IAEA International Atomic Energy Agency

EEAE ΕΛΛΗΝΙΚΗ ΕΠΙΤΡΟΠΗ ΑΤΟΜΙΚΗΣ ΕΝΕΡΓΕΙΑΣ GREEK ATOMIC ENERGY COMMISSION

IAEA Postgraduate Educational Course in Radiation Protection and the Safety of Radiation Sources

Determination of Uranium in Hair Samples

Sofia C. Papadopoulou
Biologist

Supervisor:
Dr. K. Kehagia
Environmental Radioactivity Department
Greek Atomic Energy Commission

ATHENS 2019

Cover photo: https://www.atomicheritage.org/history/uranium-mining

Abstract

Uranium is a naturally occurring radioactive heavy metal, present in many different mineral deposits, such as granites and uraninite. The redistribution of uranium in the environment may result in human intake by mainly though ingestion of food and water and inhalation. Uranium is considered as a nephrotoxic metal due to chemical effects in the proximal tubules, while radiological risks of natural uranium are of lower importance. The assessment of occupational or environmental exposure to uranium is generally carried out by analysis of urine, which reflects recent or chronic ongoing exposure. On the contrary, scalp hair analysis could be used as a bioindicator of exposure to uranium months or even years after an exposure, because uranium may be transferred by the bloodstream and accumulated into hair during growth.

The aim of this project work is the determination of uranium in hair samples by alpha spectrometry. For this purpose, hair samples from 7 non-occupationally exposed individuals, residents of 5 countries (Greece, Bosnia and Hercegovina, Portugal, UK and Australia) were collected and analyzed. The analysis procedure included sample pre-treatment, separation of uranium by ion exchange chromatography, source preparation by electrodeposition and counting by an alpha spectrometry system. According to our results, the range of activity of ^{238}U was 0.115-0.895 mBq/g which corresponds to a mass range of 9.2-71.9 ng/g. The activity of ^{234}U was found between 0.175-0.874 mBq/g. Uranium levels as well as $^{238}U/^{234}U$ ratios appear to be in accordance with the respective values from other studies in hair of non-occupationally exposed people. In addition, none of our concentrations exceeds the value of 130 ng/g reported in the ICRP (Publication 23). Moreover, the values of our study appear lower than those of people that consume water of high uranium background. The highest value that was found in our samples (0.895 mBq/g or 71.9 ng/g of ^{238}U) could be related to the dietary habits or the age of the individual. However, further experiments and epidemiological studies are needed for clearer conclusions.

Acknowledgments

The present work was part of the Postgraduate Educational Course in Radiation Protection and the Safety of Radiation Sources which took place in Athens, 2018-2019. The project work was conducted in the Environmental Monitoring Department, Greek Atomic Energy Commission. I would like to express my heartfelt thanks to my supervisor, Dr. Kehagia, for the guidance, help and support she offered to me during the whole work. I also deeply thank Mr. Xarchoulakos for the guidance and contribution to the laboratory procedures of this work.

1. Introduction

1.1 Uranium: general information, isotopes and occurrence

Uranium (U) is a chemical element with atomic number 92 and belongs to the actinide series of the periodic table. It is the heaviest naturally occurring element, having a relative atomic mass of 238.029. It was first discovered in the mineral pitchblende by Martin Heinrich Klaproth in 1789. Later, in 1896 Henri Becquerel discovered that uranium emits penetrating rays. Marie and Pierre Curie with their extensive work on radium, polonium, uranium and other elements described this "mysterious" property as radioactivity [1].

Natural uranium is a mixture of 3 primordial radioisotopes: ^{238}U (99.2742%), ^{235}U (0.7204%) and ^{234}U (0.0054%) with their relative abundance given in the parentheses. ^{238}U is the parent isotope of the uranium decay series (4n + 2) and decays to ^{234}Th. ^{234}U belongs to the uranium series and arises from the β decay of ^{234}Pa, which comes from the β decay of ^{234}Th. ^{235}U is the parent isotope of the actinium series (4n + 3) [1, 2]. All three isotopes disintegrate by α decay and, compared to human life, they have very long half-lives. Some of the nuclear properties of the natural isotopes of uranium are listed in Table 1.1.

Table 1.1: Nuclear properties of the natural isotopes of uranium [3, 4].

