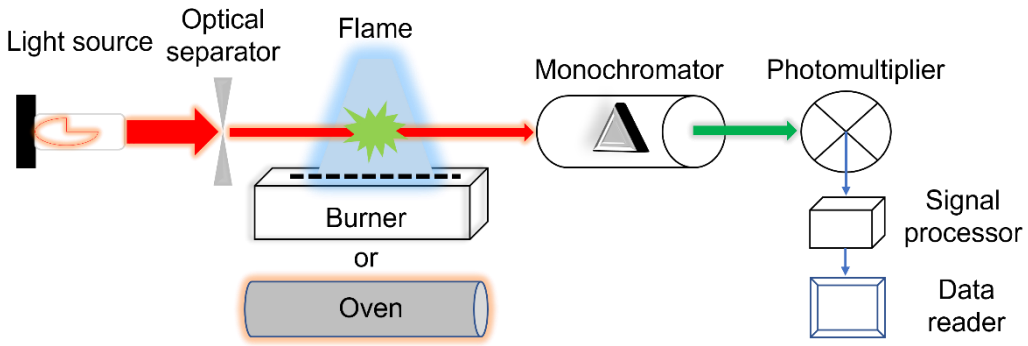


Figure 1.9. General diagram of the atomic absorption spectrophotometer (source: adapted according to [Beaty and Kerber, 1993], [Bogdevich et al., 2021])

Inductively coupled plasma mass spectrometry (ICP-MS) analytical technique (ICP-MS)

The samples intended for analysis by ICP-MS can be liquid or solid in nature, they can be introduced into the spray chamber by changing the way of introduction. Liquid samples are introduced into the spray chamber as a solution using a peristaltic pump, and solid samples are introduced after bombarding them with a laser beam and creating very fine particlesThe sample to be analyzed is introduced into an argon premixing chamber, then it is sprayed through the torch and ionized in the plasma current which can reach a temperature of ten thousand degrees Kelvin [Ammann, 2007], [Wilschefski and Baxter, 2019], [Spanos et al., 2021]. In the plasma stream the sample is dissolved, vaporized, atomized and ionized. The resulting ion beam is separated using a mass spectrometer and analyzed with an ion detector, resulting in a mass spectrum [Spanos et al., 2021], [Ene, 2021]. The application method of the ICP-MS analytical technique is schematically shown in figure 1.10.

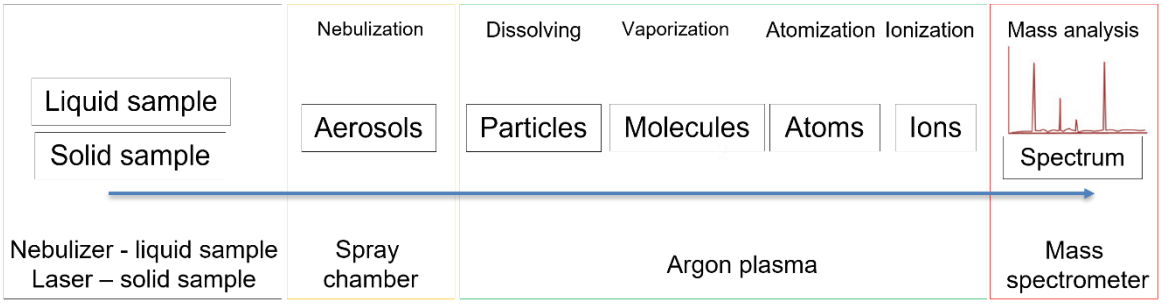


Figure 1.10. Schematic application of the ICP-MS analytical technique (source: processed according to [Spanos et al., 2021])

ICP-MS este alcătuit din șase componente principale: incinta de pulverizare a probei, torța generatoare de plasmă de argon, conurile de separare a fasciculului de ioni (interfața), lentilele optice, magnetul cu patru poli (cvadrupol) și detectorul (multiplicatorul de electroni) [Wilschefski and Baxter, 2019]. Schema de principiu a ICP-MS este reprezentată în figura 1.11.

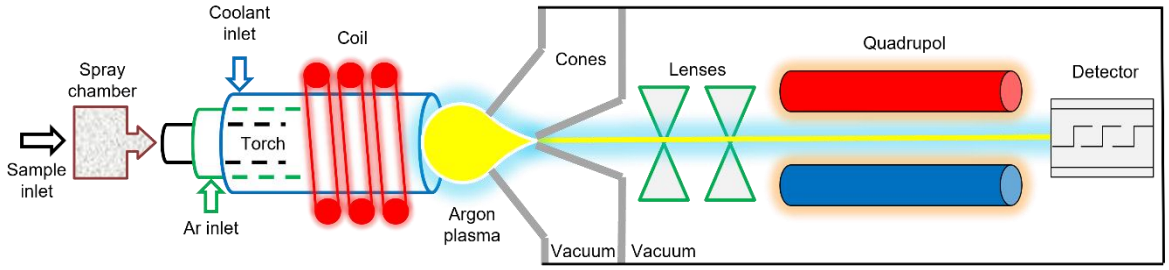


Figure 1.11. ICP-MS schematic representation (source: adapted according to [Spanos et al., 2021])

Ion Beam Analysis (IBA) – Particle Induced X-ray Emission (PIXE) and Gamma-ray Emission (PIGE)

The PIXE technique is based on X-ray spectrometry, these rays are produced when a particle induced or proton interacts with an atom. As a result of the interaction, electrons are removed from the electronic layer of the target atom, and the vacant places are occupied by electrons from higher layers. This transition is done with the emission of X-rays specific to each chemical element [IAEA, 2000], [Ghermandi, 2006], [Ishii, 2019]. Figure 1.12 shows the main phenomena that occur following the interaction between a particle induced and a target atom.

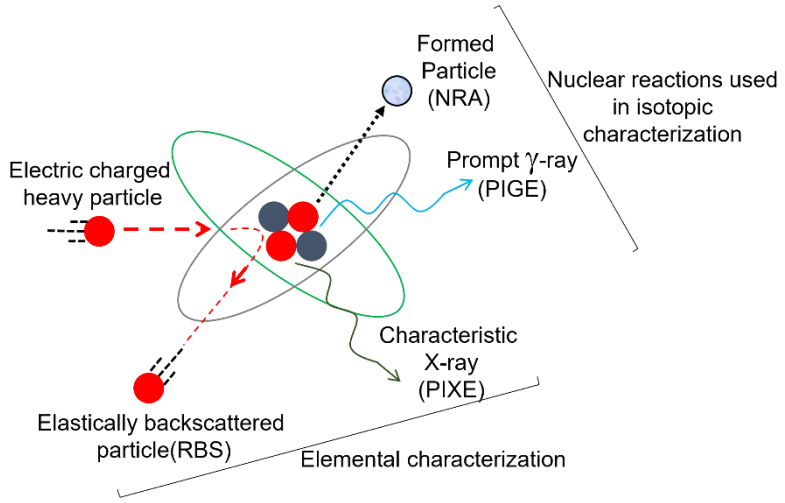
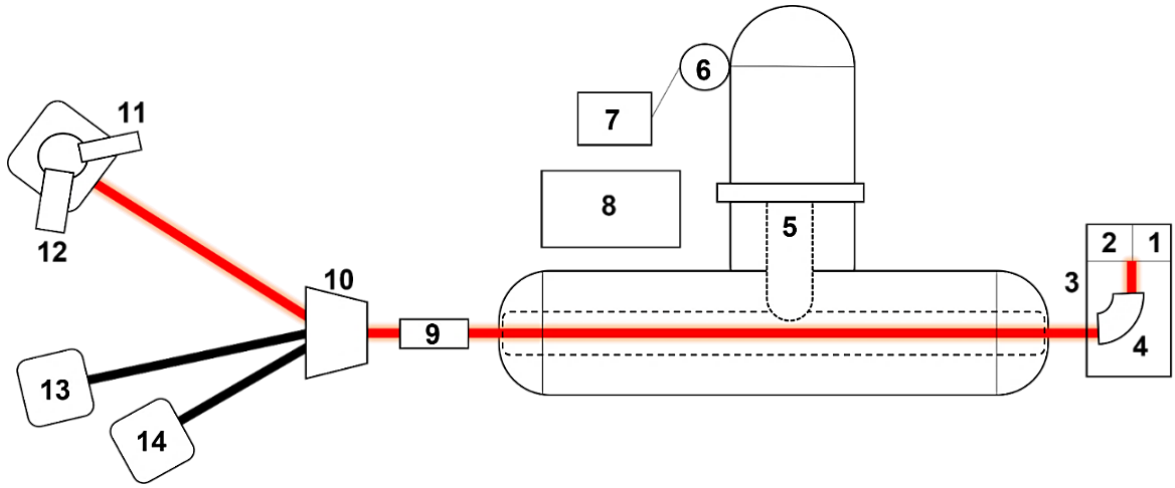


Figure 1.12. The main phenomena arising from the interaction between a particle induced and a target atom (source: adapted according to [Ene and Pantelică, 2011a], [Ene et al., 2019a])

The PIGE technique is a nuclear analysis method that is applied for the purpose of determining chemical elements with low atomic number Z, included in the interval [3; 16] and which are contained in different solid materials. With this analytical method, the prompt gamma radiation that arises from the interaction between the beam of accelerated heavy particles (such as the nuclei of: hydrogen, deuterium, tritium and helium) and the nuclei of the target sample is measured. The PIGE technique allows for elemental and isotopic analyzes

contained in a solid matrix and has the potential to achieve penetration depths of up to 500 micrometers within the sample, similar to other IBA techniques [Ene, 2006], [Ene et al., 2019a], [Zucchiatti and Corvisiero, 2013], [Dimitriou et al., 2016], [Chhillar, 2016], [Pham, 2019], [Chiari, 2023].

The most used accelerators for the implementation of IBA analytical techniques are Van de Graaff and Pelletron tandem electrostatic accelerators. Electrostatic accelerators are positioned inside a pressurized vessel, the pressure being exerted by an insulating gas. Sulfur hexafluoride is thought to be the best insulating gas, but other accelerators use a gaseous combination of nitrogen and carbon dioxide [IAEA, 2000]. The general scheme of a 3 MV Tandem accelerator is represented in figure 1.13..



1., 2. negative ion sources;
3. charge exchange channel with sodium for helium nuclei;
4. beam deflection magnet (90°);
5. Tandetron accelerator (3 MV);
6. oscillator housing with coil;
7. high power voltage supply;
8. insulating gas recovery subassembly (SF_6);
9. electrostatic cvadrupol;
10. beam deflection magnet (30°);
11. nuclear microprobe;
12. Ion Beam Analysis reaction chamber;
13. ion implantation chamber;
14. cross section measuring chamber.

Figure 1.13. General diagram of the Tandem 3 MV particle accelerator, installed at IFIN-HH, Măgurele, Ilfov (source: adapted according to [Burducea et al., 2017], [https://dfna.nipne.ro/3MV_Tandetron_EN.php])

Instrumental Neutron Activation Analysis (INAA)

The physical aspects underlying the neutron activation technique are the characteristics of the target atom's nucleus, radioactivity, and the interaction of neutrons with matter. All events that occur when a neutron interacts with a nucleus and a (neutron, gamma) type reaction is formed are represented in figure 1.14. [IAEA, 1990].

When a nucleus is hit inelastically by a neutron, the nucleus goes from its ground state to a high excited state. This high excited state of the nucleus is caused by the high binding energy between the neutron and the nucleus; on average 8 MeV is the value of the energy of the excited nucleus, and the value of its viability is between 10^{-16} and 10^{-14} seconds. This

lifetime of the excited nucleus is long enough so that it does not show signs of its activation phenomenon and short enough so that the nucleus can undergo a rapid transition to its ground state. Most of the time a radioactive nucleus is continuously de-excited by emitting characteristic gamma radiation and prompt decay. The principle of the neutron activation technique is defined by the identification and determination of the characteristic gamma radiation for the quantification of the chemical elements in the irradiated sample. Of all known chemical elements, approximately 70% of them can be analyzed using the NAA method [IAEA, 1990], [Frontasyeva et al., 2016].

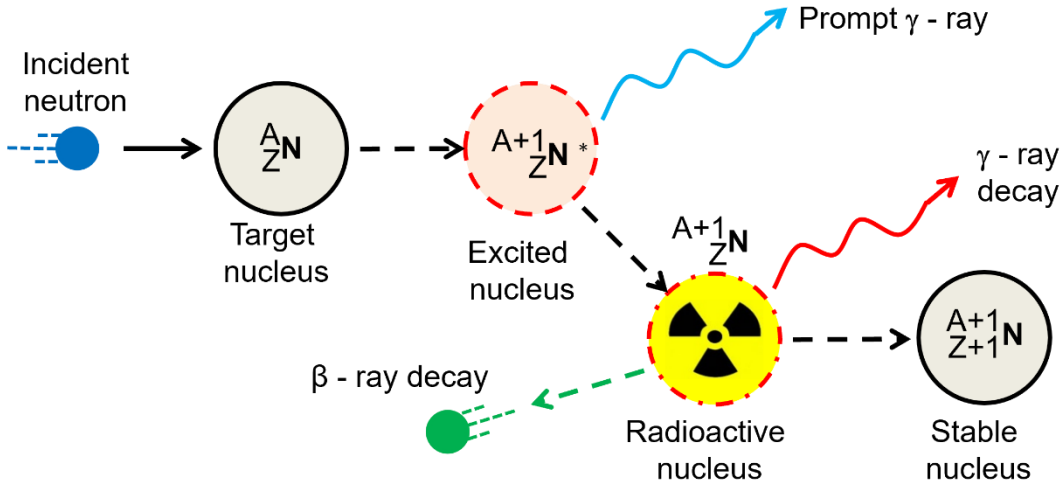


Figure 1.14. Schematic representation of the events induced by a (n, γ) type reaction (source: adapted according to [IAEA, 1990])

Three kinds of neutron sources are known: fission reactors, particle accelerators, and radioisotope neutron generators, but fission reactors provide the highest neutron fluxes, the strongest irradiations, and the highest detection sensitivity for the INAA technique. The maximum energy of neutrons from the fission of uranium nuclei is 15 MeV, and the average energy is about 2 MeV. Fast neutrons that are attenuated by elastic collisions with nuclei of moderator atoms, become thermal neutrons and achieve a vast energy distribution based on three main components, as can be seen in figure 1.15 [IAEA, 1990], [Frontasyeva, 2011].

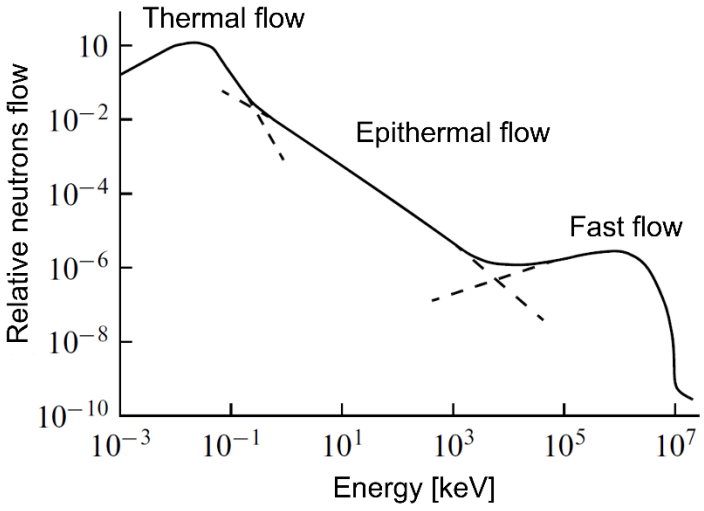


Figure 1.15. Diagram of the energy spectrum of neutrons produced and moderated in the nuclear reactor (source: adapted according to [Frontasyeva, 2011])

The energy spectrum of neutrons produced and moderated in the nuclear reactor is divided into three main components:

1. the fast neutron flow, where the neutrons resulting from fission have an energy between 0 and 15 MeV;
2. the flow of epithermal or resonance neutrons, which come from the moderation of the flow of fast neutrons, having an energy value between 1 eV and 1 MeV;
3. the thermal neutrons flow, they are in thermal equilibrium with the nuclei of the moderating elements and have an estimated energy of 0.052 eV [Frontasyeva, 2011], [Ene, 1997] .

Gamma Ray Spectrometry (GRS)

The radioactivity phenomenon occurs when an unstable nucleus decays or releases radiation in the form of energy and matter in order to transition to its ground state. There are three main types of radiation that are emitted following the decay of an unstable nucleus: α, β and γ. It is certain that the phenomenon of radioactivity occurs naturally or anthropically, some of the radionuclides are found in the components of the environment (air, water, soil) and that the interaction of radionuclides with biological species is inevitable [Zubcov and Ene, 2021], [Akinduro, 2022].

The gamma radiation detection assembly, represented in figure 1.16, consists of: detector, pulse amplifier, analog-digital converter, spectrum analyzer, respectively the display for the energy spectrum and energy windows [Ene, 1997], [IAEA, 2003], [Al-Bayati, 2017].

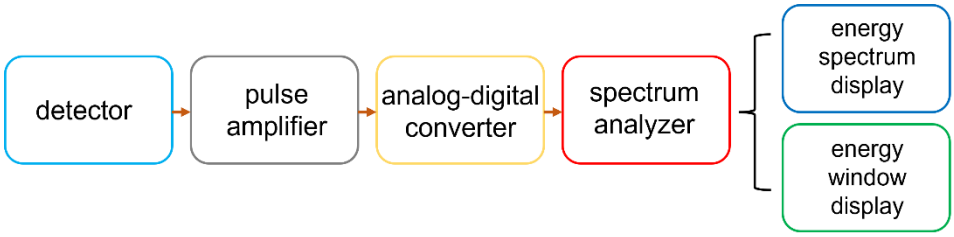
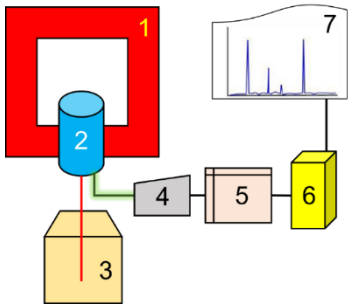


Figure 1.16. Gamma radiation detection assembly – block diagram (source: adapted according to [IAEA, 2003])

The electrical impulse passes through the amplifier, multichannel analyzer, and finally it is processed by a computer that generates a spectrum of energies for the identified gamma radiations. Given that each gamma radiation is emitted specifically by a nuclide and that the energy of these radiations is transposed into a spectrum of energies, accurate determinations can be made of the concentration of the identified nuclide. Figure 1.17 shows the principle diagram of a gamma-ray spectrometer [IAEA, 2003].

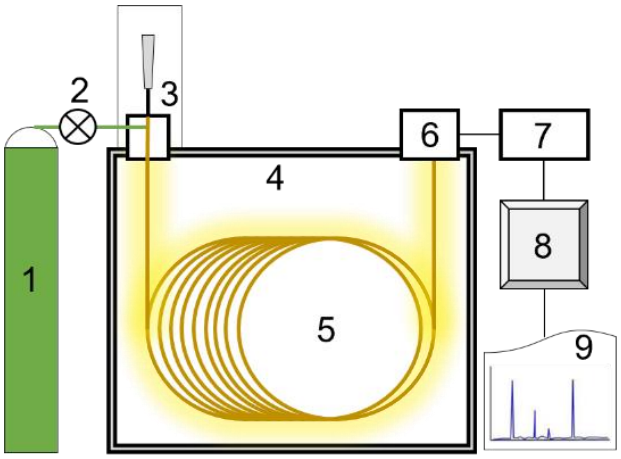


1. lead collimator shield;
2. hyperpure germanium detector;
3. liquid nitrogen canister;
4. amplifier;
5. multichannel analyzer;
6. computer;
7. energy spectrum.

Figure 1.17. Schematic representation of the gamma ray spectrometer (source: adapted according to [IAEA, 2003], [Al-Ghamdi et al., 2022])

Gas chromatographic analysis (GC)

Gas chromatography is that method of dividing a homogeneous mixture, especially of an organic nature, with the aim of qualitatively and quantitatively determining volatile fractions that have a boiling point that reaches 350^0 C or even 400^0 C. Application of the gas chromatographic method begins by injecting the sample dissolved with a solvent into the chromatographic column. The injected liquid fraction is called the stationary phase, and the mobile phase is introduced through the same column. The mobile phase is represented by a flow of carrier gases such as: nitrogen, helium, argon, etc. It is necessary that the carrier gas flow rate be constant throughout the analysis process. The stationary phase in the chromatographic column is heated to a suitable temperature to volatilize its components. The mobile phase dissolves and carries the volatilized components to the end of the column where a detector is located. As a result of the interactions between the excited molecules and the detector cells, certain electrical signals are created which are sent to the signal amplifier. Signal processing is performed by a computer, and this processing results in a chromatogram. Each peak that appears on the chromatogram highlights the presence of the analyzed components, and the area under the peak represents their concentration. The time period in which the sample injected and dissolved with the carrier gas traverses the entire length of the chromatographic column until it reaches the detector is called the retention time [Barbooti, 2015], [Shimadzu Corporation, 2020], [Teonata et al., 2021], [Sugiharto et al., 2022]. Figure 1.18 shows schematically the main components of a chromatograph.



1. carrier gas cylinder;
2. pressure reducer;
3. sample injection device;
4. oven;
5. chromatographic column;
6. detector;
7. signal amplifier;
8. signal processing computer;
9. chromatogram.

Figure 1.18. Schematic representation of the main components of a chromatograph (source: adapted according to [Mukadam et al., 2021])

In gas chromatography where a capillary column is used to improve separation when using small sample volumes, it is necessary to use a high precision detector. This detector is used for the detection of compounds with high electron affinity and has a high sensitivity for the determination of electronegative compounds such as halogens. This detector consists of an ionization chamber where the flow consisting of the mobile phase and the stable phase is continuously bombarded with beta radiation from a low-energy radioactive microsource (Ni^{60}). This results in excited molecules that disintegrate, and the released electrons are absorbed by the electric installed in the ionization chamber. The absorption of electrons by the cells of the ionization chamber is translated into an electrical signal. Due to the fact that the carrier gas can interfere with the ionization phenomenon with beta particles, for this reason the use of a combination of methane and argon gas is preferred [Barbooti, 2015], [Sugiharto et al., 2022].