Isotope	Half-life (years)	Energy of α particle* (keV)	Probability %
^{238}U	$4.468 \cdot 10^9$	4151	22.33
		4198	77.54
^{235}U	$704 \cdot 10^6$	4214.7	5.95
		4366.1	18.80
		4397.8	57.19
		4596.4	4.74
^{234}U	$2.455 \cdot 10^5$	4722.4	28.42
		4774.6	71.37

* In the Table are listed only the energies of α particles with a probability higher than 4%

Apart from the natural isotopes of uranium, there are also over 20 synthetic isotopes produced by bombardment of nuclei of elements such as uranium and thorium with protons, neutrons or other particles [5]. ^{232}U, an artificially produced α particle emitter, has found extensive use in chemical and physical studies as uranium tracer.

Uranium is a silvery-grey metal with abundance of 2-4 ppm in earth's crust and 1-3 ppb in seawater, thus it is more common than silver, mercury and cadmium. Compounds of uranium are found in hundreds of different mineral deposits, such as granites, uraninite, uranyl phosphates, arsenates, carbonates and sulfates. In the past uranium was used as a colorant in glass and other materials. Nowadays, due to its fissile properties, uranium is mainly used as fuel in nuclear power plants, either enriched in ^{235}U or not. Depleted uranium (<0.3% in ^{235}U) is used as counterweight for aircraft, in ammunition and armor and as a shielding material for radiation protection [1].

Due to natural geological formations several mineral deposits in the world, like those in Canada, Australia and Kazakhstan, contain significant quantities of uranium. In some areas uranium concentrations are increased due to anthropogenic activities involving the extraction of minerals and their processing. Examples of such activities are uranium mining, milling, combustion of coal and other fuels, and phosphate fertilizers production. Natural as well as human-related radioactive deposits of uranium belong to the so-called Naturally Occurring Radioactive Materials-NORM [1, 6].

As a heavy radioactive metal with natural occurrence, uranium can potentially be a human health hazard due to chemical and radiological effects. Environmental fate of uranium, possible routes of human exposure and health effects are discussed in the following paragraphs.

1.2 Environmental mobility of uranium

Uranium in minerals can be redistributed in the environment naturally by wind and water erosion and volcanic eruption, as well as through technological activities like those including the nuclear fuel cycle and phosphorus extraction. These processes may result in the release of uranium in air, which can then be deposited on land and surface waters. The rate of air deposition depends, among others, on uranium particle size, density, concentration and chemical form [7].

Airborne uranium deposited on land may be incorporated into soil, re-suspended in air or washed to surface water and groundwater. Factors that affect the mobility of uranium include soil porosity and particle size, oxidation-reduction potential and pH. Inorganic or organic ligands that can form soluble complexes with uranium can result in the mobility of uranium in water. Compounds that contain tetravalent uranium are insoluble in mildly acidic to alkaline conditions, while those containing the uranyl moiety $(O=U=O)^{2+}$ are highly soluble and mobile [1].

Uranium present in soluble complexes in surface water may be distributed to rivers and oceans. However, in reductive environments U^{6+} can be reduced to U^{4+} resulting in insoluble salts which can be deposited onto the sediment. Uranium can also be removed from solutions by physical processes such as adsorption onto iron or manganese oxides and thus be deposited onto sediment [7].

In theory the radioactivity ratio of ^{234}U to ^{238}U equals to unity, as secular equilibrium between ^{238}U and its progeny is established. However this appears to be the case only in undisturbed crustal rocks. Certain physical and chemical processes may result in the separation of the parent radioisotope from its progenies thus in disturbance of the equilibrium. An example of physical process is the alpha recoil ejection of ^{234}Th nucleus that causes its separation from its parent ^{238}U. Moreover, ^{234}Th is more soluble than uranium and can be washed by groundwater, thus be removed from rocks and disturb the equilibrium. Consequently, the ratio of ^{234}U to ^{238}U can appear different from unity in air, soil and water samples [8, 9].

Soluble compounds of uranium present in soil can be absorbed by plants and thus enter the trophic chain of animals and eventually humans. The main route of entry is the root system of plants, while significant translocation to aboveground parts has not been observed [10]. In aquatic animals uranium can be found at concentrations that follow a declining pattern towards higher levels of the trophic chain due to low assimilation. Bioaccumulation of uranium depends on its chemical and physical form as well as on factors regarding environmental conditions and the age of the organism [7].

1.3 Environmental levels of uranium and human exposure

As discussed, uranium can be found in air, water and food as a result of natural or technological processes. As a consequence, intake of uranium in humans is possible through inhalation and ingestion. The main route of intake for members of the public is ingestion of food and drinking water. Individuals consuming food and water in areas

with high uranium background have a higher intake potential. For occupationally exposed workers to airborne uranium such as those who work in uranium mines, in processing facilities of uranium or in the phosphate fertilizers industry the main route of intake is inhalation [7].

Environmental levels of uranium have been determined and the intake of uranium in human has been estimated by several studies conducted in different areas worldwide. In air the average urban airborne concentration has been reported at 0.05 ng/m^3 and the intake of uranium through air has been found to be extremely low.

Uranium levels in drinking water vary according to the area. For example, the average concentration in drinking water from 130 sites in Toronto was found 0.40 μg/l, whereas the respective value from 928 sites in the USA was 2.55 μg/l and 20 μg/l in New Mexico. Uranium exists in higher levels usually in smaller supplies. Such an example is some private supplies in Canada, in which a concentration of about 700 μg/l has been reported. Surveys in Finland and Ontario have resulted in an estimation of daily intake of uranium of about 2.5 μg and 0.8 μg respectively [11].

Uranium has been detected in a variety of foodstuffs. The highest concentrations have been found in shellfish. Lower levels exist in fresh vegetables, cereals and fish. From the results of studies in Japan and USA, the daily intake of uranium from food per capita is estimated from 1-4 μg [11].

1.4 Biokinetics and metabolism of uranium

Inhaled particles with AMAD[1] greater than 10 μm are expected to be removed from the tracheobronchial region and swallowed. Smaller particles can reach the lower parts of the tract (alveolar region) where the gases exchange takes place. There, uranium compounds can be absorbed to the blood at rates that depend on their solubility. Soluble compounds can be absorbed to blood within days (Inhalation Type F- fast dissolution), less soluble within weeks (Inhalation Type M-medium dissolution) and insoluble compounds can remain to the lungs even for years (Inhalation Type S-slow dissolution) [7, 12].

[1] Activity Median Aerodynamic Diameter

Ingestion is another important route of uranium intake. The ICRP[2] has developed a biokinetic model for oral exposure that can be applied to uranium. After ingestion of uranium through food or water consumption only 1-2% is absorbed by the gastrointestinal tract (GI) and transferred to blood whereas the rest is excreted with feces within few days. The absorption in GI tract depends mainly on the solubility of the uranium compounds. Uranium in blood can be associated with red blood cells. About 60% of uranium in blood is transferred directly to the bladder and about 12% is retained in renal tubules in kidneys before excretion. A significant amount of uranium is accumulated in bone and a smaller amount can be retained in the liver. In bone, uranyl ions replace calcium in hydroxyapatite complexes of bone crystals. Eventually uranium will be excreted with urine (primarily) or feces [13, 14].

The daily intake model value of uranium in reference man[3] from food and fluids has been reported to 1.9 μg and from airborne particles 0.007 μg. The daily loss of uranium has been reported as: 0.05-0.5 μg with urine, 1.4-1.8 μg with feces and 0.02 μg with hair loss [15].

1.5 Health effects of uranium

As a heavy metal, uranium poses chemical toxicity hazards. Moreover, uranium can cause radiological effects due to α particle emission. Alpha particles have a high positive charge of 2+ and large mass, thus interact highly with matter and have high stopping power. Consequently α particles are characterized by high LET (Linear Energy Transfer), meaning that they deposit all of their energy locally in matter. The deposition of energy can cause direct ionization of matter with cancer being the major latent harmful effect [16].

Radiological risks of natural uranium are in general of lower importance due to the fact that ^{238}U, the most abundant isotope, has a low decay constant as a result of its long half-life. Enriched uranium contains ^{235}U at percentages from 2-4%, thus the ratios of $^{234}U/^{238}U$ and $^{235}U/^{238}U$ are higher than those of natural uranium. Because ^{235}U and ^{234}U have higher decay constants than ^{238}U, enriched uranium has higher specific activity than natural uranium and poses increased risk of radiotoxicity.

[2] International Commission for Radiation Protection
[3] 20-30 years old Caucasian man, 70 kg, 170cm height, place of residence: Western Europe or North America

The impact of each type of toxicity depends highly on uranium compounds solubility. Chemical toxicity is of greater importance regarding soluble uranium forms. On the other hand, radiological toxicity risk is increased in case of inhalation of insoluble compounds.