II. MATERIALS AND METHODS

2.1. Sampling and preparation of samples subjected to experimental analyses

To support the experimental program developed within the present PhD thesis, technical and economic means provided by SetCar S.A. were used. from Brăila. All the samples of hazardous chemical waste were taken from inside the facilities authorized for the temporary storage of this waste. All the storage facilities are located at work point number two, called the chemical platform, within the SetCar S.A. company, Brăila (Figure 2.1).

Figure 2.1. SetCar S.A. facilities Brăila intended for the temporary storage of hazardous chemical waste - overview (source: SetCar S.A. Brăila photo gallery)

Some frames taken during solid hazardous chemical waste sampling are represented in figure 2.2 (a) and (b).

(a)

(b)

Figure 2.2. Solid hazardous waste sampling

The hazardous waste samples represented by dielectric oils containing polychlorinated biphenyls, used in high-voltage industrial electrical equipment (transformers and capacitors), were taken from inside the dedicated storage facility for this type of waste. These samples were subjected to gas chromatographic analysis. The sampling activity is illustrated in figure 2.3 (a), (b) and (c) [Sloată et al., 2017a], [Sloată and Ene, 2018a], [Sloată and Ene, 2020a].

(a)

(b)

(c)

Figure 2.3. Sampling of oil containing polychlorinated biphenyls (source: adapted according to [Sloată et al., 2017a], [Sloată and Ene, 2018a], [Sloată and Ene, 2020a])

Unknown radioactive waste was identified following a physical inventory of expired laboratory substances. On the chemical platform SetCar S.A. there is a dedicated facility for the temporary storage of these laboratory substances.

Following completion of the physical inventory of all expired laboratory substances, several vials containing radioactive material were identified. These were repackaged, weighed and provisionally labeled (Figure 2.4 (a), (b) and (c)).

After carrying out these operations, the unknown vials were subjected to analysis to determine the type of radionuclide, its activity and mass [Sloată and Ene, 2021a, b].

In addition to the vials containing unknown radioactive materials, some radioactive waste was also inventoried. This radioactive waste is represented by solid objects contaminated with radionuclides and resulted from the sorting and repackaging processes of radioactive substances (Figure 2.5 (a), (b) and (c)).

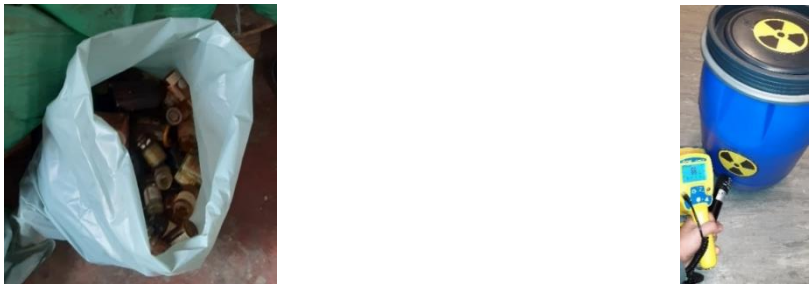
The entire amount of radioactive waste consisted of the following contaminated materials: glass, paper, plastic, ferrous and non-ferrous metal, anti-shock material used to protect glass vials against cracking and breaking, work equipment used by SetCar S.A. personnel. (gloves, coveralls, masks for respiratory protection, tweezers for shoe protection, etc.).

This waste was packed in polypropylene bags, then placed in metal and plastic drums. Finally, they were characterized from a radionuclide point of view using the in situ GRS technique [Sloată and Ene, 2021a, b].

(a) (b) (c)

Figure 2.4. Vials containing unknown radioactive substances (source: adapted according to [Sloată and Ene, 2021b])

(a)



(b) (c)

Figure 2.5. Method of packaging of unknown radioactive solid waste (source: adapted according to [Sloată and Ene, 2021b])

Ten soil samples were taken from around the former artificial fiber, pulp and paper plant, Brăila, Romania, according to the detailed map in figure 2.6. As can be seen in figure 2.6, a number of three samples (B1, B2, B3) were taken from the northern part of the compound, a number of four samples (B4, B5, B6, B7) from the western part, and a number of three samples (B8, B9, B10) were taken from the southern part. Soil samples were analyzed spectrometrically using ED-XRF, AAS, ICP-MS and IBA (PIXE-PIGE) techniques [Sloată and Ene, 2020b], [Ene and Sloată, 2021], [Ene et al., 2022b], [Sloată et al., 2022a, d].

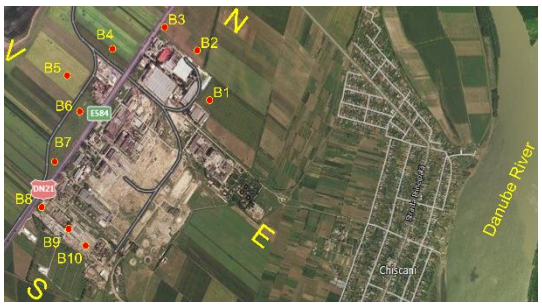


Figure 2.6. Map of soil sampling around the former artificial fiber, pulp and paper plant in Brăila (source: processed according to [Ene and Sloată, 2021], [Ene et al., 2022b], [Sloată et al., 2022a, d])

Ten soil samples, collected around the Liberty Galati metallurgical complex, Romania, were taken from different depths: 0-5 cm, 5-20 cm and 20-30 cm. Samples G1.1, G1.2 and G1.3 were taken from Vădeni commune, Brăila county, and the other samples (GC, G2.1, G2.2, G2.3, G3.1, G3.2 and G4. 1) were taken from localities belonging to Şendreni, Smârdan and Vânători communes, Galați county, respectively from Galați city. The soil sampling map around the Galați metallurgical plant can be found in figure 2.7.

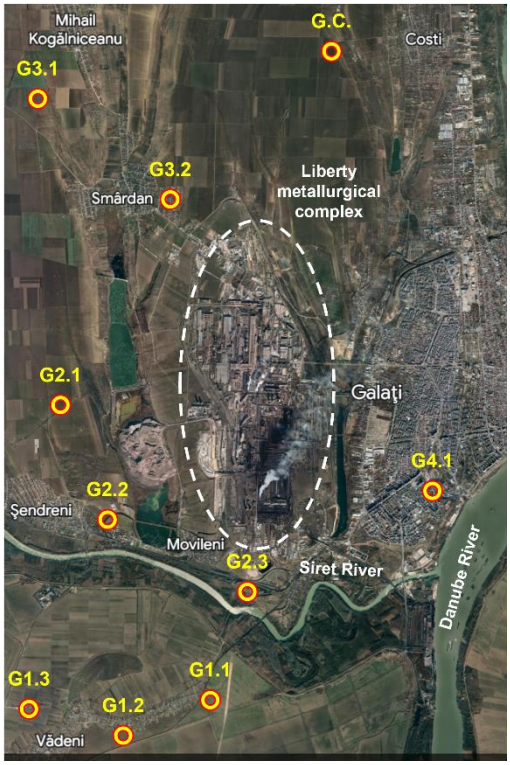


Figure 2.7. Map of soil sampling around the Galați metallurgical complex (source: processed according to [Ene et al., 2018b, c], [Ene et al., 2020b], [Ene et al., 2022a], [https://distanta.com/])

The ten soil samples were analyzed for major, minor and trace elements, including elements of industrial interest – heavy metals, actinides and rare earths, using ED-XRF and INAA analytical techniques [Ene et al., 2017a, b], [Ene et al., 2018b, c], [Moraru et al., 2019], [Ene et al., 2020b], [Ene et al., 2021b], [Ene et al., 2022a].

Another eight soil samples were collected in another sampling campaign, in the immediate vicinity of the Liberty Galați metallurgical complex, according to the map in figure 2.8, for the radiological and health risk assessment of radioactive isotopes. Table 2.2 shows the geographical coordinates of the industrial soil sampling areas according to figure 2.8.

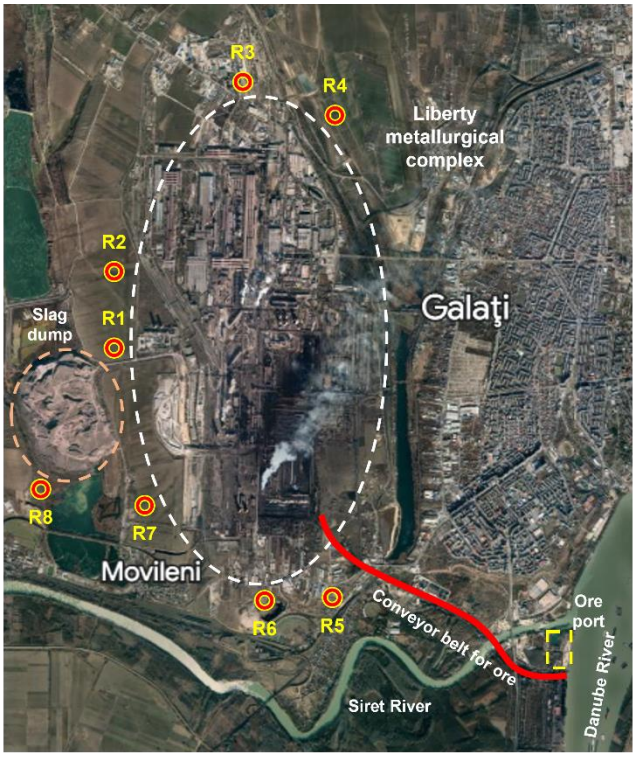


Figure 2.8. The sampling map of the eight soil samples in the immediate vicinity of the Liberty Galați metallurgical complex (source: processed according to [Ene et al., 2018a], [Ene et al., 2023a, b], [Sloată and Ene, 2018e])

The samples were taken from the soil surface (0 – 5 cm) and were radiologically analyzed by means of the GRS technique [Ene et al., 2018a], [Ene et al., 2023a, b], [Sloată and Ene, 2018e].

Figure 2.8 shows that sample R1 was taken from the area of the access road to the slag dump, and sample R2 was taken from the northern area of the slag dump. Samples R3 and R4 were collected from the northern area of the Liberty compound (Atlas), respectively the northern gate of the compound. Soil samples R5 and R6 were taken from the south-eastern area of the compound (Tirighina), respectively its south gate. Sample R7 was taken from the southwest area of the complex (Movileni), and sample R8 from the southern area of the slag dump.

The solid samples from hazardous industrial waste, including radioactive waste, were prepared inside the SetCar S.A. mobile laboratory. The oil samples containing polychlorinated biphenyls were prepared inside the main laboratory for physico-chemical determinations located on the SetCar S.A. chemical platform.

The samples from the sampling of industrial soils from Brăila and Galați counties were prepared in the SetCar S.A. mobile laboratory. and in the INPOLDE research center within the

”Dunărea de Jos” University from Galati, as mentioned in the collaboration agreement INPOLDE-SetCar, concluded on 17.03.2017. It should be mentioned that some samples of industrial waste and soils around the previously referenced plants were prepared in the laboratories of JINR (Dubna, Russian Federation), IGS (Chisinau, Republic of Moldova), IHU (Kavala, Greece) and IFIN- HH (Romania), depending on the specifics of the analytical techniques used.Probele de deșeul solid cu conținut de mercur metalic și săruri de mercur care a provenit din dezafectarea unei instalații de electroliză pentru obținerea de produse clorosodice a fost preparate în trei moduri:

1. simple preparation by taking and packing the raw sample, as can be seen in figure 2.9.

2. preparing the samples by natural drying for thirty days, applying a thin layer of waste about 0.5 cm on a polypropylene film and keeping it under the niche during the entire drying period. After drying, grinding and sieving of the samples to a grain size of 0.01 mm was applied, and finally the samples were encapsulated in Mylar foil containers dedicated to X-ray fluorescence analysis, according to Figure 2.10 (a) and (b).

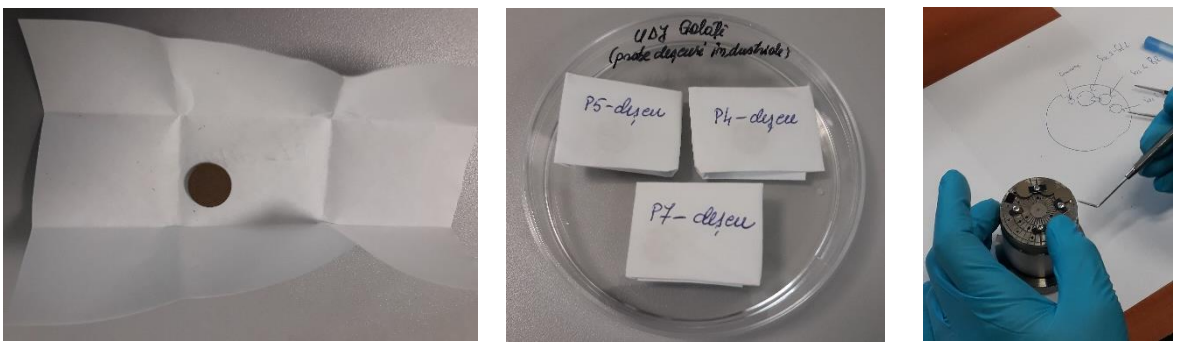
3. preparing the samples by pressing, after they were initially dried, mortared and sieved according to point 2. The samples were inserted into a mold to obtain the desired pellets. The mold was inserted into an automated hydraulic press with the load of five tons of force, the depressurization of the mold was carried out using a manual hydraulic press.

Figure 2.9. Method of packaging of raw samples of waste containing mercury and mercuric salts

(a) (b)

Figure 2.10. Preparation and encapsulation of solid waste samples containing mercury and mercury salts

The tablets obtained (10 x 1 mm) were temporarily packed in paper envelopes, and during the analysis they were positioned on a support specific to the IBA analysis, as can be seen in figure 2.11 (a), (b) and (c). All these sample preparation operations are illustrated in figure 2.12 (a), (b), (c), (d), (e), (f) and (g) [Ene et al., 2020c].



(a) (b) (c)

Figure 2.11. Samples prepared for IBA analysis: (a) and (b) samples provisionally packed in paper envelopes, (c) positioning of the samples on the support

(a) (b) (c)

(d) (f) (g)

Figure 2.12. Operations performed to obtain pelletized samples: (a) and (b) introducing the sample into the mold, (c) pressurizing the mold, (d) depressurizing the mold, (f) and (g) pelletized sample (source: adapted according to [Ene et al., 2019a, b, c])

Hazardous waste samples resulting from galvanizing processes (Figure 2.13) and pickling of metal parts (Figure 2.14) were dried in an oven at a temperature of 105^0 C for 24 hours, mortared and sieved to a grain size of 0.01 mm, then added into capsules covered with a Mylar foil. This preparation operation was performed to implement the ED-XRF analysis. The identical preparation procedure for the waste containing mercury (point 3) was used to implement the IBA analysis. [Sloată and Ene, 2018c], [Ene and, 2021b].

The ten samples of sand heavily contaminated with arsenic, represented in figure 2.15, were dried in a controlled environment for seven days where the temperature was 23^0 C and the humidity was 40%. After drying, the samples were ground and sieved to obtain a grain size of 0.01 mm. Finally, ten capsules covered with Mylar foil were formed to perform ED-XRF analysis. Applying the IBA analysis, the preparation of sand samples was carried out similar to the previous samples [Ene and Sloată, 2020].

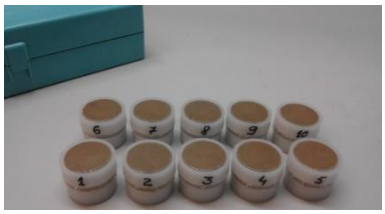


Figure 2.13 Preparation and encapsulation of solid waste samples resulting from galvanizing processes of metal parts (source: adapted according to [Sloată and Ene, 2018c, d])

Figure 2.14. Preparation and encapsulation of solid waste samples resulting from pickling processes of metal parts (source: adapted according to [Ene et al., 2021b])

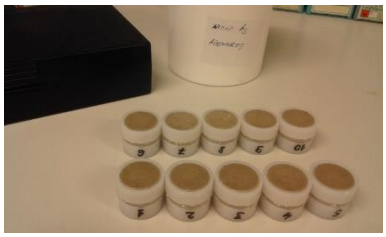


Figure 2.15. Preparation and encapsulation of sand waste samples contaminated with arsenic (source: adapted according to [Ene and Sloată, 2020])

The soil samples were separated from foreign bodies (stones, roots, leaves, stems, etc.), ground, passed through a 0.125 mm sieve and dried in an oven at 50^0 C for 48 for hours. Finally, the samples were stored in moisture- and light-free polyethylene bags and divided into subsamples for further investigation in INPOLDE partner laboratories [Sloată and, 2022a, d].

For the application of the ED-XRF analytical technique, the soil samples were packed in ten specific capsules covered with Mylar foil. This sample preparation operation is represented in figure 2.16 (a) and (b).

(a)

(b)

Figure 2.16. Preparation and encapsulation of soil samples taken from around the former chemical plant in Brăila county, in order to carry out ED-XRF analysis

The ten soil samples taken from around the Liberty metallurgical complex from Galați, from different depths: 0 cm, 5 cm and 30 cm, were dried at 105^0 C for 24 hours. After drying, the samples were mortared and sieved to a grain size of 0.01 mm. For the application of X-ray spectrometric analysis, the prepared samples were added in specific capsules covered with a Mylar foil, as shown in Figure 2.17 (a) and (b).

(a)

(b)

Figure 2.17. Preparation and encapsulation of soil samples taken from around the Liberty Galați metallurgical complex, in order to carry out ED-XRF analysis (source: [Ene et al., 2017a, b], [Ene et al., 2018b, c])

The preparation of the soil samples, subjected to INAA analysis, was carried out at the Frank Laboratory for Neutron Physics (JINR), Dubna, Russian Federation. Samples with a mass of 100 or 200 mg were wrapped in aluminum foil, then placed in small polypropylene

bags. These formed packages are placed in aluminum and Teflon containers to provide protection against the temperature inside the reactor. This procedure is used for short or long term irradiation. The Teflon container used for sample packaging and its handling mechanism are shown in figure 2.18 [Kogo et al., 2009], [Frontasyeva, 2011], [Badawy et al., 2015].

Figure 2.18. The teflon container used for sample packaging and its handling mechanism (source: adapted according to [Pavlov et al., 2016])

The samples taken from around the metallurgical complex from Galați, with the aim of being characterized from a radionuclide point of view, were packed in polypropylene bags and processed in the INPOLDE laboratory. These samples were separated from foreign bodies, dried at a temperature of 110^0 C for 48 hours, mortared and sieved until reaching a grain size of 0.01 mm. The sieved soil samples were packed in polypropylene bags, then packed in polyethylene sarpagan containers (D = 7.2 cm and h = 2.5 cm). The sarpagan type containers were sealed with adhesive tape and are represented in figure 2.19. Soil samples were stored in sarpagans for 30 days to establish the radioactive equilibrium between Ra^{226} and its radioactive gaseous descendant ^{222}Rn (half-life = 3.8 days) [Ene et al., 2018a], [Ene et al., 2020a], [Ene et al., 2023a, b].

Figure 2.19. Packaging in sarpagan type containers of soil samples taken from around the Liberty Galați metallurgical complex, in order to carry out the GRS analysis

During the preparation of samples of solid industrial waste containing hazardous chemical elements and samples of unknown radioactive materials, means of protection of bodily integrity and health against chemical and radiochemical agents were used. Certain frames captured during the preparation of the aforementioned samples are represented in figure 2.20 (a), (b) and (c), respectively in figure 2.21 (a), (b) and (c).

(a)

(b)

(c)

Figure 2.20. The equipping mode of the operating personnel with means of protection against chemical agents

(a) (b) (c)

Figure 2.21. The equipping mode of the operating personnel with means of protection against radiochemical agents (source: adapted according to [Sloată and Ene, 2021a, b])

2.2. Application of efficient spectrometric methods for sample characterization (ED-XRF, AAS, ICP-MS, PIXE, PIGE, INAA și GRS)

Application of the spectrometric method ED-XRF

The energy dispersive X-ray fluorescence (ED-XRF) spectrometric technique was applied using two portable spectrometers. The first spectrometer, the Oxford Instruments type X-MET 500, was used to characterize solid waste containing mercury and mercury salts in raw form. The X-MET 5000 spectrometer is represented in figure 2.22. The second spectrometer, the Genius 5000 XRF, manufactured by Skyray Instruments Inc. (Figure 2.23), was used to irradiate samples of industrial hazardous waste and industrial soils. These samples were irradiated for 60 and 120 seconds.

Figure 2.22. ED-XRF spectrometer, X-MET 5000, Oxford Instruments (source: adapted according to [Ene and Sloată, 2017], [Sloată and Ene, 2017a, b])

Figure 2.23. ED-XRF spectrometer, Genius 5000, Sky Instruments

Application of the spectrometric method AAS

The atomic absorption spectrometric method (AAS) was applied to determine the concentrations of toxic elements in soil samples taken around the Brăila plant. The determination of the concentrations of toxic elements was carried out based on the calibration curves made, measuring several standard samples prepared before the analyses.

The concentrations of toxic elements, from the mineralized soil sample, were determined by interpolation from the calibration curve [Ene, 2015a]. Two atomic absorption spectrometers

were used, one located in the laboratory of the INPOLDE research center, Galați, Romania (Figure 2.24), and the other in the laboratory of the Institute of Geology and Seismology (IGS), Chișinău, Republic of Moldova (Figure 2.25).

Figure 2.24. Analytik Jena AAS ContrAA 700 spectrometer from the INPOLDE laboratory, Galați, Romania

Figure 2.25. AAS AAnalyst800 spectrometer from the IGS laboratory, Chișinău, Republic of Moldova (source: adapted according to [Ene et al., 2019c])

Application of the spectrometric method ICP-MS

The ICP-MS spectrometric technique was implemented to determine some elements that are not detected by the AAS technique. The same soil samples taken from around the plant in Brăila county were analyzed, and calibration curves were made using five standard solutions of interest to which certain blank solutions were additionally added. In figure 2.26. the ICP-MS spectrometer from the equipment of the IHU laboratory, Kavala, Greece is represented.