Generally, toxicity in organs and tissues depends on the retention time at these sites. The retention time is affected by the chemical form of uranium and the route of exposure. In case of inhalation, soluble uranium compounds appear to be less toxic to lungs because they are rapidly absorbed to blood and reach distal organs, thus are mostly potent systemic toxicants. Poorly soluble and insoluble compounds tend to remain in the lungs for a prolonged period and are more likely to induce chemical and radiological pulmonary toxicity [17].

Uranium, after its release in blood circulation, accumulates primarily in bone and kidneys. It is considered as a nephrotoxic metal, due to chemical effects in the proximal tubules. Preclinical studies on laboratory animals have shown histological signs of hepatic toxicity after oral intake of uranium. Few human data are available that adequately describe the dose-response toxicity of uranium after oral exposure. Several epidemiological studies tried to associate chronic exposure to uranium from drinking water with altered kidney function by examining kidney biomarkers in urine [11]. The guideline value of uranium in drinking water from the World Health Organization concerning kidney chemical effects is 30 μg/l. In respect of radiological effects the respective guidance levels are 10 Bq/l for ^{238}U and 1 Bq/l for ^{234}U [18].

Human and animal studies have examined the potential carcinogenicity of uranium. Some studies regarding occupational exposure have found significant increases in the risk of lung cancer, although it is not clear whether uranium is the causative agent and whether the cancer is due to chemical toxicity or radiotoxicity. In general, human and animal studies have not found increases in the risk of cancer in other tissues, including the kidney and bone [7].

1.6 Hair as an indicator of exposure to uranium

The assessment of occupational or environmental exposure to uranium is generally carried out by analysis of urine because uranium is primarily excreted via this route. Urine analysis may reflect recent exposure (within days after an incident) or chronic ongoing exposure. Thus, after accidental exposure urine samples should be collected within a short time in order to be representative. Moreover, analysis of urine is of limited

value as indicator of stores, because the hemostatic mechanism operates to keep many of the components of blood constant [19]. On the contrary, determination of uranium in hair samples could yield better insights even a long time after an exposure incident [20, 21].

Human hair is a keratinous appendage that develops from large cavities called follicles. Hair follicles extend from the surface of the skin through the stratum corneum and epidermis into the dermis. Basal layers, which produce hair cells, surround the bulb. Blood vessels are in contact with the base of the bulb and carry nutrients to the growing hair [22]. Hence, metals and other toxicants present in the bloodstream may be transferred and accumulated into hair during growth. Metals such as uranium are incorporated into hair in the keratin structure by attachment to the abundant sulfhydryl group of the follicular proteins. This bond is relatively stable and resists attack from shampoos and most other preparations commonly applied to hair. Thus, human head hair is a recording filament which can reflect metabolic changes of many elements over a long period of time, as well as past contamination events [19, 23]. For these reasons, scalp hair analysis could be used as a bioindicator of exposure to uranium months or even years after an exposure incident [22]. Additional advantages of hair analysis are the easy collection, transportation and long term storage of the samples.

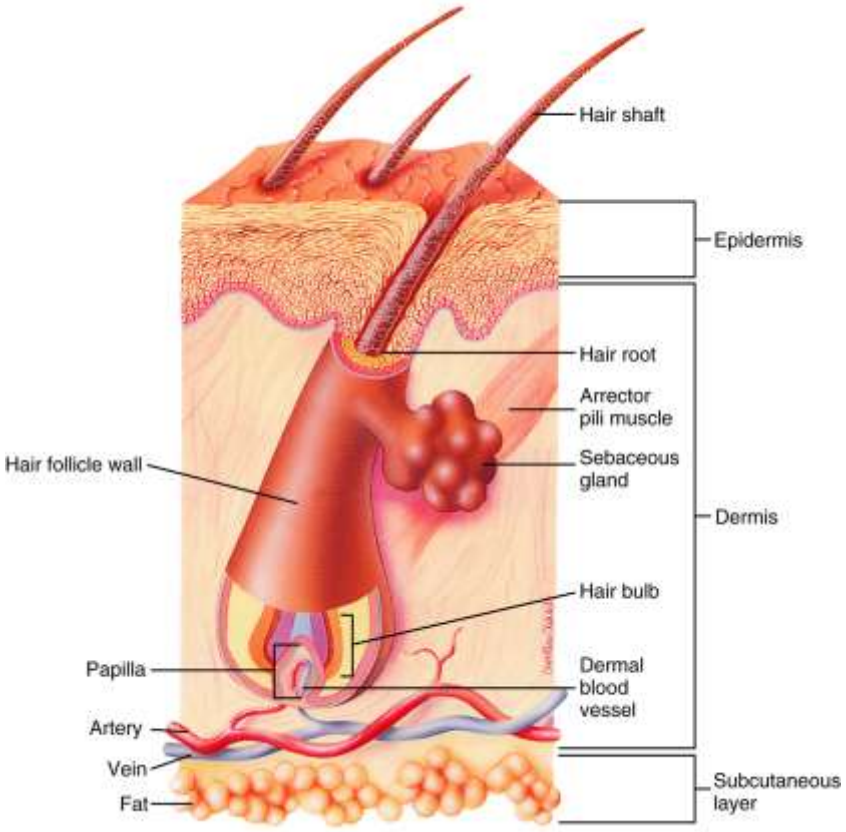

Figure 3.1: Hair anatomy [24]

2. Materials and Methods

2.1 Introduction

The aim of this project work is the determination of uranium in human hair samples of a non-occupationally exposed group by alpha spectrometry. For this purpose, a procedure of 4 steps is followed: a) sample pre-treatment for the removal of organic compounds, b) separation of uranium by ion exchange chromatography, c) source preparation by electrodeposition and d) counting by an alpha spectrometry system. In the following paragraphs the aforesaid process, as well as the calibration of the spectrometry system used, is described in detail.

2.2 Apparatus

1. High resolution alpha spectroscopy system, Alpha Analyst (Canberra)
2. Electrodeposition apparatus with a platinum anode and a cathode (stainless steel 304 polished disk of 25mm diameter and 1mm thickness).
3. ^{241}Am, ^{244}Cm, ^{239}Pu standard radionuclide source (Eckert & Ziegler)
4. DC power supply, 0 to 12 V with electrodes, E3610A (Agilent Technologies)
5. Muffle furnace (Carbolite)
6. Electronic balance (OHAUS)
7. Hot plate magnetic stirrer, SB162 (Stuart)
8. Ultrasonic cleaning bath, Starsonic 1835 (FALC Instruments)
9. Pipettes, 100-1000 ml (Eppendorf)
10. Porcelain crucibles (CoorsTek)
11. Beakers, 250 ml (TGI)
12. Glass chromatographic column
13. Plastic Pasteur pipettes
14. Volumetric cylinders, 25 ml (ISOLAB)

2.3 Reagents

1. ^{232}U tracer solution, 0.012 Bq/ml (NIST)
2. Anion exchange resin AG 1-X4, Biorad
3. conc. Nitric Acid, 65% (Merck kGaA)
4. conc. Hydrochloric acid, 37% (Merck kGaA)
5. Hydrochloric acid solution, 8M
6. Hydrochloric acid solution, 0.1M
7. conc. Sulfuric acid, 95% (VWR)
8. Ammonium sulfate (Merck kGaA)
9. Ammonia solution, 25% (Riedel de Haen)
10. Thymol blue pH indicator (Sigma-Aldrich)
11. Ethanol, absolute (Merck kGaA)

2.4 Sample collection and pre-treatment

The group of study comprised 7 adult volunteers, residents of 5 different countries. The hair samples were collected from the occipital part of the head with stainless steel scissors and stored in sealed plastic bags. The volunteers kindly provided information regarding their age, country of residence (listed in Table 2.1), dietary habits and water consumption.

Table 2.1: Samples information.

Sample code	Sample mass (g)	Gender	Age	Country of residence
S-1	1.08	Female	26	Bosnia and Herzegovina
S-2	1.03	Female	27	Portugal
S-3	2.67	Female	35	Greece
S-4	3.17	Male	41	Greece
S-5	2.20	Male	65	Greece
S-6	1.22	Female	23	Australia
S-7	1.68	Female	41	United Kingdom

In the pre-treatment step, each sample was placed into a porcelain crucible, weighed and spiked uniformly with 0.5 ml of ^{232}U tracer solution of known activity (0.012 Bq/ml), and let for few minutes to dryness. The use of the tracer aims at the determination of the activity concentration and the chemical yield of the procedure, which is used in the final

calculations. Then, each crucible was placed on a hot plate (200-250 °C) and samples were wet ashed by alternately adding 3 ml of nitric acid (HNO_3, 65%) and equal volume of hydrochloric acid (HCl, 37%) 3-4 times (18-24 ml in total). Finally, the samples underwent dry ashing in a muffle furnace at 500 °C for at least 6 hours.