Figure 2.26. Agilent 7700X ICP-MS ICP-MS spectrometer from IHU laboratory, Kavala, Greece (source: adapted according to [Spanos et al., 2021], [Ene et al., 2019c])

Application of the spectrometric methods PIXE and PIGE

IBA analytical techniques (PIXE, PIGE) were put into practice using the Tandem particle accelerator with a working voltage of three million volts, from IFIN-HH, Măgurele, Ilfov, Romania, and its main components are represented in figure 2.27 (a), (b), (c) and (d) [Ene et al., 2019a, b, c].

(a) (b) (c) (d)

Figure 2.27. Main components of the Tandem 3 MV accelerator: (a) particle source, (b) Tandetron accelerator, (c) electromagnetic lines for particle transport and (d) IBA reaction chamber (source: adapted according to [Ene et al., 2019a, b, c], [Ene et al., 2020c])

Application of the spectrometric method INAA

The instrumental analytical neutron activation method (INAA) was implemented using the neutron irradiation channels of the IBR-2 research nuclear reactor at the Frank Laboratory for Neutron Physics, JINR, Dubna, Russian Federation (Figure 2.28).

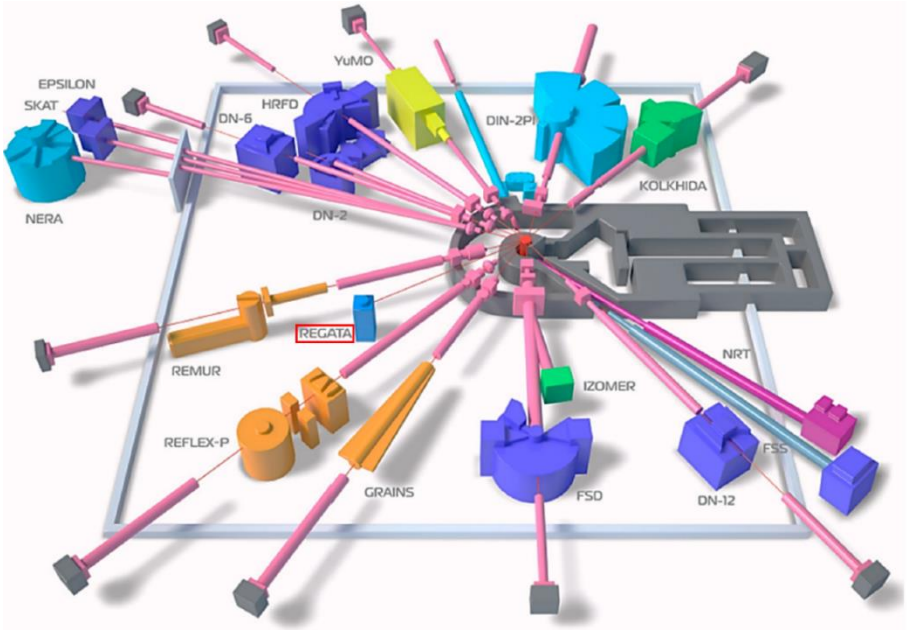


Figure 2.28. Complex structure of the IBR-2 research nuclear reactor and configuration for neutron irradiation of environmental and biological samples - REGATA, Dubna, Russian Federation (source: adapted according to [Frontasyeva, 2005], [Shvetsov, 2017], [Ene et al., 2017c], [Ene et al., 2018b, c], [Ene et al., 2019c])

Application of the spectrometric method GRS

The low-background high-resolution gamma spectrometry technique was put into practice at the GamaSpec laboratory within IFIN-HH, Măgurele, Ilfov, Romania. The purpose of applying this spectrometric technique was to determine the concentration of natural and artificial radionuclides in industrial soil samples. In the composition of the technological assembly of the gamma spectrometer, represented in figure 2.29 (a), (b), (c) and (d), there is a semiconductor detector made of high purity germanium for the gamma radiation detection.

(a) (b) (c) (d)

Figure 2.29. The technological assembly of the gamma spectrometer within the GamaSpec laboratory, IFIN-HH, Măgurele, Ilfov, Romania: (a) the lead tower, (b) the positioning of the gamma radiation detector inside the lead tower, (c) the positioning of the sample to be measured on the surface the detector and (d) the electronic equipment required for data acquisition (source: adapted according to [Ene et al., 2018a], [Ene et al., 2019c], [Ene et al., 2020a])

Complementary to the low-background gamma ray spectrometry, the in-situ gamma ray spectrometry technique was applied. This spectrometric method was applied for the radionuclide characterization of samples of radioactive materials and waste identified in the premises of the SetCar S.A. chemical platform, Brăila.

The portable spectrometer belongs to the Nuclear Research Institute from Mioveni, Argeș, România (RATEN ICN) and is shown in figure 2.30. (a) and (b).

(a) (b)

Figure 2.30. Canberra Inspector 1000 portable gamma ray spectrometer – property of RATEN ICN Pitesti: (a) Canberra Inspector 1000 spectrometer and (b) IPROL - 1 probe (source: adapted according to [Sloată and Ene, 2021a, b])

Application of radiometric methods

Throughout the application of the radioactive materials and waste inventory procedures, the gamma dose rate was measured. This radiation fund was measured to ensure the radiological protection of the personnel involved in the inventory activity. Another reason why the gamma radiation background was measured was to establish a proper work program with the radioactive sources. The gamma radiation background measurements were performed using the CoMo 170 radiometric device manufactured by Nuvia Instruments Gmbh, Germany, represented in figure 2.31.

Figure 2.31. Nuvia Instruments CoMo 170 radiometric device – property of SetCar S.A. Brăila

The measurements regarding the suspected contamination were carried out using the CoMo 170 – Nuvia Instruments contaminometer, represented in figure 2.32.

Figure 2.32. Contaminometer CoMo 170 Nuvia Instruments – property of SetCar S.A. Brăila (source: adapted according to [Sloată and Ene, 2021a, b])

Application of the chromatographic method GC-EDC

The gas chromatographic technique was implemented using an Agilent GC-ECD device, model 7890A, property of SetCar S.A. Braila (figure 2.33). The Agilent 7890A chromatograph has an electron capture detector, which contains an artificial radioactive micro source of ^{63}Ni with a nuclear activity of 15 mCi [Sloată et al., 2017a], [Sloată and Ene, 2019b], [Sloată et al., 2022b, c].

Figure 2.33. Gas Chromatograph Agilent 7890A – SetCar S.A. Brăila

III. OWN EXPERIMENTAL RESULTS ON THE CHARACTERIZATION OF HAZARDOUS INDUSTRIAL WASTE AND SOILS

3.1. Characterization of the hazardous waste generated following the decommissioning of some installations in the chemical industry

3.1.1. Characterization of the hazardous waste generated following the decommissioning of an industrial electrolysis facility

On the national level, it was executed by the company SetCar S.A. from Brăila, a decommissioning work of an electrolysis installation that uses elemental mercury as a cathode. This electrolysis facility was located inside the former chemical plant in Dolj County, România. Following the decommissioning of the electrolysis plant, it was also necessary to decontaminate the area where it was located because the soil was heavily contaminated with mercury [Sloată and Ene, 2017a], [Sloată et al., 2023a].

Figure 3.1 (a) and (b) show some images from the decommissioning of the electrolysis plant and the decontamination of the work area.

(a) (b)

Figure 3.1. Images during decommissioning of the electrolysis plant and decontamination of the work area: (a) decommissioned electrolysis plant and (b) decontamination of the work area (source: adapted according to [Sloată and Ene, 2017a, b])

After the completion of the decommissioning and decontamination works, approximately one hundred tons of hazardous waste with a high mercury content resulted. For the rapid determination of the contamination degree of the waste contaminated with elemental mercury, a number of ten samples were taken, which were packed in the raw state in Mylar foil and subjected to ED-XRF analysis. The results of the preliminary analysis applied to the ten unprocessed samples of waste containing mercury are presented in table 3.1.

After applying the aforementioned ED-XRF analysis, the ten waste samples were prepared and subjected to ED-XRF analysis again. The samples were irradiated for 60 and 120 seconds and the results can be found in table 3.2. Figure 3.2 shows the spectrum of energies obtained after irradiation for 60 s of sample HG1.

Table 3.1. Mercury concentrations obtained from the analysis, by applying the ED-XRF method, of waste samples containing mercury in raw form
(source: processed according to [Sloată and Ene, 2017a, b])

Sample No.	1	2	3	4	5	6	7	8	9	10
c [ppm]	11154	11163	12627	12271	10624	10784	12078	12309	11384	12150

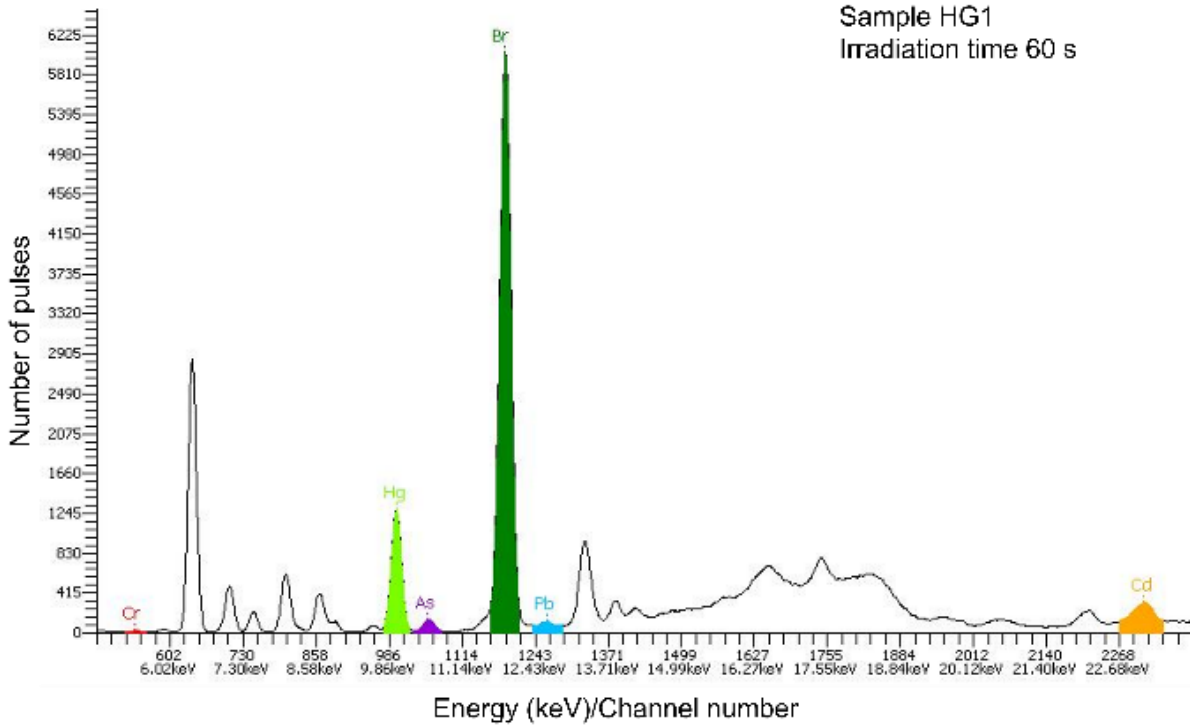


Figure 3.2. The energy spectrum obtained after irradiation for 60 s of sample HG1.

The concentration values of the chemical elements of interest determined varied as follows:

The highest **chromium** concentration value (296.81ppm) was identified in sample 10 (120 s), and the lowest concentration value (93.94 ppm) in sample 4 (120 s). The average value of all chromium concentrations from the 10 samples analyzed at different times was calculated, and it is 123.01 ppm;

Copper recorded the highest concentration value (3736.73 ppm) in sample 8 (60 s), and the lowest concentration value (542.55 ppm) in sample 4 (120 s). The average value calculated for all copper concentrations obtained from the analysis of the ten samples at different times is 2323.33 ppm;

Mercury recorded the lowest concentration value (543.70 ppm) in sample 7 (120 s), the highest concentration value (1760.96 ppm) in sample 3 (60 s), and the average value calculated for all concentrations of mercury obtained from the analysis of the ten samples at different times is 1171.97 ppm;

It is noteworthy that the average value of mercury concentration determined from the raw waste samples is 10 times higher than the average mercury concentration determined from the prepared waste samples. This may be caused by the fact that mercury-containing waste samples (raw and prepared) differ greatly in grain size and homogeneity. The analysis of raw samples in-situ is quick and advantageous for "screening" type investigations, while laboratory analyzes of processed samples have greater precision, matrix effects being minimized.

Comparing the results obtained by irradiating for 60 seconds and 120 seconds the 10 waste samples with mercury content resulted in the optimization of the analysis errors related to the concentrations of the identified elements, by using a longer irradiation time. The degrees of error optimization for all the concentrations of the analyzed chemical elements (Cr, Cu and Hg) varied as follows: Cr - between 1.33 and 1.51%, Cu - between 0.13 and 1.44%, and Hg - between 1.37 and 3.7% [Sloată et al., 2023a].

The ED-XRF analytical technique applied for the identification of the previously mentioned chemical elements was complemented with the accelerated ion beam analytical

techniques (IBA) PIXE and PIGE for the identification of other elements of interest. Element F (9656±337.96 ppm) was identified following the application of PIGE analysis, and element P (11680±151.84 ppm) was identified following the application of PIXE analysis [Sloată et al., 2023a, b].

The average concentrations calculated for eight elements determined by the ED-XRF analytical method and the concentrations of three elements determined by the IBA (PIXE-PIGE) methods, were compared with the national regulations regarding the acceptance parameters of hazardous waste for disposal on dedicated landfilds.

At the same time, all the selected elements were compared and other elements identified in research from the specialized literature. Table 3.2 systematically shows the comparison between the values of the element concentrations determined in the waste samples with mercury content from this research and the element concentrations from the Romanian standard, respectively from other similar researches.

Table 3.2. The comparison between the element concentration values determined in the waste samples containing mercury from this research and the element concentration values from the Romanian regulations, respectively other similar researches

Chemical element	Waste code	Parameter [Ordinul 95, 2005]		Waste HG [Bloom et al., 2003]	Waste HG [Zagury et al., 2009]
	HG	*LS2	**LS10	HG_1	HG_2
	c [ppm]	s. u. [ppm]	s. u. [ppm]	c [ppm]	c [ppm]
F	9656	200	500	-	-
Cr	123,01	25	70	-	-
Cu	2323,33	50	100	-	-
Hg	1171,97	0,5	2	73300	11500

*LS2 - L/S = 2 l/kg
**LS10 - L/S = 10 l/kg

From the systematized comparison (table 3.4) it can be seen that the value of the concentrations of the elements in this research exceeded or not the value of the concentrations of the referenced elements as follows:

The **fluorine** concentration is about 50 times higher than the value of parameter LS2 and almost 20 times higher than the value of parameter LS10;

The **chromium** concentration is 5 times higher compared to the LS2 parameter value and almost 2 times higher compared to the LS10 parameter value;

The average value of the **copper** concentration is 46 times higher than the value of the LS2 parameter, respectively 23 times higher than the value of the LS10 parameter;

Mercury, the concentration of this chemical element of great interest is 2340 times higher than the LS2 parameter value and 580 times higher than the LS10 parameter value.

3.1.2. Characterization of the hazardous waste generated following the decommissioning of an industrial distillation plant

In Romania, a work was carried out to dismantle some industrial distillation columns, which resulted in significant amounts of hazardous waste containing arsenic, specified in table 3.3. The dismantling work was accompanied by a decontamination work on a total area of 800 m^2 inside the plant.

This work was executed by SetCar S.A. Brăila in the perimeter of the chemical plant in Mureș County, Romania. Certain frames during the execution of the works can be seen in figure 3.3 (a), (b), (c), (d), (e), (f) and (g) [Sloată and Ene, 2018b], [Ene and Sloată, 2020].

Table 3.3. Quantities of waste containing arsenic generated following the dismantling of the distillation plant and the decontamination of the work area (source: processed according to [Sloată and Ene, 2018b], [Ene and Sloată, 2020])

Hazardous waste name	The quantity [kg]
metallic and non-metallic waste contaminated with hazardous substances	81000
waste containing arsenic	59000
refractory waste containing arsenic	29000
waste insulating material	9000
liquid waste	10000

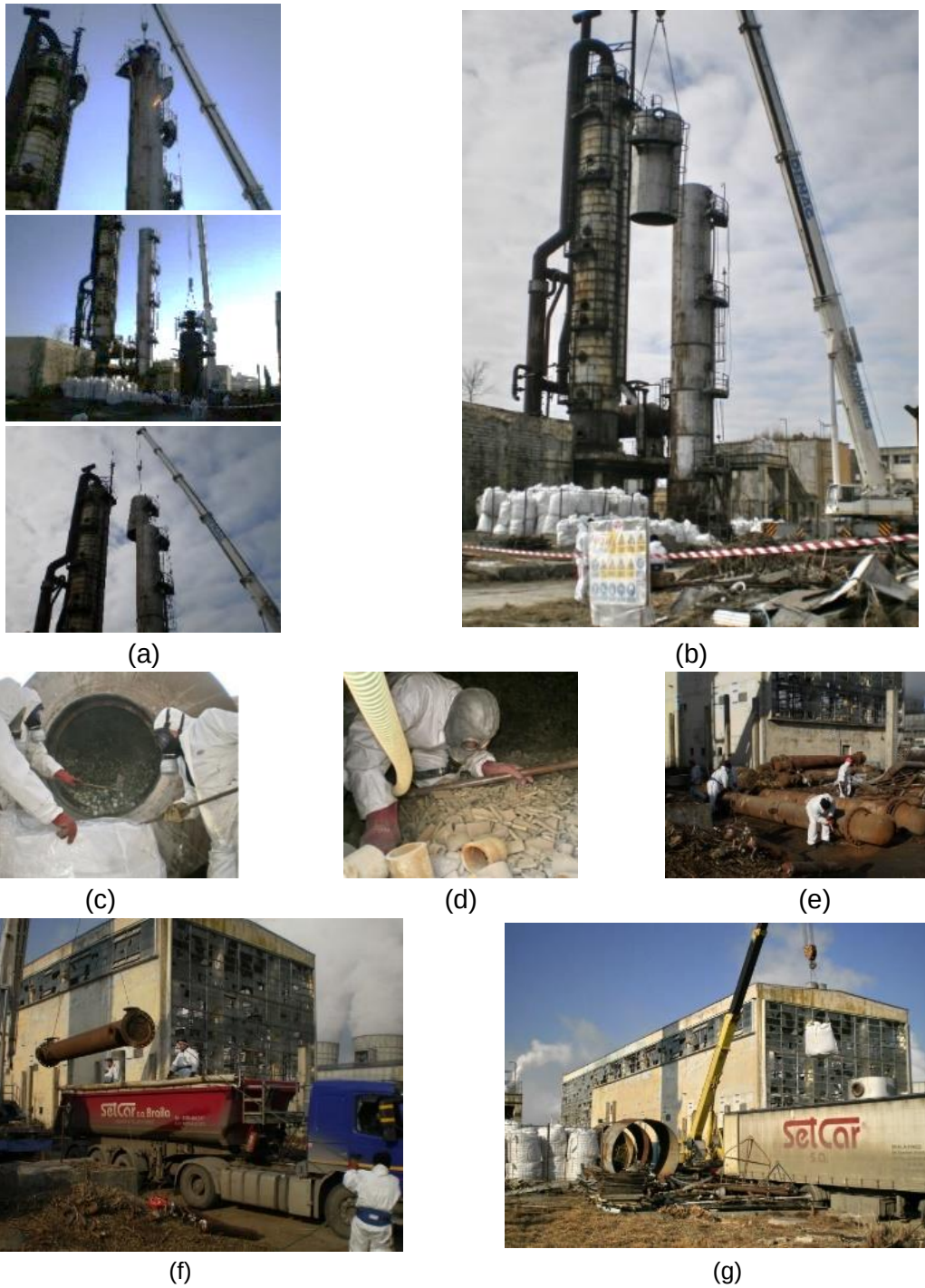


Figure 3.3. Frames during the works performed on the platform of the chemical plant in Mureș County, Romania: (a) and (b) dismantling of industrial distillation columns, (c), (d) and (e) taking over solid waste containing arsenic, (f) and (g) ensuring the transport of waste under optimal conditions (source: adapted according to [Sloată and Ene, 2018b])

After taking and preparing the contaminated sand samples, ED-XRF, PIXE and PIGE analytical techniques were applied to determine the concentrations of toxic elements [Sloată et al., 2023b]. Using the ED-XRF technique, the samples were irradiated for 60 and 120 seconds respectively, and the results are presented in table 3.4. (a) and (b). Figure 3.4 shows the spectrum of energies obtained after irradiation for 60 s of sample AS1.

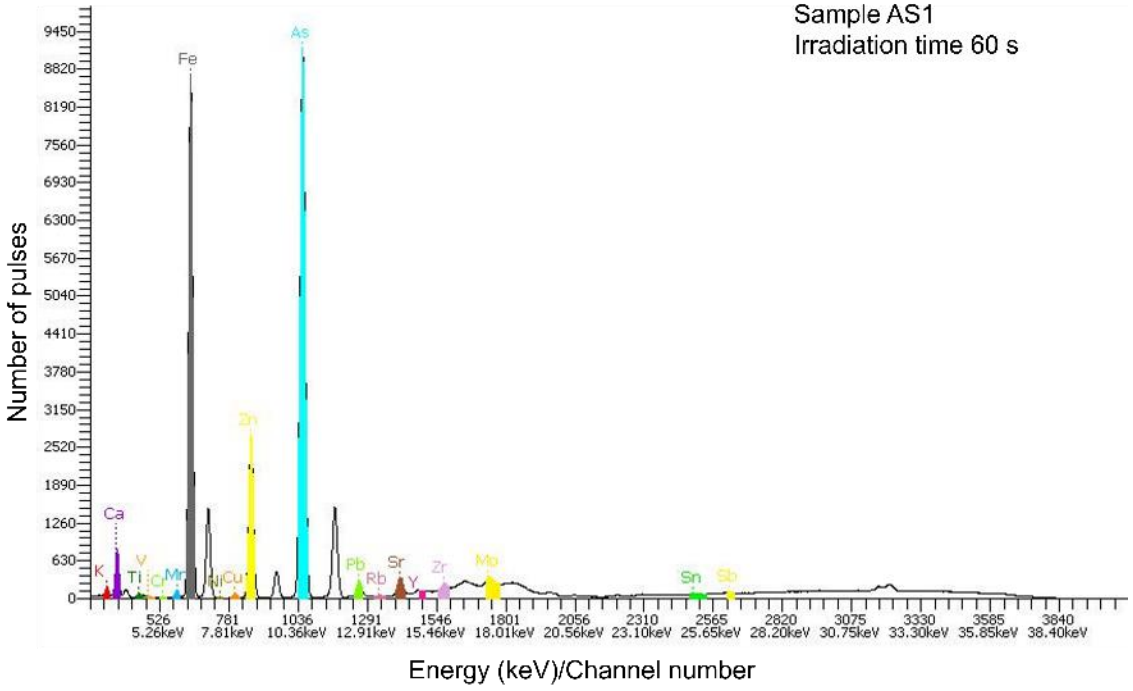


Figure 3.4. The energy spectrum obtained after 60 s irradiation of sample AS1 (source: adapted according to [Sloată and Ene, 2018b], [Ene and Sloată, 2020])

Table 3.4. Determination of chemical elements of interest from waste samples containing arsenic (Waste Code - AS) by applying the ED-XRF analytical method: (a) determination of Cd, Cr, Cu, Ni and Zn concentrations, (b) determination of As, Mo, Sb and Pb concentrations (source: processed according to [Ene and Sloată, 2020], [Sloată and Ene, 2018b])

(a) determination of Cd, Cr, Cu, Ni and Zn concentrations

Irradiation time [s]	Sample No.	Chemical element									
		Cd		Cr		Cu		Ni		Zn	
		c [ppm]	±e [ppm]	c [ppm]	±e [ppm]	c [ppm]	±e [ppm]	c [ppm]	±e [ppm]	c [ppm]	±e [ppm]
60	1	42,23	1,12	239,20	12,55	447,29	11,02	107,87	5,66	12300,37	54,98
	2	55,65	1,41	252,41	13,23	541,62	12,46	82,62	4,59	14887,57	61,33
	3	44,54	1,16	228,18	11,76	360,03	9,44	140,09	6,79	11967,36	52,60
	4	42,53	1,14	359,13	17,00	528,74	12,29	150,97	7,52	13097,49	57,48
	5	46,70	1,18	167,89	9,32	425,29	10,41	79,49	4,26	11278,73	51,19
	6	14,33	0,42	240,54	12,47	405,52	10,30	128,61	6,47	11969,83	53,66
	7	37,61	1,02	222,84	11,81	379,60	9,94	106,98	5,58	11566,16	52,85
	8	25,82	0,74	299,23	14,76	480,05	11,48	120,67	6,21	13096,00	56,72
	9	6,75	0,21	207,15	11,34	360,05	9,79	141	7,08	10550,43	51,21
	10	31,24	0,86	657,68	24,61	410,31	10,33	133,97	6,66	11818,07	53,10
120	1	33,72	0,66	255,53	9,40	481,61	8,21	99,81	3,79	12225,88	39,11
	2	33,86	0,68	298,98	10,77	469,53	8,27	122,73	4,60	14914,71	44,23
	3	43,54	0,81	198,86	7,61	372,11	6,90	95,46	3,56	11787,92	37,47
	4	45,59	0,87	329,76	11,26	446,91	7,84	167,15	5,72	12605,86	39,63
	5	12,91	0,27	187,62	7,26	419,94	7,39	69,14	2,70	10643,64	35,54
	6	22,97	0,47	212,64	8,10	363,52	6,89	109,12	4,03	12909,35	39,69
	7	41,00	0,78	217,69	8,34	403,89	7,40	108,27	4,05	11276,69	37,49
	8	11,45	0,25	236,89	8,94	498,63	8,42	113,79	4,25	13090,90	40,69
	9	38,40	0,76	229,78	8,62	365,18	6,94	101,42	3,81	10625,00	36,14
	10	17,45	0,37	601,41	16,73	382,58	7,13	145,96	5,13	12699,61	39,60

(b) determination of As, Mo, Sb and Pb concentrations

Irradiation time [s]	Sample No.	Chemical element							
		As		Mo		Sb		Pb	
		c [ppm]	±e [ppm]	c [ppm]	±e [ppm]	c [ppm]	±e [ppm]	c [ppm]	±e [ppm]
60	1	13108,48	34,50	10,32	0,27	107,36	11,40	912,07	11,50
	2	13056,10	34,89	9,83	0,29	0,76	0,23	867,56	11,37
	3	12446,26	32,61	10,29	0,27	21,31	4,05	875,19	10,93
	4	12901,17	34,67	7,59	0,25	197,58	16,12	871,82	11,40
	5	11373,48	31,25	10,16	0,27	2,44	0,68	738,21	10,09
	6	13456,71	34,60	10,39	0,27	0	0	824,50	10,83
	7	11300,19	31,76	7,05	0,24	141,28	13,16	785,19	10,60
	8	13723,55	35,30	10,34	0,27	137,43	13,07	860,97	11,18
	9	11574,93	32,62	9,89	0,28	130,32	12,78	775,95	0
	10	12599,09	33,34	10	0,28	254,96	17,95	794,90	10,60
120	1	12727,98	24,26	9,04	0,19	145,00	9,61	937,96	8,32
	2	12810,64	24,90	9,96	0,21	103,78	8,17	868,87	8,20
	3	12392,48	23,36	10	0,20	93,19	7,33	803,86	7,53
	4	12549,78	24,03	10,50	0,19	43,51	4,77	819,31	7,77
	5	11563,08	22,53	10,33	0,19	26,29	3,35	767,34	7,35
	6	13049,71	24,26	10,83	0,19	204,70	11,42	806,89	7,63
	7	11630,38	23,15	5,48	0,15	50,96	5,26	806,14	7,71
	8	13799,55	25,40	10,43	0,19	94,38	7,61	843,74	7,94
	9	11789,14	23,15	10,23	0,20	103,91	7,92	779,25	7,54
	10	12529,47	23,91	10,16	0,20	141,55	9,42	868,26	7,96

Using the PIGE analytical technique, the following chemical elements were determined: Na (41740±7050 ppm) and Al (2820±33600 ppm). Applying the PIXE analytical technique it was possible to determine the following chemical elements: Si (128760±643.8 ppm), Ti (3760±105.28 ppm) and Fe (94880±474.4 ppm)

After the implementation of the irradiation of the ten samples of waste contaminated with arsenic, for 60 and 120 seconds, the optimization of the errors was obtained for the concentrations of the chemical elements identified in the waste containing arsenic: Ni, Zn and As. The degrees of error optimization for the previously mentioned elements varied as follows: Ni - between 1.3 and 1.48%, Zn - between 1.36 and 1.46%, respectively As - between 1.37 and 1, 43%.

Nine chemical elements and their average concentrations determined by the ED-XRF analytical method and three other chemical elements determined by the PIXE and PIGE analytical methods were compared to the concentration values specified in the Romanian standard and in other research. The Romanian regulations refer to the acceptance parameters for the final disposal of hazardous waste in dedicated landfilds. The systematized comparison made between the element concentration values determined in this research, the concentration values specified in the Romanian regulations and the concentration values determined in other research is presented in table 3.5.

Table 3.5. The comparison between the values of the element concentrations determined in the waste samples waste containing arsenic from this research and the element concentration values from the Romanian normative, respectively another research

Chemical element	Waste code	Parameter [Ordinul 95, 2005]		Waste AS [Zhang et al., 2023]
	AS	*LS2	**LS10	AS_1
	c [ppm]	s. u. [ppm]	s. u. [ppm]	c [ppm]
Cr	282,17	25	70	-
Ni	116,26	20	40	-
Cu	427,12	50	100	1376
Zn	12265,58	90	200	2043
As	12519,11	6	25	17407
Mo	9,64	20	30	-
Cd	32,41	3	5	570
Sb	100,04	2	5	-
Pb	830,40	25	50	-

*LS2 - L/S = 2 l/kg

**LS10 - L/S = 10 l/kg

Systematized comparison from table 3.8. demonstrates that the vast majority of elements determined in this research have concentration values that exceed the comparative values as follows:

Chromium is 11 times more concentrated than the LS2 parameter value and 4 times more concentrated than the LS10 parameter value;

Nickel has a concentration almost 6 times higher than the LS2 parameter value and almost 3 times higher than the LS10 parameter value;

The **copper** concentration value is approximately 9 times higher than the LS2 parameter value, 4 times higher than the LS10 parameter value, but is 3 times lower than the value obtained in the AS1 sample;

Zinc registers a concentration value 136 times higher than the LS2 parameter value and 61 times higher than the LS10 parameter value. Compared to the value obtained in AS1, it is 6 times higher;

Arsenic, the concentration of this element of interest is much higher than the LS2 parameter value (2086 times higher), and 500 times higher than the LS10 parameter value. Compared to the value identified in the AS1 sample, it has a concentration approximately 40% lower;

Molybdenum has a concentration 50% lower than the LS2 parameter value;

Cadmium is about 11 times more concentrated than the LS2 parameter value and about 7 times more concentrated than the LS10 parameter value. On the other hand, the cadmium concentration in the AS1 sample is approximately 18 times higher than the cadmium in the AS sample;

Antimony has a concentration 50 times higher than the value of the LS2 parameter and 20 times higher than the value of the LS10 parameter;

Lead is 33 times more concentrated than the LS2 parameter value and about 17 times more concentrated than the LS10 parameter value.

3.2. Characterization of hazardous industrial waste resulting from the production activity of some economic operators in Romania

3.2.1. Characterization of hazardous waste resulting from the electrical and electronic equipment manufacturing industry

The galvanizing process is based on chemical and electrochemical methods and is used to obtain new properties, mainly anticorrosive, of metallic and non-metallic surfaces [Wang ș.a., 2023].

In Romania, industrial galvanizing processes are applied by a private company from Timiș County. The field of activity of this company is represented by the production of electrical and electronic equipment. The management of solid waste resulting from galvanizing processes is ensured by the company SetCar S.A. from Brăila [Sloată and Ene, 2018c, d].

The galvanizing waste samples were taken from inside the temporary hazardous waste storage facilities, located on the SetCar S.A. chemical platform.

After taking and preparing the samples, they were analyzed using ED-XRF and PIGE analytical techniques. The irradiation of the samples with the ED-XRF spectrometer was carried out in two stages in which they were analyzed for 60 and 120 seconds, and the results are found in table 3.6 (a) and (b). The energy spectrum resulting from the irradiation of the GV1 sample for 60 s is presented in figure 3.5.

The following chemical elements and their concentrations were determined by the PIGE nuclear analytical method: Al (710±91 ppm) and Si (350±12.8 ppm) [Sloată ș.a., 2023b].

Table 3.6. Determination of chemical elements of interest from galvanizing waste samples (Waste Code - GV) by applying the ED-XRF analytical method: (a) determination of Cr, Ni, Cu, Zn and Pb concentrations, (b) determination of Mo, Fe, Sb, As concentrations (source: processed according to [Sloată and Ene, 2018c, d])

(a) determination of Cr, Ni, Cu, Zn and Pb concentrations

Irradiation time [s]	Sample No.	Chemical element									
		Cr		Ni		Cu		Zn		Pb	
		c [ppm]	±e [ppm]	c [ppm]	±e [ppm]	c [ppm]	±e [ppm]	c [ppm]	±e [ppm]	c [ppm]	±e [ppm]
60	1	3260,49	70,25	71807,32	174,20	1147,86	21,01	1219,79	18,92	102,49	3,57
	2	3068,52	67	62593,60	160,21	1087,65	20,10	1345,45	19,63	92,25	3,26
	3	3189,07	68,72	63496,60	162,13	1015,31	19,46	1371,34	19,93	109,59	3,69
	4	3169,62	68,15	69803,18	169,14	1038,73	19,61	1194,18	18,42	76,49	2,81
	5	3123,92	67,91	59601,76	156,97	1035,63	19,66	1265,78	19,08	106,22	3,61
	6	3174,43	68,88	57799,38	155,45	1001,57	19,42	1319,44	19,62	114,52	3,81
	7	2983,50	65,91	57409,30	153,24	973,17	18,91	1326,12	19,46	108,82	3,65
	8	3099,75	66,93	53880,13	147,71	929,84	18,35	1380,25	19,78	86,59	3,12
	9	3239,49	68,32	53199,70	146,35	891,65	17,89	974,2	16,35	111,56	3,68
	10	3300,23	70,38	67328,17	167,91	1110,04	20,54	1517,31	21,15	97,75	3,44
120	1	3273	49,48	70310,85	121,16	1100,75	14,44	1215,12	13,27	104,42	2,54
	2	3017,03	46,92	62897,85	113,49	1104,21	14,32	1336,27	13,82	101,76	2,47
	3	3186,88	48,69	68233,49	119,13	1138,55	14,67	1353,71	14,03	106,77	2,57
	4	3248,04	48,93	62582,71	113,52	1040,13	13,91	1291,06	13,61	101,95	2,48
	5	3054,02	46,82	57187,40	107,30	976,45	13,29	1219,51	13,05	109,06	2,56
	6	3189,60	48,65	58761,75	110,43	1055,01	14,07	1337,17	13,92	110,08	2,62
	7	3169,87	48,38	60138,11	111,46	1061,15	14,08	1324,63	13,82	98,25	2,42
	8	3165,71	47,82	53504,50	103,98	951,59	13,13	1477,49	14,48	104,95	2,50
	9	3227,24	48,12	53187,24	103,28	937,49	12,97	1038,78	11,95	112,97	2,62
	10	3317,15	49,70	67337,88	118,25	1084,95	14,29	1520,37	14,91	101,12	2,48

(b) determination of Mo, Fe, Sb, As concentrations

Irradiation time [s]	Sample No.	Chemical element							
		Mo		Fe		Sb		As	
		c [ppm]	±e [ppm]	c [ppm]	±e [ppm]	c [ppm]	±e [ppm]	c [ppm]	±e [ppm]
60	1	6,03	0,24	414309,27	622,11	0	0	110,36	2,82
	2	8,09	0,28	418677,87	616,03	65,15	9,52	107,80	2,74
	3	7,85	0,28	427289,47	625,34	50,44	8,20	170,64	3,76
	4	7,61	0,27	401206,16	602,83	0	0	86,42	2,44
	5	7,95	0,28	425748,17	623,71	24,33	5,11	108,83	2,77
	6	5,16	0,22	433522,89	632,97	56,02	8,78	112,06	2,83
	7	9,98	0,31	427564,86	621,74	0	0	128,59	3,07
	8	9,10	0,29	452875,60	636,75	24,48	5,08	166,32	3,65
	9	6,95	0,26	459377,04	639,45	0	0	99,22	2,60
	10	7,20	0,27	430762,89	631,49	118,16	13,52	91,74	2,54
120	1	7,43	0,19	410169,59	435,09	0	0	101,58	1,90
	2	6,16	0,17	412671,13	432,18	0	0	112,99	1,99
	3	6,87	0,18	418092,80	438,42	0	0	175,95	2,72
	4	7,66	0,19	422513,41	438,52	56,82	6,22	104,70	1,91
	5	6,73	0,18	425470,07	435,14	32,02	4,29	110,25	1,94
	6	6,77	0,18	429380,26	443,82	16,54	2,75	102,41	1,90
	7	4,88	0,15	426420,76	441,27	0	0	117,04	2,04
	8	6,02	0,17	446105,89	446,43	0	0	167,88	2,60
	9	7,30	0,18	456994,54	450,13	30,41	4,13	94,42	1,79
	10	7,79	0,19	426611,58	442,54	14,35	2,47	93,42	1,81

As a result of the irradiation of the ten galvanizing waste samples, for 60 and 120 seconds, the optimization of the specific errors of the concentrations of the studied elements was obtained. The oscillation mode of the optimization degrees for all the studied elements is as follows: Cr - between 1.4 and 1.45%, Ni - between 0.01 and 1.46%, Cu - between 1.39 and 1.49%, Zn - between 1.4 and 1.46%, Mo - between 1.01 and 1.6%, Pb - between 1.36 and 1.51%, Sb - between 0 and 1.57%, As - between 1.36 and 1.55%, Fe - between 0.70 and 7.04%.

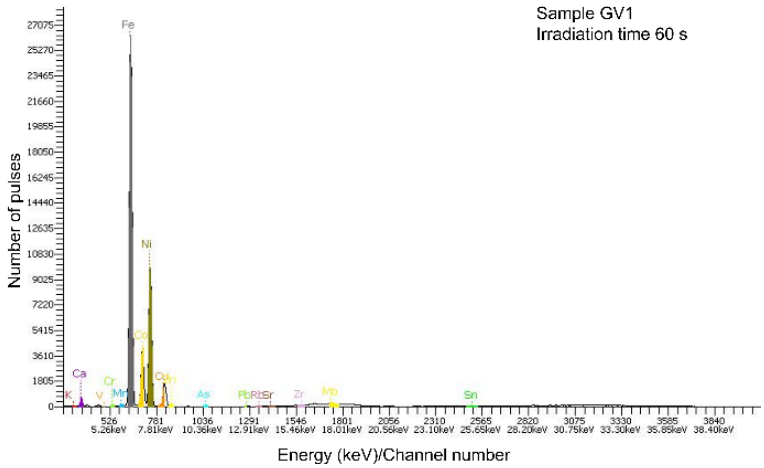


Figure 3.5. The energy spectrum resulting from the irradiation of the GV1 sample for 60 s (source: adapted according to [Sloată and Ene, 2018c, d])

The average values of the concentrations of the nine chemical elements determined by the ED-XRF method were put in parallel with the values of the concentrations of the elements specified in the Romanian regulations and in other similar researches.

The regulation refers to the conditions for accepting hazardous waste at special surface deposits. The parallel achieved regarding the values is reproduced in table 3.7, and from it the following observations can be made:

The concentration of **fluorine** is half of the LS2 parameter value;

Chromium has a concentration 126 times higher than the value of the parameter LS2, 45 times higher than the value of the parameter LS10, about 12 times higher than the value obtained in the GV1 sample, 8 times higher than the value obtained in sample GV2, 96 times higher than the value obtained in sample GV3, almost 92 times higher than the value obtained in sample GV4 and approximately 79 times higher than the value obtained in sample GV5;

Nickel is more than 3000 times more concentrated than the LS2 parameter value, more than 1500 times more concentrated than the LS10 parameter value and more than 2000 times more concentrated than the value identified in the GV2 sample. This element has a concentration 40 times higher than the value identified in the GV1 sample and more than 8 times higher than the value identified in the GV3 sample, respectively the value identified in the GV4 sample. Compared to the value identified in the GV5 sample, it is more than 9 times higher;

The average value of the **copper** concentration is 20 times higher than the value of parameter LS2 and 10 times higher than the value of parameter LS10. This is 12 times higher than the concentration identified in the GV2 sample. Instead, the copper concentration values identified in the GV3, GV4 and GV5 waste samples are more than 7 times higher than the copper value identified in the GV waste sample;

Zinc has a concentration about 15 times higher than the value of the parameter LS2 and a concentration more than 6 times higher than the value of the parameter LS10, respectively the concentration value of the GV1 sample. This element has a very high concentration compared to zinc concentrations in waste samples GV2, GV3, GV4 and GV5;

Arsenic is almost 20 times more concentrated than the LS2 value and almost 5 times the LS10 value. Compared to the value obtained from the GV3 sample, it is 16 times more concentrated, and compared to the values obtained from the GV4 and GV 5 samples, it is almost 19 times, respectively almost 16 times more concentrated;

Molybdenum does not record concentration values higher than the parameter values specified in the standard;

Antimony has a concentration value 12 times higher than the LS2 parameter value and 5 times higher than the LS10 parameter value;

The **iron** concentration value is clearly higher than the values identified in the GV1 and GV2 samples. This value is several thousand times higher than the referenced values;

The **silicon** concentration is more than 6 times higher than the value identified in the GV1 sample.

Table 3.7. The comparison between the element concentration values determined in the galvanizing waste samples from this research and the element concentration values from the Romanian regulations, respectively other researches

Chemical element	Waste code	Parameter [Ordinul 95, 2005]		Waste GV [Stojković et al., 2023]		Waste GV [Wang et al., 2023]		
	GV	*LS2	**LS10	***GV1	****GV2	GV3	GV4	GV5
	c [ppm]	s.u. [ppm]	s.u. [ppm]	c [ppm]	c [ppm]	c [ppm]	c [ppm]	c [ppm]
Cr	3172,88	25	70	266	380,4	32,9	34,53	40,21
Ni	61553,05	20	40	1518	29,4	7050	7250	6550
Cu	1034,09	50	100	-	85	8009	7609	8201
Zn	1301,40	90	200	203	64	50,36	60,23	52,49
As	118,13	6	25	-	-	7,3	6,3	7,6
Mo	7,18	20	30	-	-	-	-	-
Sb	24,44	2	5	-	-	-	-	-
Pb	102,88	25	50	18	-	86,5	76,8	92,5
Fe	3260	-	-	87,9	55,8	-	-	-
Si	350	-	-	55,5	-	-	-	-

*LS2 - L/S = 2 l/kg
**LS10 - L/S = 10 l/kg
***GV1 - alkaline galvanizing waste
****GV2 - acid galvanizing waste

3.2.2. Characterization of hazardous waste resulting from the maritime shipbuilding industry

The company SetCar S.A. from Brăila deals with the management of the solid waste generated as a result of the pickling processes carried out by an economic operator from Tulcea city, Romania, whose field of activity is the construction of maritime ships.

The ten pickling waste samples were taken from inside the temporary hazardous waste storage facilities owned by SetCar S.A. from Brăila. Following the sample collection and preparation steps, they were analyzed using IBA non-destructive multi-element nuclear methods (PIXE-PIGE). The energy spectrum is represented in figure 3.6.