2.5 Separation of uranium by ion exchange chromatography

After the pre-treatment of the samples, separation of uranium by ion exchange chromatography followed. Shortly, 2.5 g of anion exchange resin, slurring in approximately 10 ml of 8N HCl solution, were loaded into a 13-mm-ID glass chromatographic column. The pre-condition of the resin was performed by the gradual addition of 50 ml 8N HCl, which was discarded. Subsequently, the sample ash from the pre-treatment step was dissolved in a small amount of 8N HCl (heating is used if necessary) and the sample solution was loaded into the column. The column was rinsed by adding 100-125 ml of 8N HCl, which was discarded. Uranium was eluted with 100 ml of 0.1N HCl. The eluate was collected in a 250 ml beaker and after that evaporated on a hotplate to almost dryness. When the eluate's volume was approximately 5 ml, 1 ml of conc. nitric acid was added and the procedure continued until dryness.

2.6 Source preparation

The sources for alpha spectrometry were prepared by electrodeposition of uranium onto stainless steel disks, according to the following procedure: The residue from §2.5 was dissolved in 15 ml electrolyte solution, which consisted of 1M ammonium sulfate adjusted to pH 3.5 (1.98g $(NH_4)_2SO_4$ dissolved in 15 ml distilled H_2O. Then, 2 drops of conc. H_2SO_4 were added). The electrodeposition cell, with a platinum anode and a polished stainless steel cathode disk was prepared, and the distance between anode and cathode was adjusted to 1 cm. Then, electrodes were connected to the DC power supply and the electrolytic cell. The sample solution was added to the electrodeposition cell with a pasteur pipette and the cell was submerged to water. Current was adjusted to 1.2 Amperes, the power was turned on and the electrodeposition was carried out for 1 hour. One minute before the end, 1 ml of ammonia solution 25% was added into the cell. The addition of ammonia aims at the fixing of uranium on the cathode disk. Promptly, the power supply was turned off, the electrodes were disconnected and the source was quickly removed from the cell. Finally, the source was rinsed with distilled H_2O and ethanol and air dried.

2.7 Counting by alpha spectrometry

The uranium sources were measured by alpha spectrometry for 7200 minutes. The equipment used is a fully automated and integrated alpha spectroscopic system from Canberra with 12 passivated implanted planar silicon (PIPS) detectors and an active area of 600 mm^2. The system is computer controlled by software (Genie 2000 Alpha Analyst V2.0B), which coordinates all operations such as detector set-up and calibration, quality assurance, background collection, sample analysis and control of electronics. The chambers are automatically air vented at sample loading and unloading, while during measurements the pressure inside the chamber remains at very low predefined levels. The counting efficiency of the system is 24%.

2.7.1 Calculations

After the measurement of the samples the specific activity of the uranium isotopes is calculated, taking into account a series of parameters which are further discussed. Calculations are performed automatically by the system's software according to the measurement protocol which is defined before the start of the measurements and includes all parameters needed. The following formulas represent the main calculations performed and are expressed in a simplified way.

2.7.1.1 Chemical recovery

The radiochemical procedures performed during the analysis of uranium in hair and biological samples in general, result always in a small loss of quantity of the analyte. For this reason, it is necessary to calculate the radiochemical recovery factor, which is the fraction of uranium that remains intact after the end of the analysis. The determination of the chemical recovery (R) is executed by the following formula, according to the measurement of the tracer ^{232}U used.

$$R = \frac{N_{tracer}}{A_{tracer} \cdot t \cdot \eta}$$

Where N_{tracer} the total net counts of the tracer, A_{tracer} the activity of the tracer at the time of measurement, t counting time in seconds and η the counting efficiency of the detector (discussed in § 2.7.2).

2.7.1.2 Activity concentration

The activity concentration or specific activity of the sample is calculated according to the formula:

$$C_A = \frac{N_{sample} \cdot A_{tracer}}{N_{tracer}}$$

Where N_{sample} the total net counts of the sample, A_{tracer} the activity of the tracer at the time of measurement, N_{tracer} the total net counts of the tracer.