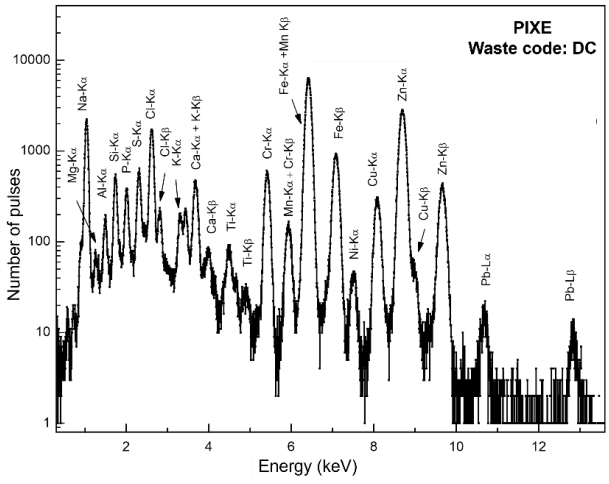


Figure 3.6. The energy spectrum obtained following the analysis of the pickling waste by the PIXE method (source: adapted according to [Ene et al., 2019a])

Using the PIGE analytical method, a number of two chemical elements and their concentrations were determined as follows: Na (43240±1683 ppm) and Al (3000±313 ppm). Using the PIXE method, four chemical elements and their concentrations were determined as follows: Ti (1090±54.83 ppm), Fe (161800±550.12 ppm), Zn (208000±1019.20 ppm) and Cr (9890 ±123.63 ppm).

As was done in the case of the previously studied waste, in this case five chemical elements and their concentrations were selected in order to compare them with the Romanian standard and with other concentrations of chemical elements determined in other similar researches. This comparison is shown in table 3.8.

Table 3.8. The comparison between the element concentration values determined in the pickling waste samples from this research and the element concentration values from the Romanian regulations, respectively other similar researches

Chemical element	Waste code: DC	Parameter [Ordinul 95, 2005]		Waste DC [Aciu et al., 2021]	Waste DC [Xu et al., 2022]					
		*LS2	**LS10	DC1	DC2	DC3	DC4	DC5	DC6	DC7
	c [ppm]	s.u. [ppm]	s.u. [ppm]	c [ppm]	c [ppm]	c [ppm]	c [ppm]	c [ppm]	c [ppm]	c [ppm]
Na	43240	-	-	945	-	-	-	-	-	-
Al	3000	-	-	333	-	-	-	-	-	-
Cr	9890	25	70	-	0,002	0,005	0,012	0,001	0,006	0,001
Zn	208000	90	200	16,51	174,3	54,9	3,6	167,3	23,6	34,5
Fe	161800	-	-	10	-	-	-	-	-	-

*LS2 - L/S = 2 l/kg
**LS10 - L/S = 10 l/kg

From the systematized comparison presented in table 3.8, the following aspects can be noted:

Sodium has a value 45 times higher than the value of the parameter DC1;

Aluminum is 9 times more concentrated than the value obtained from sample DC1;

The **chromium** concentration value is about 400 times higher than the LS2 parameter value and 141 times higher than the LS10 parameter value. Compared to the values obtained from samples DC2-7 it is of the order of hundreds of thousands and even millions of times higher;

Zinc is the most concentrated element determined in this research and has a value of the order of thousands even hundreds of thousands of times higher than all other values referenced in other works [Aciu et al., 2021], [Xu et al., 2022];

Iron is more than 16000 times more concentrated than the value identified in the DC1 sample.

3.3. Management of radioactive waste containing nuclear materials

The appearance of nuclear materials containing natural uranium and thorium inside the temporary storage facilities for hazardous waste owned by SetCar S.A. Brăila, are the result of managing expired laboratory chemicals for more than two decades. The nuclear materials were identified inside the temporary storage facilities following a physical inventory of all expired laboratory chemicals in stock [Sloată and Ene, 2021a, b].

The inventory of these hazardous wastes was put into practice with the aim of establishing the method of their final disposal according to their chemical nature. The results of the inventory are presented in table 3.9. Figure 3.7 (a), (b), (c) and (d) show part of the vials containing uranium and thorium salts, respectively vials containing unidentified radioactive substances [Sloată and Ene, 2021a, b].

Table 3.9. Results obtained from physical inventory of all expired laboratory chemicals in stock

Listed substance category	The quantity [kg]
Organic solvents	9030
Other organic substances	13700
Acids	5620
Alkalis	7833
Metallic mercury	7
Recoverable inorganic salts	1010
Other known organic and inorganic salts	16900
Unidentified substances	17000
Uranium and thorium salts	80
Unknown radioactive substances	20
Total	71200

(a) (b) (c) (d)

Figure 3.7. Identification of vials containing nuclear material and unidentified radioactive substances: (a) and (b) vials containing uranyl acetate, (c) and (d) vials containing thorium nitrate (source: adapted according to [Sloată and Ene, 2021a, b])

All these radioactive substances containing materials of nuclear interest (^{238}U and ^{232}Th) have a special management regime and need to be declared to the National Nuclear Regulatory Authority (CNCAN). The personnel operating and responsible for the management of these substances have been trained and qualified in the open sources of ionizing radiation field.

This radioactive waste was sorted, weighed, repackaged and specified in the provisional physical inventory [Sloată and Ene, 2021a]. Annex 1 shows frames during the repacking and weighing operations of all radioactive substances containing nuclear materials, respectively of radioactive waste.

After the implementation of all the previously described operations, the provisional physical inventory was drawn up. The physical inventory of nuclear material is designed according to the following specifications: unique nuclear safeguards code/batch, number of objects in the batch, open source type, manufacturer, chemical formula, nuclear material form, aggregation state, color, packaging type, material nuclear quantity and the nuclear element quantity.

The physical inventory of radioactive waste (solid materials contaminated with ^{238}U, ^{232}Th and their descendants) is designed respecting the following aspects: the packaging type in which the waste is found, the identifier and the packaging mass, the radioactive waste type,

the net mass of the waste, the gross mass of the package, respectively the type, mass and activity of the radionuclide contained in the radioactive waste.

In order to finalize the physical inventory of all radioactive waste, it was necessary to apply in-situ gamma spectrometry to identify the radionuclides inside the repackaged substances, including the identification of the radionuclides that contaminated the solid materials.

The entire amount of nuclear materials and radioactive waste were temporarily stored in a special storage facility arranged and approved by CNCAN. The temporary storage was carried out in compliance with the basic requirements of the legislation regarding the application of safeguards control in the nuclear field and physical protection.

Some of the basic requirements refer to the following aspects: specifying the operating personnel exposed to ionizing radiation who have access to the nuclear material storage, storing the materials in sheet metal files secured with a lock and seal, displaying the physical inventory inside the storage, equipping the storage with a fan for the evacuation of radon and thoron, equipping the storage with motion sensors and cameras, securing the access door with a lock, seal and alarm system in case of unauthorized opening. Annex 2 shows some images about how to store the nuclear materials, including radioactive waste, and the appearance of the temporary storage facility.

The operation of temporary storage of the radioactive materials was preceded by the operation of transporting them to an institution authorized in the nuclear field and recognized by CNCAN. All the services of receiving, transporting ADR class 7, final storage of nuclear materials and processing of radioactive waste were provided by the Nuclear Research Institute belonging to RATEN from Pitesti, Argeș, Romania. The services listed above were put into practice only by obtaining transfer/carriage authorizations from CNCAN. By transfer is understood the placing under safeguard control of all nuclear materials and radioactive waste from SetCar S.A. Brăila to RATEN ICN Pitesti and implicitly the change of owner of these radioactive materials. It is mentioned that the transport/transfer of nuclear materials and radioactive waste was accompanied by SetCar S.A. staff responsible for this activity. In annex 3 are presented some images from the time of the previously mentioned operation.

Gamma radiation spectrometry was applied for the radiological characterization of twenty-one vials containing radioactive substances and seven containers containing solid materials contaminated with ^{238}U, ^{232}Th and their descendants.

The presence of element ^{238}U was identified in nine vials analyzed. The concentration and activity of this element has the following values for each vial: vial 1 has a concentration of 49.1 g and an activity of 610.5 kBq; the content in vial 2 is 9.3 g, and the activity is 116 kBq; vial 3 has a concentration of 11.4 g and an activity of 142.3 kBq; the concentration of 2.4 g and the activity of 29.6 kBq is found in vial 4; a concentration of less than 1 gram and an activity of only 9 kBq to be found in vial 5; in vial 6 a concentration of 20 g and an activity of 233 kBq were identified; 55 grams and 701 kBq activity was identified in vial 7; vial 8 has a concentration of 31 g and an activity of 464 kBq; the last vial (9) contains 0.25 g and an activity of 3.34 kBq.

The concentration of element ^{232}Th was identified in twelve vials. This element recorded the following concentration and activity values as follows: the first vial has a concentration of 368.8 g and an activity of 1497.6 kBq; concentration of 290.5 g and activity of 1179.7 kBq was identified in the second vial; the third vial contains 384.5 g with an activity of 1561.3 kBq; in vial 4 there is a concentration of 507.5 g with an activity of 2060.9 kBq; a concentration of 490.3 g and an activity of 1991.2 were determined in vial 5; in vial 6, concentration and activity values of 430.1 g and 1746.8 kBq were determined; vial 7 contains 91.5 g with an activity of 371.7 kBq; the concentration value in vial 8 is 4.8 g and the activity value is 19.5 kBq; vial 9 contains 15.2 g with an activity of 61.6 kBq; in vial 10 is found a concentration of 9.1 g and an

activity of 36.8 kBq; the lowest values of concentrations (0.18 and 0.16) and activities (656 and 727) were obtained from vials 11 and 12.

All these determinations of ^{238}U and ^{232}Th concentrations established the classification of nuclear materials in the final physical inventory. The classification was preceded by the assignment of a unique nuclear safeguard code "BRSETCAR".

Regarding the seven containers, it can be said that the use of gamma-ray spectrometric analysis identified the presence of natural uranium and thorium as follows: in container B1, a concentration of 13.7 g with an activity of 170.5 kBq was identified;thorium concentration values (2.7; 4.1; 59.1; 10 and 1.2 g), respectively activity values (11.2; 16.8; 239.8; 40.8 5 kBq) have were registered by analyzing containers B2, B3, B4, B5 and B6; in container B7, the presence of element ^{238}U with a content of 3.7 g and an activity of 45.7 kBq was identified, including the presence of element ^{232}Th with a concentration of 1.59 g and an activity of 6470 kBq.

The project for the total management of nuclear materials and radioactive waste, identified and processed within the SetCar S.A. company, did not end after their transfer to RATEN ICN. This project was completed after the temporary storage for the radioactive materials was declared to be a regular storage and relieved of duties from nuclear field.

The certificate issued by CNCAN declaring the storage is relieved of duties from nuclear field was obtained following a radiological expertise.This radiological expertise proved that there were not ^{238}U and ^{232}Th contaminations inside and in the immediate vicinity of the storage.

The declaration of nuclear materials is strictly necessary to comply with international laws on nuclear safeguards field.

Besides the fact that the managed substances are nuclear materials of interest, they are chemicals of high toxicity and contain long-lived radionuclides like ^{238}U and ^{232}Th.

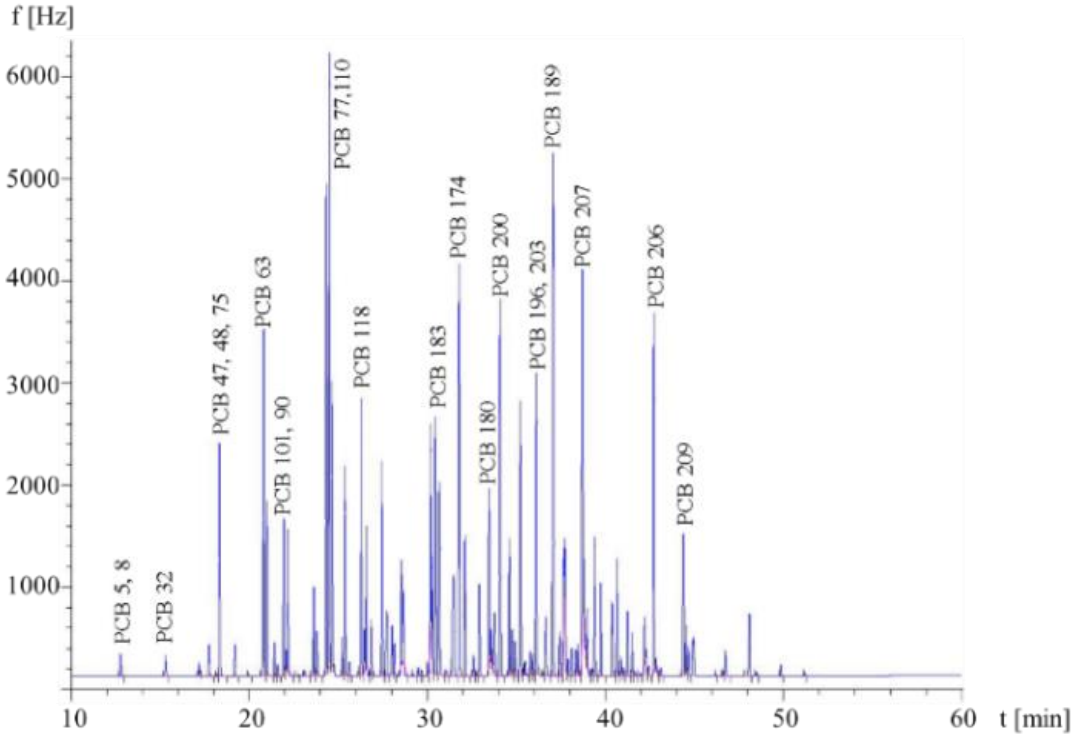
3.4. Determination of concentrations of polychlorinated biphenyl families in dielectric fluids of high voltage electrical equipment

The spread of PCBs in the environment is a serious problem because of their persistent and toxic properties. The toxic effects are caused by the hydrophobic property of PCBs, which causes them to bioaccumulate in adipose tissues of animals and humans. In 1999, the law on limiting PCB concentrations in transformer and capacitor oil was changed from 50 to 2 mg/l for liquid waste [Saeedi et al., 2017], [Sloată et al., 2022b].

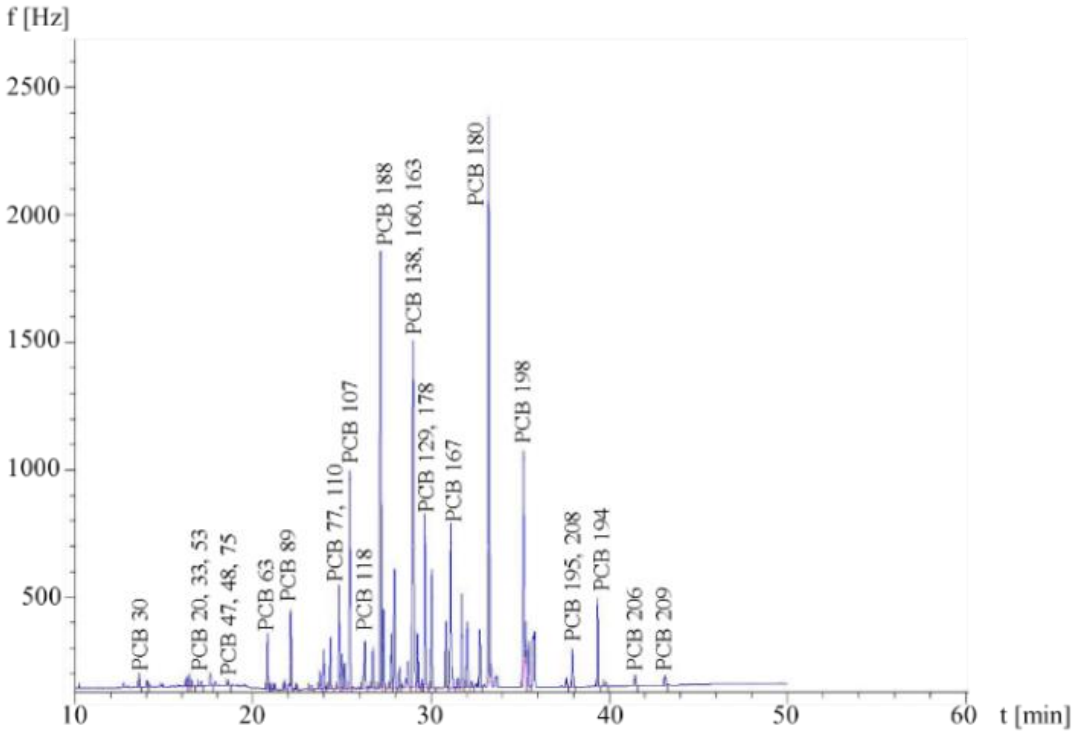
The initial phase of the experimental program meant collecting samples of PCB-contaminated industrial oil from inside high-voltage electrical transformers originating in Romania and Indonesia. After analyzing the samples qualitatively and quantitatively using the gas chromatographic method, they recorded high values for the content of all identified PCB families [Sloată and Ene, 2019b], [Sloată et al., 2022b].

Table 3.10 (a) and (b) shows the most important PCB isomers and their concentration identified as a result of the analysis of industrial oil samples from electrical transformers from Romania and Indonesia.

Figure 3.8 shows the chromatograms obtained from the analysis of industrial oil samples.



(a)



(b)

Figure 3.8. The chromatograms obtained from the analysis of industrial oil samples contaminated with PCBs: (a) the chromatogram obtained from the analysis of the oil sample from Romania and (b) the chromatogram obtained from the analysis of the oil sample from Indonesia (source: adapted according to [Sloată et al., 2022b, c])

Table 3.10. Identification of PCB isomers in industrial oils and determination of their concentrations: (a) concentrations of PCB isomers determined from the oil sample taken from Romania and (b) concentrations of PCB isomers determined from the oil sample taken from Indonesia (source: processed according to [Sloată et al., 2022b, c])

(a) concentrations of PCB isomers determined from the oil sample taken from Romania

Timpul de retenție [s]	Numele alotropului de PCB	Concentrația [ppm]	Timpul de retenție [s]	Numele alotropului de PCB	Concentrația [ppm]
12,802	PCB 5, 8	656,38	28,04	PCB 141	654,20
15,306	PCB 32	639,83	28,16	PCB 179	1255,01
17,191	PCB 22, 51	2464,31	28,555	PCB 130	345,06
17,766	PCB 52, 69	584,01	28,66	PCB 176	775,35
18,188	PCB 49	5983,86	29,225	PCB 138, 160, 163	13018,71
18,348	PCB 47, 48, 75	86,70	29,516	PCB 158	3015,76
19,229	PCB 37, 42, 59	622,96	29,698	PCB 129, 178	6277,02
19,995	PCB 96	7998,24	30,019	PCB 187	2627,10
20,818	PCB 63	58,71	30,192	PCB 183	196,33
21,01	PCB 70, 74	115,70	30,689	PCB 167	139,41
21,43	PCB 91	734,64	31,081	PCB 128	4939,68
21,617	PCB 66, 95	2086,25	31,488	PCB 185	168,25
21,959	PCB 101, 90	166,31	31,805	PCB 174	83,15
22,083	PCB 56, 60	1168,64	32,125	PCB 177	249,36
22,193	PCB 89	204,38	32,603	PCB 201, 157, 173	1508,70
22,762	PCB 99	11149,26	32,769	PCB 172	14323,54
23,119	PCB 83	2965,65	32,938	PCB197	461,02
23,634	PCB 97	286,76	33,486	PCB 180	222,26
23,813	PCB 87, 115	539,64	33,786	PCB 200	675,93
24,344	PCB 136	61,83	35,245	PCB 170, 190	126,28
24,509	PCB 77, 110	42,41	35,413	PCB 198	16330,93
24,654	PCB 82, 151	106,00	35,49	PCB 199	7302,49
25,251	PCB 135	851,93	35,927	PCB 196, 203	2003,34
25,383	PCB 107	122,10	37,676	PCB 189	1233,04
25,63	PCB 123, 149	2151,66	37,894	PCB 195, 208	3584,58
26,49	PCB 118	698,69	38,722	PCB 207	175,06
26,597	PCB 114, 143	240,97	39,407	PCB 194	301,48
26,851	PCB 146	556,06	39,751	PCB 205	453,20
27,466	PCB 105	116,99	41,513	PCB 206	1023,09
27,738	PCB 127, 168	362,05			

(b) concentrations of PCB isomers determined from the oil sample taken from Indonesia

Timpul de retenție [s]	Numele alotropului de PCB	Concentrația [ppm]	Timpul de retenție [s]	Numele alotropului de PCB	Concentrația [ppm]
13,637	PCB 30	206,54	27,771	PCB 105	261,80
14,089	PCB 18	206,54	27,946	PCB 127, 168	289,39
16,289	PCB 25	206,54	28,235	PCB 179	317,06
16,43	PCB 31	206,54	28,712	PCB 176	317,06
16,582	PCB 28	206,54	28,995	PCB 138, 160, 163	289,39
17,113	PCB 20, 33, 53	234,13	29,27	PCB 137	289,39
17,633	PCB 45	234,13	29,506	PCB 158	289,39
18,623	PCB 47, 48, 75	234,13	29,667	PCB 129, 178	317,06
20,832	PCB 63	234,13	30,042	PCB 183	317,06
21,001	PCB 70, 74	234,13	30,857	PCB 128	289,39
21,247	PCB 66, 95	261,80	31,108	PCB 167	289,39
21,797	PCB 56, 60	234,13	31,492	PCB 185	317,06
22,145	PCB 89	261,80	31,737	PCB 174	317,06
22,477	PCB 79, 113	261,80	32,046	PCB 177	317,06
23,294	PCB 83	234,13	32,315	PCB 156, 171	317,06
23,797	PCB 97	261,80	32,735	PCB 172	317,06
23,993	PCB 87, 115	261,80	33,247	PCB 180	317,06
24,371	PCB 136	289,39	35,207	PCB 198	344,66
24,846	PCB 77, 110	261,80	35,319	PCB 170, 190	317,06
24,989	PCB 82, 151	289,39	35,51	PCB 199	344,66
25,159	PCB 135	289,39	37,627	PCB 189	317,06
25,461	PCB 107	261,80	37,943	PCB 195, 208	400,00
26,279	PCB 118	261,80	39,35	PCB 194	344,66
26,759	PCB 114, 143	289,39	39,814	PCB 205	344,66
27,185	PCB 188	317,06	41,467	PCB 206	372,25
27,36	PCB 132, 153	289,39			

Table 3.11 shows a comparison of the calculated statistical parameters (minimum and maximum value of PCB concentration, respectively average of total PCB concentrations) for six different industrial oil samples. One sample each of the six is from Romania (U1), Indonesia (U2) (current research) and the Republic of Moldova (U3), and three samples are from Turkey (U4, U5 and U6).

Table 3.11. Comparison of calculated statistical parameters for PCB concentrations in oils (source: processed according to [Sloată et al., 2022b])

Calculated statistical parameters	Total PCB content determined from transformer oil samples [ppm]					
	Sample from Romania	Sample from Indonesia	Sample from Moldova [1]	Sample from Turkey [2]		
	U1	U2	U3	U4	U5	U6
Minim	42,41	206,54	1,986	-	-	-
Maxim	16330,93	400	2,682	-	-	-
Average	2157,5	248	2,247	150	0,06	1,37

[1] - [Bogdevich and Cadocinicov, 2005]
[2] - [Pelitli et al., 2015]

As can be seen in table 3.11, the minimum concentration of PCB in sample U1 is about 5 times lower than the concentration of PCB obtained in sample U2, but 21 times higher than the concentration of PCB in sample U3. The minimum concentration of PCBs in sample U2 is 104 times higher than the concentration of PCBs in sample U3. The maximum concentration of PCBs in sample U1 is 41 times higher than the concentration of PCBs in sample U2 and more than 6000 times higher than the concentration of PCBs in sample U3, and the maximum concentration of PCBs in sample U2 is about 150 times higher than the maximum PCB concentration in sample U3.

The last statistical parameter calculated and taken into account is the average concentration of PCB isomers in the analyzed or referenced oil samples. The average value of PCB concentrations identified in sample U1 is approximately 9 times higher than the average value of PCB concentrations identified in sample U2 and 960 times higher than the average value of PCB concentrations identified in sample U3. Compared to the average values of PCB concentrations identified in samples U4, U5, U6, it is very high and extremely high.

The average concentration of PCB isomers obtained from sample U2 is 110 times higher than the average concentration of PCB isomers obtained from U3. The same average value is approximately 2 times higher than the value of the average concentration of PCB isomers obtained from U4 and extremely high compared to the values of average concentrations of PCB isomers obtained from samples U5 and U6, respectively.

3.5. Determination of the content of heavy metals in the soils located around the former artificial fiber plant from Brăila county

In Brăila county, just 10 km from the city of the same name, Romania, a chemical plant was built for the production of artificial fibers, as well as cellulose derivatives (paper, cardboard, etc.). The technological processes for the production of artificial fibers were based on chemical and electrochemical methods to obtain the finished material [Ene and Sloată, 2021].

From these processes we can list: obtaining carbon sulfide (CS_2), sodium sulfide (Na_2S), sulfuric acid (H_2SO_4), obtaining chlorine gas (Cl_2) and sodium hydroxide (NaOH) by electrochemical methods using a mercury cathode (Hg) and catalysts made of heavy metals (Cd, Ni, Zn), cellofibres, etc. [Ene and Sloată, 2021], [Sloată and, 2022a, d]. Ten soil samples were taken from around the former chemical plant in Brăila county, and they were prepared in the laboratory with the aim of being subjected to ED-XRF, AAS and ICP-MS analyses. This

research was implemented to determine the content of heavy metals in soil and to carry out an assessment of their ecological risk in industrial soils.

The pXRF technique can quickly detect elements that have a very low level. concentrations (ppm), being a complementary tool to the expensive and time-consuming destructive techniques AAS and ICP-MS [Ene et al., 2011a], [Ene et al., 2019b], [Ene and Sloată, 2020], [Sloată et al., 2022a].

Following the analyzes carried out with the help of the three analytical techniques (XRF, AAS, ICP-MS), 23 chemical elements and their concentrations were determined. The main chemical elements (heavy metals and trace elements) determined using the three analysis methods (XRF, AAS, ICP-MS) are represented in table 3.12 (a), (b) și (c). Table 3.12 (c) shows the concentration values of other major chemical elements determined only by the ED-XRF method, after irradiation for 120 seconds. The energy spectrum resulting from the analysis of sample B1 is illustrated in figure 3.9.

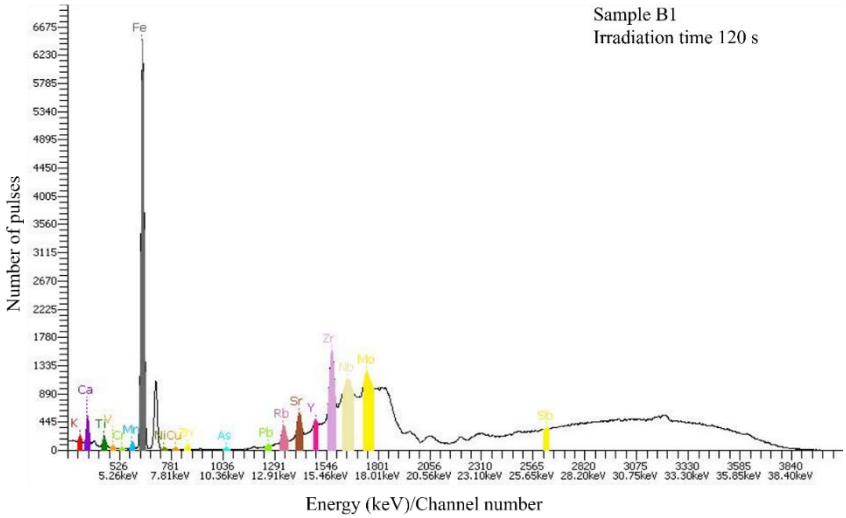


Figure 3.9. The energy spectrum resulting from the analysis of sample B1 by ED-XRF

The values of element concentrations determined by the three methods were compared with the values specified in the Romanian regulations regarding soil pollution with heavy metals and with the average values of their concentrations determined in the European surface soil and in the upper continental crust [Wedepohl, 1995], [Ordinul 756, 1997], [Salminen, 2005]. The comparison between the values of the element concentrations determined in this research and the values referenced in the Romanian standard and in other research can be found in table 3.13.

Following the comparison, the following observations can be made:

Arsenic recorded slightly higher values in samples B1, B2, B3, B4 and B6 compared to the average value in the upper continental crust (C);

The concentration of **calcium** in samples B1 and B3 are slightly higher than the average in the upper continental crust (C), and the concentration in samples B5, B6, B9 and B10 are about 30% higher than the average value in the European surface soils (E);

The value obtained for **cadmium** in samples B1-B9 are higher than the normal limit in the legislation (N) and much higher compared to the average value in the European surface soils (E), respectively the average value in the upper continental crust;

For **cobalt**, values below the legal limits and below the values specified in the works [Salminen, 2005], [Wedepohl, 1995] were obtained;

Chromium recorded values twice the normal value (N) and approximately twice the values specified in the works [Salminen, 2005], [Wedepohl, 1995];

Copper only in samples B2 and B4 has a slightly increased concentration compared to the average value in the upper continental crust;

Iron and **potassium** - the concentration values of these elements rank below the values specified in the works [Salminen, 2005], [Wedepohl, 1995];

Manganese in all ten analyzed soil samples recorded concentration values higher than the average value in the upper continental crust;

Molybdenum is slightly more concentrated than the action limit value (S2) and 10 times more concentrated than the values specified in the works [Salminen, 2005], [Wedepohl, 1995];

Niobium has a concentration, in samples B2, B4 and B7 2% higher than the average value in the upper continental crust (C), and in samples B1, B3, B5, B6, B8, B9 and B10 it has a concentration of 10, respectively 100 percent higher than the average value in the upper continental crust (C);

The **nickel** concentrations in the ten samples considerably exceed the normal value (N) and the average value in the upper continental crust (C), and in samples B6-B8 it recorded higher concentrations compared to the average value in the European surface soils (E);

Lead has in sample B6 a concentration twice as high as the action limit value (S2), in all samples the values even exceed twice the normal value (N). In sample B8, it has a concentration 3 times higher than the value specified in the paper [Wedepohl, 1995], and in all other samples the values are almost double the value specified in the paper [Wedepohl, 1995]. In samples B3, B4-B10 the concentrations are higher than the value specified in the paper [Salminen, 2005];

Rubidium only in sample B4 has a slightly increased concentration compared to the value specified in the paper [Salminen, 2005];

Antimony did not record values above the legal limits, instead it recorded concentration values in samples B1, B2, B3, B5, B7 and B10 even 4 times higher than the value specified in the work [Salminen, 2005], and compared to the value specified in the paper [Wedepohl, 1995] recorded values even 10 times higher;

Strontium in samples B5 and B6 has slightly higher concentration values compared to the average value in the surface soils of our continent (E);

Titanium recorded values 30% higher than the average value in the upper continental crust (C) in all analyzed samples**;**

Vanadium in samples B2, B5 and B7 has a 20% higher concentration than the normal value (N) and the average value in the upper continental crust (C);

Zinc in all samples it has a higher concentration than the value specified in the paper [Wedepohl, 1995], in samples B3, B4 and B5 the concentrations are more than twice the value specified in the paper [Wedepohl, 1995] and all these exceed the normal limit (N). The values specified in the job are exceeded [Salminen, 2005] in all samples, less so in samples B1 and B3.

The values of **zirconium** concentrations obtained from all 10 samples significantly exceed the values specified in the works [Salminen, 2005], [Wedepohl, 1995].

Based on the results obtained from the application of ED-XRF, AAS and ICP-MS analytical techniques and the toxicological risk assessment approach, the values of the geoaccumulation index, the pollution index and the enrichment factor indices were calculated and presented in table 3.14 (a), (b) and (c).

Table 3.12. Determination of the chemical elements from the soils sampled around the former plant from Brăila county: (a) determination of B, As, Sn, Mn, V, Sb and Mo concentrations, (b) determination of Co, Zn, Cu, Ni, Cd, Pb and Cr concentrations and (c) determination of K, Ca, Ti, Fe, Rb, Zr, Sr, Nb and Y concentrations (source: processed according to [Sloată et al., 2022a], [Ene et al., 2022b])

(a) determination of B, As, Sn, Mn, V, Sb and Mo concentrations

Sample code	Chemical element, concentration and error [ppm]						
	B	As	Sn	Mn	V	Sb	Mo
B1	28,22±1,94	3,51±0,24	0	726,49±15,76	44,68±0,69	2,82±0,08	10,55±0,14
B2	18,22±1,27	3,10±0,22	0	772,66±16,28	51,54±0,78	3,66±0,12	10,52±0,14
B3	7,92±0,54	2,68±0,18	2,87±0,14	782,40±16,49	30,01±0,48	4,33±0,03	10,33±0,14
B4	17,44±1,28	2,61±0,19	0	676,92±14,99	39,75±0,61	0,2±<0,000	10,71±0,14
B5	4,04±0,27	1,96±0,13	6,08±0,28	781,21±16,58	67,48±1,00	1,91±0,04	10,61±0,14
B6	0,61±0,04	2,52±0,17	0	748,60±16,17	41,10±0,64	0,2±<0,000	10,45±0,14
B7	<0,15±<0,000	1,56±0,11	9,98±0,42	763,82±16,20	57,46±0,86	1,51±0,03	10,38±0,14
B8	<0,15±<0,000	1,25±0,08	0	638,50±14,44	28,26±0,44	0,2±<0,000	10,77±0,14
B9	<0,15±<0,000	1,04±0,07	0,69±0,03	729,24±15,91	39,58±0,62	0,66±0,01	10,47±0,14
B10	<0,15±<0,000	0,94±0,06	0,93±0,05	718,65±15,71	31,56±0,50	3,58±0,12	10,56±0,14

(b) determination of Co, Zn, Cu, Ni, Cd, Pb and Cr concentrations

Sample code	Chemical element, concentration and error [ppm]						
	Co	Zn	Cu	Ni	Cd	Pb	Cr
B1	7,27±0,36	59,39±17,82	11,66±2,33	32,65±5,72	1,05±0,26	26,08±7,35	62,18±2,76
B2	6,84±0,34	89,83±17,97	15,86±3,17	32,82±5,74	1,74±0,36	33,69±9,50	62,39±2,75
B3	8,11±0,41	56,69±11,34	1,89±0,38	29,88±5,23	1,30±0,27	28,03±7,90	61,47±2,76
B4	7,42±0,37	102,43±20,49	14,69±2,94	30,85±5,4	1,55±0,33	39,05±11,01	61,85±2,74
B5	5,87±0,29	110,17±22,03	10,73±2,15	33,79±5,91	1,75±0,37	44,38±12,52	64,37±2,82
B6	6,62±0,33	124,87±24,97	13,17±2,63	38,74±6,78	1,76±0,37	210,70±59,42	61,75±2,78
B7	6,98±0,35	89,50±17,90	11,96±2,39	43,84±7,67	1,24±0,26	46,43±10,27	63,39±2,77
B8	6,61±0,33	97,61±19,52	11,1±2,22	45,52±7,97	1,75±0,37	53,50±11,83	67,62±2,81
B9	6,19±0,31	63,04±12,61	9,61±1,92	34,12±5,97	1,46±0,31	41,83±9,25	66,19±2,84
B10	6,38±0,32	83,51±16,70	12,87±2,57	35,20±6,16	0,48±0,10	46,19±10,22	59,19±2,73

(c) determination of K, Ca, Ti, Fe, Rb, Zr, Sr, Nb and Y concentrations

Sample code	Chemical element, concentration and error [ppm]								
	K	Ca	Ti	Fe	Y	Zr	Nb	Rb	Sr
B1	19855,08±643,12	30717,99±449,04	4575,06±104,30	28777,19±86,82	3,64±0,07	366,57±1,77	20,06±0,24	84,99±1,19	110,17±1,38
B2	20827,64±651,00	26827,10±410,01	4368,11±103,83	28920,59±86,61	3,88±0,07	362,41±1,75	32,23±0,37	80,40±1,15	114,90±1,41
B3	19780,63±643,76	36051,03±495,40	4530,37±104,51	29036,48±87,29	4,07±0,08	363,74±1,76	10,90±0,13	81,53±1,17	123,85±1,47
B4	19846,81±637,90	23320,96±382,47	4625,74±103,51	29782,66±87,16	3,75±0,07	369,26±1,77	7,91±0,10	89,14±1,21	115,23±1,40
B5	18568,19±634,28	47888,16±520,60	4158,30±105,35	2871,65±87,47	5,55±0,10	341,57±1,70	10,61±0,13	74,31±1,13	146,44±1,61
B6	19526,56±644,47	47142,10±518,59	4363,96±105,07	29237,80±87,98	5,50±0,10	316,53±1,60	12,75±0,16	72,75±1,11	149,33±1,63
B7	20079,61±644,05	28919,71±431,11	4343,14±104,03	28905,04±86,75	3,94±0,07	345,75±1,69	9,48±0,12	84,55±1,19	118,85±1,43
B8	19312,67±630,05	21719,38±374,10	4570,54±103,13	29898,98±87,00	3,84±0,07	366,17±1,75	18,82±0,22	85,51±1,18	112,72±1,38
B9	20469,58±654,59	41227,39±506,59	4390,77±105,02	28210,12±86,84	4,24±0,08	350,79±1,73	12,71±0,16	80,47±1,17	124,44±1,48
B10	20091,43±647,87	41366,44±504,83	4444,03±104,60	28171,15±86,46	4,27±0,08	331,95±1,65	17,25±0,21	80,00±1,16	121,43±1,46

Table 3.13. The comparison between the values of the concentrations of the elements determined in this research and the values specified in the Romanian normative and in other researches (source: processed according to [Sloată et al., 2022a])

Chemical element	Results form this research [ppm]			The Romanian regulations for soils [ppm] [1]			Data from specialized literature [ppm]	
	Min.	Max.	Med.	N	S1	S2	E [2]	C [3]
As	0,94	3,1	2,12	5	15	25	11,6	2,0
Ca [g/kg]	21,71	47,88	34,51	-	-	-	35,4	29,45
Cd	0,48	1,76	1,41	1	3	5	0,28	0,10
Co	5,87	8,11	6,83	15	30	50	10,4	11,6
Cr	59,19	67,62	63,04	30	100	300	94,8	35
Cu	1,89	15,86	11,35	20	100	200	17,3	14
Fe [g/kg]	2,87	29,89	26,3	-	-	-	38,0	30,89
K [g/kg]	18,56	20,82	19,83	-	-	-	20,2	28,65
Mn	638,5	782,4	733,85	900	1500	2500	810	527
Mo	10,33	10,77	10,54	2	5	10	0,94	1,4
Nb	7,91	32,23	15,27	-	-	-	10,6	26
Ni	29,88	45,52	35,74	20	75	150	37,3	18,6
Pb	26,08	210,7	56,99	20	50	100	32,6	17
Rb	72,75	89,14	81,37	-	-	-	86,8	110
Sb	0,2	4,33	1,91	5	12,5	20	1,04	0,31
Sn	0	9,98	2,06	20	35	50	4,48	2,5
Sr	110,17	149,33	123,74	-	-	-	130	316
Ti [g/kg]	4,15	4,62	4,43	-	-	-	6,09	3,117
V	28,26	67,48	43,14	50	100	200	68,1	53
Y	3,64	5,55	4,27	-	-	-	22,7	20,7
Zn	56,69	124,87	87,7	100	300	600	68,1	52
Zr	316,53	369,26	351,47	-	-	-	251	237

N - Normal Value; S1 - Alert limit; S2 - Action limit; E - Average in the European surface soils;C - Average in the upper continental crust; [1]- [Ordinul 756, 1997]; [2] - [Salminen, 2005]; [3] - [Wedepohl, 1995]

Table 3.14. Evaluation of toxicological risk factors: (a) values of the geoaccumulation index of toxic elements in industrial soils, (b) values of the pollution index with toxic elements of industrial soils and (c) values of the enrichment factor with toxic elements of industrial soils (source: processed according to [Sloată et al., 2022a])

(a) values of the geoaccumulation index of toxic elements in industrial soils

Sample code	I_{geo} value												
	Zn	As	Ni	V	Cr	Mn	Cd	Mo	Sb	Pb	Cu	F	P
B1	-0,78	1,01	-0,78	-1,19	-1,19	-0,74	1,81	-0,36	0,91	-0,91	-1,15	0	2,08
B2	-0,19	0,83	-0,77	-0,99	-1,19	-0,65	2,54	-0,36	1,29	-0,54	-0,71	0	2,36
B3	-0,85	0,62	-0,90	-1,77	-1,21	-0,63	2,11	-0,39	-1,79	-0,80	-0,45	0	1,48
B4	0,00	0,58	-0,86	-1,36	-1,20	-0,84	2,37	-0,33	-2,91	-0,32	-0,82	0	1,61
B5	0,11	0,17	-0,73	-0,60	-1,14	-0,64	2,54	-0,35	0,35	-0,14	-1,27	0	2,46
B6	0,29	0,53	-0,53	-1,31	-1,20	-0,70	2,55	-0,37	-2,91	2,11	-0,98	0	1,72
B7	-0,19	-0,16	-0,35	-0,83	-1,17	-0,67	2,05	-0,38	0,01	-0,07	-1,12	0	1,48
B8	-0,07	-0,48	-0,30	-1,85	-1,07	-0,93	2,55	-0,33	-2,91	0,13	-1,23	0	1,37
B9	-0,70	-0,74	-0,71	-1,37	-1,10	-0,74	2,28	-0,37	-1,17	-0,23	1,89	0	2,03
B10	-0,29	-0,90	-0,67	-1,69	-1,26	-0,76	0,68	-0,35	1,26	-0,08	-1,01	0	1,75

Legend		
Class	I_{geo} value	Soil quality
0	I ≤ 0	unpolluted
1	0< I< 1	unpolluted to moderately polluted
2	1< I< 2	moderately polluted
3	2< I< 3	moderate to highly polluted
4	3< I< 4	highly polluted
5	4< I< 5	highly to extremely polluted
6	5< I< 6	extremely polluted

(b) values of the pollution index with toxic elements of industrial soils

Sample code	PI value												
	Zn	As	Ni	V	Cr	Mn	Cd	Mo	Sb	Pb	Cu	F	P
B1	0,87	3,03	0,88	0,66	0,66	0,90	3,70	1,17	2,83	0,80	0,67	0	6,34
B2	1,32	2,67	0,88	0,76	0,66	0,95	6,14	1,17	3,66	1,03	0,92	0	7,68
B3	0,83	2,31	0,80	0,44	0,65	0,97	4,56	1,15	0,43	0,86	1,10	0	4,19
B4	1,50	2,25	0,83	0,58	0,65	0,84	5,47	1,19	0,20	1,20	0,85	0	4,57
B5	1,62	1,69	0,91	0,99	0,68	0,96	6,14	1,18	1,91	1,36	0,62	0	8,26
B6	1,83	2,17	1,04	0,60	0,65	0,92	6,19	1,16	0,20	6,46	0,76	0	4,93
B7	1,31	1,34	1,18	0,84	0,67	0,94	4,38	1,15	1,51	1,42	0,69	0	4,18
B8	1,43	1,08	1,22	0,42	0,71	0,79	6,17	1,20	0,20	1,64	0,64	0	3,88
B9	0,93	0,90	0,91	0,58	0,70	0,90	5,13	1,16	0,67	1,28	5,56	0	6,11
B10	1,23	0,81	0,94	0,46	0,62	0,89	1,70	1,17	3,58	1,42	0,74	0	5,04

Legend		
Class	PI value	Soil pollution degree
1	PI <1	absent
2	1< PI< 2	low
3	2< PI< 3	moderate
4	3< PI< 5	intensive
5	PI >5	very intensive

(c) values of the enrichment factor with toxic elements of industrial soils

Sample code	EF value												
	Zn	As	Ni	V	Cr	Mn	Cd	Mo	Sb	Pb	Cu	F	P
B1	0,97	3,38	0,98	0,73	0,73	1,00	4,12	1,31	3,15	0,89	0,75	0	7,07
B2	1,38	2,80	0,92	0,79	0,69	1,00	6,43	1,23	3,84	1,08	0,96	0	8,05
B3	0,86	2,39	0,83	0,46	0,67	1,00	4,72	1,19	0,45	0,89	1,14	0	4,33
B4	1,80	2,69	0,99	0,70	0,78	1,00	6,55	1,42	0,24	1,43	1,02	0	5,46
B5	1,68	1,75	0,94	1,03	0,70	1,00	6,37	1,22	1,98	1,41	0,64	0	8,56
B6	1,98	2,35	1,12	0,65	0,70	1,00	6,70	1,26	0,22	6,99	0,82	0	5,34
B7	1,39	1,42	1,25	0,89	0,71	1,00	4,65	1,22	1,60	1,51	0,73	0	4,43
B8	1,82	1,37	1,55	0,53	0,90	1,00	7,83	1,52	0,25	2,08	0,81	0	4,92
B9	1,03	1,00	1,02	0,65	0,78	1,00	5,70	1,29	0,74	1,43	6,17	0	6,79
B10	1,38	0,91	1,06	0,52	0,70	1,00	1,91	1,32	4,04	1,60	0,84	0	5,68

Legend	
EF value	Enrichment degree in soil
< 2	deficit to minimal enrichment
2-5	moderately enriched
5-20	significantly enriched
20-40	very enriched
> 40	extremely enriched

3.6. Determination of the concentrations of heavy metals and trace elements in the soils located around the metallurgical complex from Galati

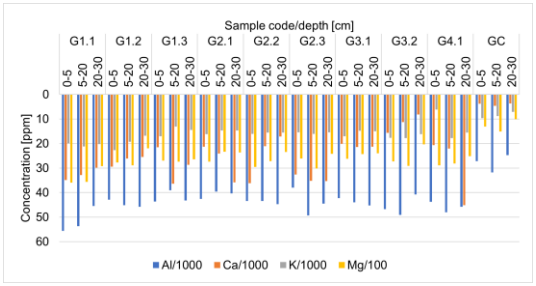
The purpose of this research is to measure the level of soil pollution with toxic chemical elements around the metallurgical plant in Galati, Romania and to compare the results obtained in this work with the results of other similar scientific contributions. The activity of this metallurgical complex began in 1965 and continues today.

It can be said that it remains the most important metallurgical complex in Romania and in SE Europe, but its activity also represents a large source of pollution of environmental factors (air, soil, water) [Popescu et al., 1996], [Ene et al., 2009a], [Ene et al., 2010a].

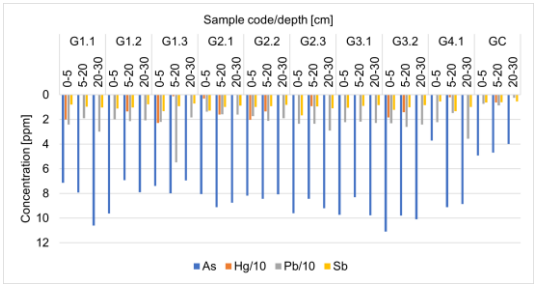
Instrumental neutron activation analysis (INAA), using fast, thermal or epithermal neutrons, is successfully applied for the determination of trace elements, heavy metals, actinides, lanthanides in metallurgical, pharmaceutical, biological, environmental samples, etc.. One among the advantages of the INAA method is the fact that it uses the high intensity of the neutron beams resulting from the moderation of fission neutrons and the large cross sections of moderated neutrons for the identification of a large number of chemical elements [Ene and Frontasyeva, 2013]..

Using the INAA technique, the concentration of 40 chemical elements can be determined simultaneously with detection limits lower than 1 ppm, without the application of laborious acid digestion processes, etc. [Abdo et al., 2017], [Ene et al., 2019b, c]. The ED-XRF analytical technique was used in complementarity with the INAA method to complete the database in this research with values of the concentrations of the elements that could not be determined by the nuclear method.

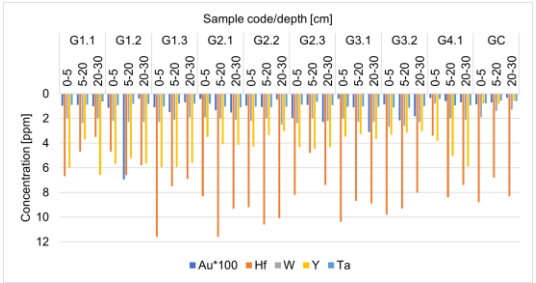
By means of the two methods of analysis, a number of 43 major, minor and trace chemical elements were identified from the soils sampled around the metallurgical complex in Galati. The distribution of the values of the concentrations of the identified elements according to the depth of soil sampling is presented in figure 3.10 (a), (b), (c), (d), (e), (f), (g), (h), (i) and (j).



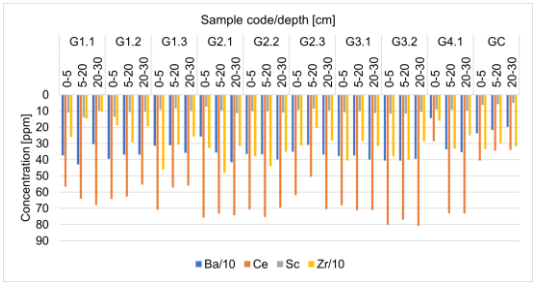
(a) the distribution of element concentration values: Al, Ca, K și Mg



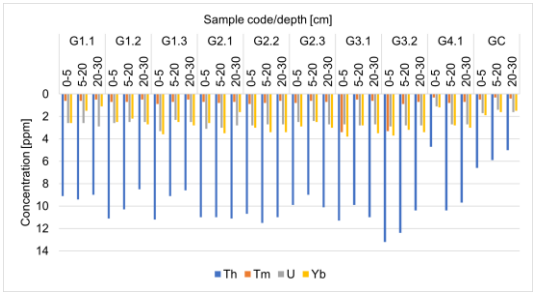
(b) the distribution of element concentration values: As, Hg, Pb și Sb



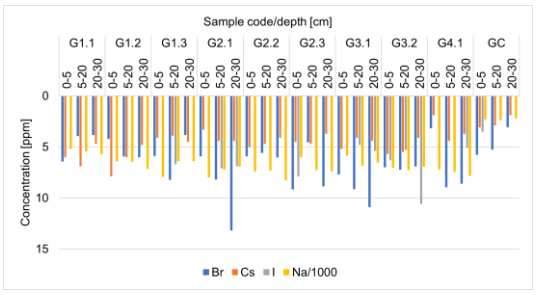
(c) the distribution of element concentration values: Au, Hf, W, Y și Ta



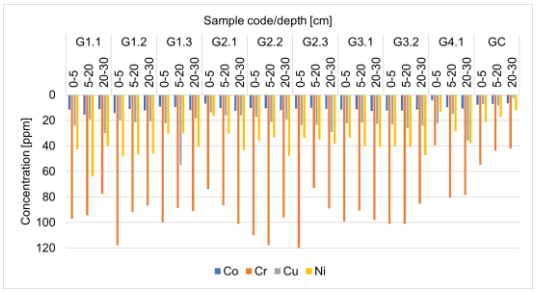
(d) the distribution of element concentration values: Ba, Ce, Sc și Zr



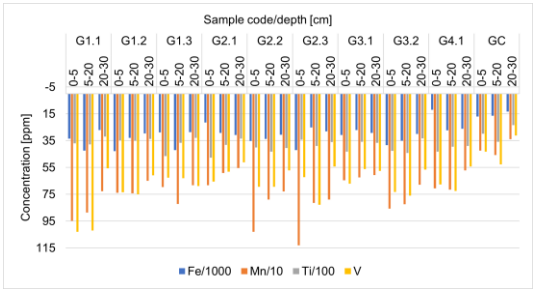
(e) the distribution of element concentration values: Th, Tm, U și Yb



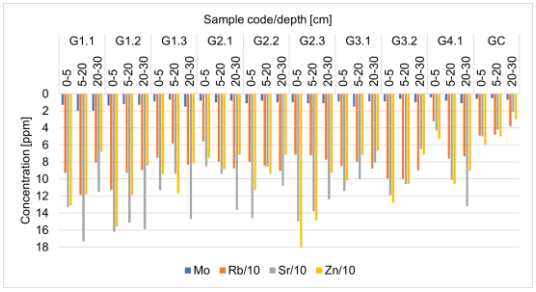
(f) the distribution of element concentration values: Br, Cs, I și Na



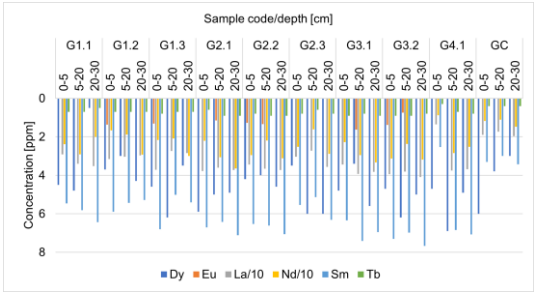
(g) the distribution of element concentration values: Co, Cr, Cu și Ni



(h) the distribution of element concentration values: Fe, Mn, Ti și V



(i) the distribution of element concentration values: Mo, Rb, Sr și Zn



(j) the distribution of element concentration values: Dy, Eu, La, Nd, Sm și Tb

Figure 3.10. Distribution of the values of the concentrations of the identified elements according to the sampling depth of the soil samples: (a) the distribution of element concentration values: Al, Ca, K and Mg, (b) the distribution of element concentration values: As, Hg, Pb and Sb, (c) the distribution of element concentration values: Au, Hf, W, Y and Ta, (d) the distribution of element concentration values: Ba, Ce, Sc and Zr, (e) the distribution of element concentration values: Th, Tm, U and Yb, (f) the distribution of element concentration values: Br, Cs, I și Na, (g) the distribution of element concentration values: Co, Cr, Cu and Ni, (h) the distribution of element concentration values: Fe, Mn, Ti and V, (i) the distribution of element concentration values: Mo, Rb, Sr și Zn and (j) the distribution of element concentration values: Dy, Eu, La, Nd, Sm and Tb.

Based on the results obtained from the analysis to determine the concentrations of heavy metals in the industrial soil samples and the risk assessment approach, the values of the migration index on the depth of the soil were calculated. The migration indices values of the elements identified in the soil samples are shown in table 3.15 (a) and (b).

Table 3.15. Toxicological risk factors assessment: (a) the migration index values of the elements: As, Au, Ba, Br, Co, Cr, Cs, Cu, Hg, I, Mn, Mo, Ni, Pb, Rb, Sb, Sc, Sr, V, W, Zn and Zr and (b) the migration index values of the elements: Al, Ca, Ce, Dy, Eu, Fe, Hf, K, La, Mg, Na, Nd, Sm, Ta, Tb, Th, Ti, Tm, U, Y and Yb

(a) the migration index values of the elements: As, Au, Ba, Br, Co, Cr, Cs, Cu, Hg, I, Mn, Mo, Ni, Pb, Rb, Sb, Sc, Sr, V, W, Zn and Zr

Sample code	DMI value																					
	As	Au	Ba	Br	Co	Cr	Cs	Cu	Hg	I	Mn	Mo	Ni	Pb	Rb	Sb	Sc	Sr	V	W	Zn	Zr
G1.1	19,95	18,54	17,70	15,91	18,41	17,47	17,56	19,14	5,04	0	17,28	20,09	18,37	19,14	18,00	19,38	18,06	17,99	16,21	18,44	15,95	14,42
G1.2	17,32	18,44	18,03	19,80	17,59	16,96	16,23	18,55	20,03	0	17,85	17,95	18,12	18,55	17,30	16,90	17,18	18,22	17,65	18,53	15,83	18,75
G1.3	18,15	17,09	18,84	17,22	19,40	17,89	18,68	18,45	5,86	20,00	18,36	20,48	19,50	18,45	18,67	15,72	18,66	19,36	18,72	17,54	17,95	15,77
G2.1	18,71	22,74	20,29	21,58	20,76	19,63	19,55	19,01	17,50	24,93	17,43	18,46	22,07	19,01	20,14	16,76	20,12	20,25	17,30	18,75	18,25	18,43
G2.2	18,29	16,06	18,70	18,38	18,95	17,88	17,54	18,84	11,02	0	16,80	17,76	19,50	18,84	18,85	17,62	18,63	16,73	17,60	18,81	16,50	18,14
G2.3	18,09	18,71	18,46	17,83	18,41	16,77	17,64	19,17	20,03	5,00	16,68	18,75	18,88	19,17	18,66	16,26	18,45	17,55	18,04	17,88	14,41	17,65
G3.1	18,27	25,31	18,54	19,75	18,65	18,23	17,52	18,45	24,00	25,29	18,07	18,64	19,16	18,45	18,44	17,43	18,49	16,94	17,63	18,94	16,41	17,09
G3.2	17,89	21,09	18,23	18,30	18,11	17,70	17,09	18,55	11,54	20,52	17,43	18,60	18,95	18,55	17,95	16,78	17,92	16,08	17,42	17,70	16,03	17,34
G4.1	21,52	21,07	21,67	21,84	21,79	20,97	20,85	20,33	20,14	30,00	17,56	22,17	22,22	20,33	21,37	20,55	18,68	22,45	17,56	21,84	20,46	20,17
G.C.	17,49	15,06	17,57	16,03	17,76	17,14	16,52	15,38	20,03	5,00	17,56	18,89	16,09	15,38	17,40	17,72	17,38	15,26	17,35	16,63	15,77	18,06

(b) the migration index values of the elements: Al, Ca, Ce, Dy, Eu, Fe, Hf, K, La, Mg, Na, Nd, Sm, Ta, Tb, Th, Ti, Tm, U, Y and Yb

Sample code	DMI value																				
	Al	Ca	Ce	Dy	Eu	Fe	Hf	K	La	Mg	Na	Nd	Sm	Ta	Tb	Th	Ti	Tm	U	Y	Yb
G1.1	17,55	15,01	19,10	13,62	0,00	17,76	15,60	18,44	19,14	17,54	18,73	17,87	19,01	17,02	17,11	18,31	17,77	17,65	18,77	18,52	14,62
G1.2	18,61	17,70	17,76	18,86	5,00	16,73	19,27	17,07	18,07	17,51	18,77	20,66	17,86	17,86	18,33	17,27	18,23	17,11	18,16	18,25	18,58
G1.3	18,24	19,59	17,26	17,62	5,00	18,52	15,96	17,53	17,08	18,25	17,34	19,65	17,21	17,18	17,73	17,16	16,82	15,95	16,98	18,09	17,08
G2.1	18,07	20,47	18,24	17,50	20,00	19,83	18,92	17,89	18,25	17,66	17,71	20,36	18,55	19,64	20,00	18,37	16,82	18,41	17,92	19,04	17,01
G2.2	18,45	15,02	18,31	18,67	12,70	17,77	18,76	18,19	18,67	17,40	18,76	18,41	18,65	18,48	18,85	18,48	18,40	16,74	18,17	16,82	18,88
G2.3	19,05	18,68	18,78	20,48	0,00	16,32	17,60	18,36	18,93	18,14	19,20	18,73	18,83	18,36	18,18	18,36	18,60	17,62	18,62	18,35	18,39
G3.1	18,62	18,57	18,52	18,84	20,00	18,05	17,61	17,73	18,80	17,95	18,85	19,91	18,76	18,36	18,27	18,15	17,55	10,00	18,35	18,51	17,82
G3.2	17,85	15,62	18,35	18,71	10,24	17,35	17,53	18,00	18,46	17,32	18,29	18,27	18,50	17,88	17,88	17,39	17,45	11,33	18,18	17,95	17,91
G4.1	18,55	21,61	21,73	18,70	0,00	21,25	21,20	21,59	21,87	17,79	18,69	21,91	21,99	21,41	21,94	21,07	17,88	21,39	21,62	20,12	21,71
G.C.	18,08	18,32	17,52	15,31	0,00	17,39	17,95	17,11	18,45	17,51	18,19	19,23	18,44	16,94	18,33	17,20	17,61	17,08	17,98	17,19	17,30

Legend		
Class	DMI value	Migration degree
0	<5	very low
1	5-10	moderate
2	10-20	high
3	>20	very high

3.7. Radiological characterization of the soils located around the metallurgical complex from Galati

This research has as its first objective the determination for the first time of the activity concentrations of the main natural and artificial radionuclides in the soil located around the metallurgical complex from Galați, Romania. The second objective is to assess the radiological risk to the health of the population in the region and calculate the public exposure doses to ionizing radiation emitted by soil radionuclides.

The low-background high-resolution gamma spectrometry technique was applied to determine the activity and mass concentrations of radionuclides in the industrial soils sampled around the metallurgical complex, and the results are found in table 3.16 (a), (b) and (c). The statistical parameters calculated for the concentrations of the main radionuclides are represented in table 3.17. The gamma radiation spectra corresponding to soil sample R6 (figure 3.11) and the natural background in the laboratory (figure 3.12) indicate the presence of peaks resulting from the activity of natural radionuclides and the artificial radionuclide ^{137}Cs [Ene et al., 2023a].

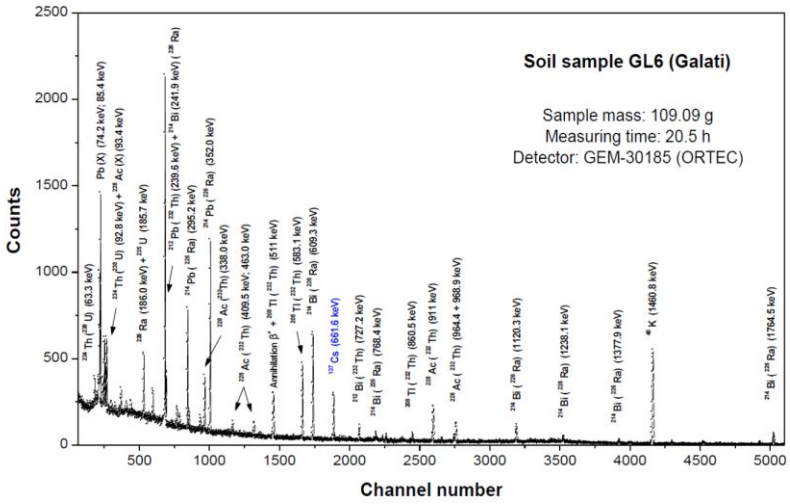


Figure 3.11. The gamma radiation spectrum obtained from the analysis of soil sample R6 (source: adapted according to [Ene et al., 2023a])

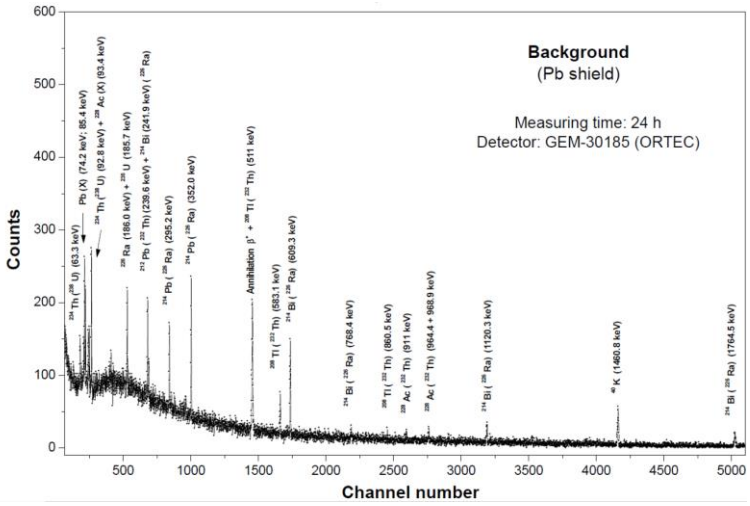


Figure 3.12. Gamma radiation spectrum obtained from the measurement of the natural background in the laboratory and the lead shield (source: adapted according to [Ene et al., 2023a])

Table 3.16. The activity concentration of the radionuclides identified in the soils sampled around the metallurgical complex from Galati: (a) determining the activity concentration of radioactive isotopes: ^{226}Ra, ^{214}Pb, ^{214}Bi, ^{238}U, ^{235}U, ^{210}Pb and ^{232}Th , (b) determining the activity concentration of radioactive isotopes: ^{228}Ac, ^{212}Pb, ^{208}Tl, ^{40}K, ^{137}Cs, ^{241}Am and ^{60}Co and (c) determination of mass concentration of radioactive isotopes: ^{238}U, ^{232}Th și ^{40}K (source: processed according to [Ene et al., 2023a, b])

(a) determining the activity concentration of radioactive isotopes: ^{226}Ra, ^{214}Pb, ^{214}Bi, ^{238}U, ^{235}U, ^{210}Pb and ^{232}Th

Sample code	Measurement time [h]	Radioactive isotope													
		^{226}Ra		^{214}Pb		^{214}Bi		^{238}U		^{235}U		^{210}Pb		^{232}Th	
		c [Bq/kg]	±e [Bq/kg]	c [Bq/kg]	±e [Bq/kg]	c [Bq/kg]	±e [Bq/kg]	c [Bq/kg]	±e [Bq/kg]	c [Bq/kg]	±e [Bq/kg]	c [Bq/kg]	±e [Bq/kg]	c [Bq/kg]	±e [Bq/kg]
R1	5,28	46,3	2,5	45,1	2,7	47,5	4,2	47	18	1,4	0,6	43	32	41,6	1,4
R2	17	32,0	1,4	32,9	2,0	31,1	1,9	36	11	0,7	0,2	59	20	35,0	1,9
R3	5,5	36,2	1,8	36,8	2,5	35,5	2,7	43	14	0,5	0,4	43	37	33,2	1,6
R4	7,08	36,1	2,1	37,7	2,9	34,5	3,2	42	25	0,9	0,5	49	39	35,5	1,7
R5	14,6	35,4	1,6	36,1	2,0	34,7	2,6	28	7	1,0	0,5	57	22	36,6	1,4
R6	20,5	40,1	1,6	39,8	2,2	40,4	2,2	32	7	0,7	0,3	37	31	36,7	1,4
R7	13,5	32,1	1,5	32,3	1,9	31,9	2,4	41	13	0,9	0,4	53	38	31,7	1,4
R8	7	28,9	1,7	30,9	2,1	27,0	2,8	37	10	1,3	0,6	37	32	33,6	1,6

(b) determining the activity concentration of radioactive isotopes: ^{228}Ac, ^{212}Pb, ^{208}Tl, ^{40}K, ^{137}Cs, ^{241}Am and ^{60}Co

Sample code	Measurement time [h]	Radioactive isotope													
		^{228}Ac		^{212}Pb		^{208}Tl		^{40}K		^{137}Cs		^{241}Am		^{60}Co	
		c [Bq/kg]	±e [Bq/kg]	c [Bq/kg]	±e [Bq/kg]	c [Bq/kg]	±e [Bq/kg]	c [Bq/kg]	±e [Bq/kg]	c [Bq/kg]	±e [Bq/kg]	c [Bq/kg]	±e [Bq/kg]	c [Bq/kg]	±e [Bq/kg]
R1	5,28	42,1	3,3	42,1	2,8	40,8	3,6	563	36	7,3	0,9	<4,7	-	<1,3	-
R2	17	37,0	1,6	34,1	2.7	43,0	2,8	519	31	11,6	1,0	<2,2	-	<0,6	-
R3	5,5	35,5	2,7	32,4	2,6	31,8	2,9	435	28	13,5	1,0	<4,4	-	<1,2	-
R4	7,08	36,4	2,1	35,2	3,7	34,8	2,9	494	30	4,6	0,7	<3,8	-	<1,1	-
R5	14,6	37,0	1,9	37,1	2,4	35,5	2,7	490	29	7,9	0,6	<2,8	-	<0,8	-
R6	20,5	36,6	1,6	36,8	2,7	36,6	2,7	485	27	10,8	0,7	<2,4	-	<0,6	-
R7	13,5	31,6	2,0	32,7	2,1	30,6	3,0	508	30	1,2	0,3	<2,7	-	<0,7	-
R8	7	33,2	2,2	33,4	2,6	34,2	3,3	542	37	0,9	0,4	<3,4	-	<1,1	-

(c) determination of mass concentration of radioactive isotopes: ^{238}U, ^{232}Th și ^{40}K

Sample code	Measurement time [h]	Radioactive isotope					
		^{238}U		^{232}Th		^{40}K	
		c [ppm]	e± [ppm]	c [ppm]	e± [ppm]	c [g/kg]	e± [g/kg]
R1	5,28	3,8	1,5	10,2	0,5	17,8	1,1
R2	17	3,1	0,8	8,6	0,3	16,4	1,0
R3	5,5	3,4	1,1	8,2	0,4	13,7	0,9
R4	7,08	3,4	2,0	8,7	0,4	15,6	0,9
R5	14,6	2,6	1,2	9,0	0,3	15,5	0,9
R6	20,5	2,6	0,6	9,0	0,3	15,3	0,9
R7	13,5	3,3	1,1	7,8	0,3	16,0	0,9
R8	7	3,0	0,8	8,3	0,4	17,1	1,2

Tabelul 3.17. Statistical parameters calculated for the concentrations of the main radionuclides determined in the analyzed soils (source: processed according to [Ene et al., 2023a, b])

Parameter	^{226}Ra [Bq/kg]	^{238}U [Bq/kg]	^{232}Th [Bq/kg]	^{40}K [Bq/kg]	^{137}Cs [Bq/kg]	^{238}U [ppm]	^{232}Th [ppm]	^{40}K [g/kg]
Min.	28,9	28	31,7	435	0,9	2,2	7,8	13,7
Max.	46,3	47	41,6	563	13,5	3,8	10,2	17,8
Av.	35,9	38,1	35,5	504,5	7,23	3,09	8,73	15,93
S.D.	5,4	6,2	3	38,9	4,70	0,5	0,72	1,24
V.C. (%)	15,1	16,3	8,5	7,7	65,1	16,2	8,3	7,8

Av. - average; S.D. - standard deviation; V.C. = variation coefficient.

Table 3.18 (a) and (b) show radiological risk indices and statistical parameters calculated based on the results obtained from the analysis of industrial soils.

Table 3.18. The results obtained after calculating the radiological risk indices (a) and (b) the statistical parameters (source: processed according to [Ene et al., 2023a, b])

(a) radiological risk indices

Sample code	DR_{NAT} [nG/h]	DR_{TER} [nG/h]	DR_{TOT} [nG/h]	Ra_{eq} [Bq/kg]	I_G	H_{ex}	AED [mSv/y]	ELCR [$\times 10^{-4}$]	AGD [mSv/y]
R1	69,99	70.9	102,95	149,1	1,10	0,40	0,087	3,0	0,494
R2	57,57	59,01	91,04	122	0,91	0,33	0,072	2,5	0,408
R3	54,92	56,59	88,65	117,2	0,86	0,32	0,069	2,4	0,387
R4	58,72	59,29	91,36	124,9	0,93	0,34	0,073	2,5	0,415
R5	58,86	59,85	91,87	125,4	0,93	0,34	0,073	2,6	0,416
R6	60,85	62,19	94,22	129,8	0,96	0,35	0,076	2,7	0,429
R7	55,16	55,31	87,34	116,5	0,87	0,31	0,068	2,4	0,391
R8	56,25	56,36	88,36	118,7	0,89	0,32	0,069	2,4	0,400

(b) statistical parameters

Min.	54,92	55,31	87,34	116,5	0,86	0,31	0,068	2,4	0,387
Max.	69,99	70,90	102,95	149,1	1,10	0,40	0,087	3	0,494
Av.	59,04	59,94	91,97	125,5	0,93	0,34	0,074	2,6	0,418
S.D.	4,86	4,96	4,96	10,6	0,08	0,03	0,006	0,2	0,034
V.C. (%)	8,2	8,3	5,4	8,4	8,1	8,4	8,3	8,3	8,1

Av. - average; S.D. - standard deviation; V.C. = variation coefficient.

Based on the activity values and the methodology proposed, it was calculated the outdoor absorbed dose rate at 1 m above the ground surface due to γ-rays emission in air from ^{226}Ra, ^{232}Th, and ^{40}K natural radionuclides (DR_{NAT}) and to all detected terrestrial radionuclides (DR_{TER}), including the artificial radionuclide ^{137}Cs, although this one had a small contribution to the terrestrial dose rate (Table 3.18).

Also, Table 3.18 shows the results of the total absorbed dose in air, DR_{TOT}, originated both from terrestrial and cosmic radiation. The values (average/(range)) for absorbed dose rates (59.94/(55.31–70.90) nGy h^{-1} for D_{TER}, 91.97/(87.34–102.95) nGy h^{-1} for D_{TOT}) are comparable with those reported for Romania, 59/(20–125) and 92/(52–163) nGy h^{-1}, respectively, with a slight exceeding of the mean values in the industrial sites which recorded higher radioactivity levels.

To evaluate the radiological hazards resulting from soil radioactivity, radium equivalent activity (Ra_{eq}), representative gamma index (I_G), external hazard index (H_{ex}), annual effective dose (AED), excess lifetime cancer risk (ELCR), and annual gonadal dose rate (AGD) were calculated (Table 3.18).

Compared with the recommended values (Ra_{eq}=370 Bq kg^{-1}, I_G<1, H_{ex}<1, AED=0.070 mSv y^{-1}, ELCR=2.9 × 10^{-4}, AGD=0.300 mSv y^{-1}), our results indicate higher values for AED in sites nos. 1,2,4,5 and 6; for I_G and ECLR in site no.1, and for AGD in all sites. As a result, gamma radiation emitted from the soil samples around metallurgical complex from Galați might pose health hazards for the inhabitants of the area.

IV. GENERAL CONCLUSIONS, ORIGINAL CONTRIBUTIONS AND PERSPECTIVES

General conclusions

The PhD thesis, entitled: "***Performant analytical techniques used for the toxic substances monitoring and industrial waste management***", was designed to highlight a way in which a physico-chemical characterization of hazardous industrial waste can be made regardless of whether it is of an inorganic, organic or radiological nature. It is considered that the content of this doctoral thesis deals with the determination of the content of toxic chemical and radiological substances in industrial soil samples located in the immediate vicinity of some active or inactive industrial facilities in the Brăila-Galați region, in southeastern Romania.

The experimental results obtained as a result of the analyzes applied and exposed in this thesis, can contribute to changing the way of interpretation regarding the management of hazardous industrial waste and the impact it has on environmental factors, ecosystems and implicitly human health.

The major economies of the world face very serious problems related to the control of industrial emissions of gaseous pollutants into the atmosphere, the generation of large volumes of solid and liquid industrial waste, the pollution of water and soil with toxic chemical elements, the health status of the population, etc. At the same time, the governments of the world's major economic powers are adopting plans and measures to reduce the impact of industrial pollutants on environmental factors.

At the level of the European Union, laws have been implemented that regulate the transfer of hazardous waste between member states, the method of final storage of industrial waste, their recycling strategy, etc. From the specialized literature, it is understood that the European states that annually generate the largest quantities of hazardous waste are not among the countries that export the largest quantities of such waste. This phenomenon probably does not occur because considerable efforts are being made to develop applicable technologies in hazardous industrial waste treatment/recycling operations. According to statistics, Romania has generated in the last 7 years a total amount of hazardous waste of less than one million tons each year and ranks among the top small generators of hazardous waste in the EU.

Thanks to the contribution of scientists throughout history, nowadays we can use high-performance analytical techniques to determine the content of toxic substances in samples of various matrices. These techniques have demonstrated that they can be applied without a large consumption of material resources and time.

The non-destructive analytical technique ED-XRF has been successfully applied to the determination of toxic chemical elements in industrial waste matrices such as wastes with high mercury and arsenic content from the decommissioning of industrial facilities and wastes resulting from industrial galvanizing and pickling processes. metal surfaces. It should be noted that this technique has also been applied to the determination of heavy metal content in industrial soils alongside other destructive techniques such as AAS, ICP-MS and INAA.

Accelerated Ion Beam Nondestructive Analysis (IBA) – Particle Induced X-ray Emission (PIXE) and Gamma (PIGE) techniques have contributed substantially to the determination of the content of toxic elements with atomic number Z less than 20 or more large, from hazardous industrial waste samples. By means of these techniques the concentrations of elements such as fluorine, chlorine, sulphur, phosphorus and sodium were determined and thus a connection could be made between the content of chemical elements in a sample of hazardous waste and the way it was obtained following the industrial process from which have result.

The gamma spectrometry method applied in-situ was very beneficial because it was possible to determine the content of long-lived radionuclides such as ^{238}U and ^{232}Th, their mass and nuclear activity, from unknown radioactive waste samples later classified as materials of nuclear interest. Radiometric methods made it possible to differentiate between solid materials contaminated with ^{238}U and ^{232}Th and uncontaminated ones, respectively to determine the flow of gamma radiation to which the operating personnel were subjected during the physical inventory of nuclear materials. The "nuclear program" that took place within the company SetCar S.A. from Brăila is a complete example of the application of good practices for the management of nuclear materials and radioactive waste containing long-lived radionuclides.

The analytical technique of gas chromatography was applied to determine the concentrations of 209 PCB types contained in industrial transformer oils from 4 different countries. The results obtained following the application of this method made it possible to compare the degrees of contamination of oils with PBC and it was observed that the oil contained in the transformer from Romania was the most contaminated with PCB.

The low-background high-resolution gamma spectrometric method demonstrated that there are significant concentrations of natural and artificial radionuclides in the soils sampled around the metallurgical complex from Galați, and based on the results obtained, a radiological health risk assessment was carried out the population living near this complex.

The characterization of the soils sampled around the former chemical plant from Brăila County was carried out using ED-XRF, AAS and ICP-MS analysis methods. Following the analyzes carried out and the results obtained, a toxicological risk assessment was carried out, from which it emerged that the soils around this former compound are polluted with heavy metals and that they represent a real threat to the health of the population in the area, especially from due to the fact that these soils are exploited agriculturally.

The instrumental technique of neutron activation analysis (INAA) was able to simultaneously determine a number of 40 chemical elements from the soil samples taken around the metallurgical complex from Galați. In this case the ED-XRF analytical method was used to determine the content of heavy metals in the soil that the INAA analytical method cannot identify because the isotopes of those chemical elements do not activate in the neutron field. The results of the analyzes identified very high concentrations of mercury, chromium, zinc, etc. in the analyzed industrial soil samples. These results were used to calculate some pollution indices on the basis of which a toxicological risk assessment can be carried out. The toxicological risk assessment highlighted the fact that the industrial soils sampled around the metallurgical complex are highly polluted with heavy metals and represent a major factor in degrading the health of the population living in that area. This soil pollution persists or may expand due to the activity of the metallurgical complex.

It is very important to note that there are geological repositories for the safe final disposal of hazardous waste and facilities that are suitable for processing this waste. Some industrial facilities are designed to treat hazardous waste in order to recover some chemical elements such as metallic mercury, nickel, chromium, zinc, etc.. Other industrial facilities are capable of treating PCB-contaminated oils from industrial transformers to dechlorinate and recycle the oil. There are industrial facilities specially designed for the decontamination of metallic and non-metallic component parts of high-voltage electrical equipment contaminated with PCBs with the aim of recovering and reusing them from an economic point of view.

Original contributions

The PhD thesis "***Performant analytical techniques used for the toxic substances monitoring and industrial waste management***" focused on the adaptation and optimization

of some high-performance analytical techniques (ED-XRF, AAS, ICP-MS, PIXE, PIGE, INAA, GRS and GC) for the compositional characterization and radiological evaluation of hazardous industrial waste and industrial soils. The main original contributions are:

- optimizing the application of the ED-XRF method to reduce the analysis error values by improving the peak-background ratio in the energy spectra. This optimization was put into practice by increasing the irradiation time of hazardous industrial waste samples;

- characterization of trace elements composition of industrial waste containing hazardous substances from the decommissioning of some industrial facilities or resulting from the industrial activities of some economic operators on the territory of Romania in order to establish the best criteria for managing this waste. The characterization of hazardous industrial waste was carried out with the help of ED-XRF, PIXE and PIGE analytical techniques;

- adoption of the best practices related to the total management of materials of nuclear interest and radioactive waste represented by solid materials contaminated with ^{238}U and ^{232}Th. Compliance with national and international norms in the nuclear field, the application of analytical gamma spectrometry methods for the identification of ^{238}U and ^{232}Th from unknown samples and the use of radiometric equipment to determine the gamma radiation flow to which the operating personnel were subjected during the physical inventory of nuclear materials, were at basis for carrying out the operation of the total management of all nuclear and radioactive materials. By obtaining these experimental results, a contribution was made to the updating of national and international databases regarding holders or former holders of interest nuclear materials and radioactive waste;

- establishing the degree of PCB contamination of oils from high-voltage industrial electrical equipment to make a parallel between the concentrations obtained in this research and the results obtained in other scientific contributions from abroad, respectively to establish the technological parameters of the installation, property of SetCar S.A. Braila, for the dehydration, dechlorination and reuse of these oils. The determination of the PCB content in industrial transformer oils contributed to the updating of the inventory regarding the quantities of hazardous waste with PCB content located on the territory of Romania;

- determining the elemental composition of the soils and performing the ecological and toxicological risk assessment related to the health of the population that agriculturally exploits the soils polluted with heavy metals located around the former chemical plant in Brăila county. This ecotoxicological risk assessment was carried out based on the results obtained following the application of complementary analytical methods ED-XRF, AAS, ICP-MS and PIGE for the analysis of industrial soil samples and a set of soil pollution/contamination indices;

- determining the compositional scheme of the soils and performing the ecological and toxicological risk assessment related to the health status of the population living in the vicinity of the Galati metallurgical complex using the experimental data resulting from the application of INAA and ED-XRF instrumental and non-destructive analytical techniques for the analysis of soil samples industrial and simple pollution and ecotoxicological indices;

- the assessment of the mobility and the risk of migration in the depth of the soil of a large number (42) of chemical elements (metals, rare earths, actinides, lithogenic elements, trace elements) detected in the industrial area of the Galati metallurgical complex;

- radiological risk assessment, related to the health of the population living near the Galati metallurgical complex, based on the results obtained following the application of the analytical technique of high-resolution and low-background gamma spectrometry on industrial soil samples. The results of this study will contribute to the updating of national databases on the content of natural and artificial radionuclides in industrial soils and international databases on the radioactivity of soils around steel enterprises.

Perspectives

The most important perspectives in the scientific field are formulated as follows:

✓ expansion of the experimental program supported by the use of high-performance techniques for the characterization of other industrial waste containing hazardous substances in order to achieve optimal traceability regarding the total management of this waste;

✓ characterization of the soils around the active or inactive industrial facilities from Brăila city and county for the toxicological and radiological risk assessment related to the health status of the population living in the vicinity of these industrial facilities;

✓ optimization of industrial plants capable of processing hazardous waste already owned by SetCar S.A. Braila for improving their treatment/decontamination efficiency;

✓ development of already existing experimental industrial plants, property of SetCar S.A. Brăila, respectively of the new technologies designed for the treatment of dangerous waste such as: metallic mercury, waste water contaminated with petroleum products, soil contaminated with petroleum products, etc.;

✓ publication in the scientific field of the experimental data resulting from the application of the optimization and development methods of the SetCar S.A. installations. designed to treat industrial waste and to expand the experimental program on the characterization of industrial waste containing hazardous substances.

ANNEXES

Annex 1. Frames during the repackaging and weighing operations of all radioactive substances containing nuclear materials, respectively of radioactive waste: (a), (b) and (c) repacking of radioactive substances containing nuclear materials by appropriately equipped operating personnel, (d) provisional labeling of vials containing uranyl perchlorate and thorium nitrate, (e) and (f) vials containing nuclear material identified and prepared for weighing, (g) weighing a vial containing nuclear material, (h) provisional labeling of vials containing unidentified radioactive substances, (i), (j), (k) and (l) weighing solid materials contaminated with ^{238}U, ^{232}Th and their descendants (glass, metal, plastic and used protective equipment), (m) specific labeling of a container containing contaminated solid materials, (n), (o) and (p) weighing containers containing contaminated solid materials (source: adapted according to [Sloată and Ene, 2021a, b])


(a)


(b)


(c)


(d)


(e)


(f)


(g)


(h)


(i)

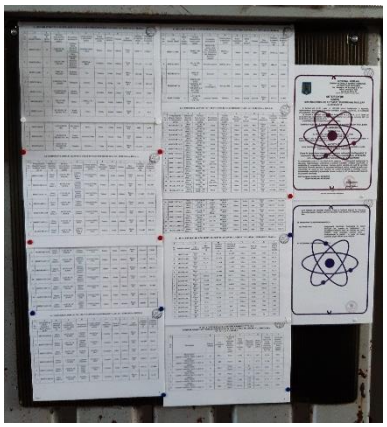

(j)


(k)


(l)

Annex 2. Representation of the storing nuclear materials way, including radioactive waste and the layout of the temporary storage: (a) placement of the hazard warning panel and nomination of personnel who have access to the temporary storage facility, (b) location of physical inventory and holding authorization inside the temporary storage facility, (c) location of the fan for exhausting radioactive gases (radon and thoron), (d) arrangement of vials with nuclear materials containing ^{232}Th inside the closet, (e) arrangement of vials with nuclear materials containing ^{238}U inside the closet, (f), (g) and (h) the closet model used for the storage of nuclear materials and the method of sealing and (i) internal aspect representation of the temporary storage and the way of storing radioactive waste inside it

(a)



(b)

(c)

(d)

(e)

(f)

(g)

(h)

(i)

Annex 3. Images during the transportation/transfer of nuclear materials and radioactive waste: (a), (b) and (c) packing vials containing nuclear materials to avoid their destruction during transport, (d) measuring the gamma dose rate, in contact with the vehicle, before carrying out the transport/transfer, (e) and (f) labeling metal barrels containing radioactive waste and loading them into the transport vehicle, (g) and (h) how to sign transport vehicles according to ADR class 7 norms

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

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2. PROJECT JOINT OPERATIONAL PROGRAMME BLACK SEA BASIN 2014-2020, CODE BSB165, Title: Creating a system of innovative transboundary monitoring of the transformations of the Black Sea river ecosystems under the impact of hydropower development and climate change (HydroEcoNex), Project coordinator Ene Antoaneta (Dunarea de Jos University of Galati).

3. RESEARCH PROJECT 2017 JINR-Romania no. 80, Investigation of advanced functional materials using atomic and nuclear analytical techniques and imaging microscopy, Theme no. 03-4-1128-2017/2019, Investigations of Neutron Nuclear Interactions and Properties of the Neutron, Protocol No. 4613-4-17/19, Director Romania**:** Ene Antoaneta.

4. RESEARCH PROJECT 2019 JINR-Romania no. 63, Assessment of industrial impact on agroecosystems and human health risk in Romania using nuclear and related analytical techniques, JINR Theme no. 03-4-1128-2017/2019, Investigations in the Field of Nuclear Physics with Neutrons, Leaders from Romania: Ene Antoaneta (Project Director, UDJ Galati), Stihi Claudia (Project Responsible, Valahia University of Targoviste).

5. RESEARCH PROJECT 2017 JINR-Romania no. 81, Applied research on air and soil pollution with toxic elements using nuclear and related analytical techniques, Theme no. 03-4-1128-2017/2019, Investigations of Neutron Nuclear Interactions and Properties of the Neutron,

Protocols Nos. 4619-4-17/19,4613-4-17/19,4610-4-17/19, Leaders from Romania: Stihi Claudia (Project Director, Valahia University of Targoviste), Ene Antoaneta (Co-director, UDJ Galati), Dan-Gabriel Ghita (Co-director, IFIN-HH Magurele).

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11. GRANT DE CERCETARE INTERVENT nr. 9187/2023, Cercetări privind aplicațiile interdisciplinare ale tehnicilor avansate de analiză și control în studii de mediu, sănătate și știința materialelor (UDJ) Galați, România. Ene Antoaneta (Director de Proiect, UDJ Galati).