2.7.1.3 Minimum Detectable Activity

The calculation of the Minimum Detectable Activity for a given radionuclide at the 95% confidence level is based on the Curries deviation, with one simplified formula being:

$$MDA = \frac{2.71 + 4.66 \cdot \sqrt{bkg}}{\eta \cdot t \cdot R \cdot Y \cdot m \cdot K_s}$$

Where bkg the total background counts at the energy of interest, Y the yield (or branching ratio) of the emitted particles of given energy for a specific radionuclide and K_s the activity correction factor (for long lived radionuclides such as uranium K_s=1). The above formula takes into account both kinds of errors – false positive and false negative, and yields the smallest level of activity which can be detected with 95% confidence, while also having 95% confidence that "activity" is not detected falsely from a null sample.

2.7.2 Calibration and Quality assurance of the alpha spectrometry system

Energy and efficiency calibration of the alpha spectroscopic system is performed periodically and after changes in the conditions (e.g. change of detectors) using a standard reference source containing ^{241}Am, ^{244}Cm and ^{239}Pu. The source comprises a stainless steel disk of 0.65 mm thickness, 24.1 mm diameter and 19 mm active area. The main characteristics of the source are listed in Table 2.2.

Table 2.2: The characteristics of the standard reference source.

Isotope	Activity* (Bq)	Energy Range (keV)	Half-Life (years)	Uncertainty** (%)
Am-241	3.113	5280-5600	432.58	3.0
Cm-244	3.390	5650-5870	18.11	2.8
Pu-239	4.959	4950-5240	24100	2.8

* Activity shown refers to August 1st 2015. ** Uncertainty: Relative expanded uncertainty, k=2.

For the energy and efficiency calibration the source is placed in each chamber and measured for 30 minutes. The software determines the centroid and peak range for each chamber according to the energies of alpha particles defined by the user. In the software system, the calibration data from the standard are entered into a "Certificate File", with these data being used for subsequent efficiency calibrations. The software will automatically correct for source decay. The energies of alpha particles of each radionuclide as well as the corresponding yield are given below.

Table 2.3: Alpha particles emitted by the radionuclides of the standard source

Isotope	Energy (keV)	Probability (%)
Am-241	5485.7	84.45
Cm-244	5804.9	76.70
Pu-239	5155.5	70.79

The counting efficiency (η) of each detector is calculated according the following formula:

$$\eta = \frac{N}{t \cdot A \cdot Y}$$

Where N the net counts at the given energy, t the counting time in seconds, A the activity of the standard source, Y the yield (or branching ratio) of the emitted particles for a specific radionuclide.

The quality assurance of the system is performed before each series of measurements to ensure the quality of the results. For this purpose, the standard reference source is measured by each detector for 1 minute. In addition, a pulser check is performed for the electronics check of each chamber. The results of the quality assurance performed are listed in Table 2.4.

Table 2.4: Quality assurance results

Detector	Radionuclide	Peak range	Centroid	Pulser (keV)
A11A	Pu-239	654-718	701	
	Am-241	757-840	807	5000
	Cm-244	866-934	909	
A11B	Pu-239	621-706	686	
	Am-241	748-824	792	5000
	Cm-244	845-916	893	
A12A	Pu-239	648-726	704	
	Am-241	758-848	811	4998
	Cm-244	845-916	893	
A12B	Pu-239	638-718	697	
	Am-241	750-840	803	5000
	Cm-244	868-928	905	
A13A	Pu-239	626-710	687	
	Am-241	745-827	793	5001
	Cm-244	850-912	893	
A13B	Pu-239	688-771	752	
	Am-241	806-897	861	4999
	Cm-244	926-992	966	
A14A	Pu-239	644-708	684	
	Am-241	742-824	790	5001
	Cm-244	850-910	891	
A14B	Pu-239	631-709	683	
	Am-241	738-820	788	5002
	Cm-244	852-908	889	
A15A	Pu-239	632-709	688	5002
	Am-241	747-830	793	
	Cm-244	850-914	894	
A15B	Pu-239	631-708	686	
	Am-241	742-828	791	5001
	Cm-244	855-910	892	
A16A	Pu-239	634-696	680	
	Am-241	749-813	787	5001
	Cm-244	846-901	886	
A16B	Pu-239	646-706	688	
	Am-241	747-828	795	4999
	Cm-244	856-916	895	

3. Results and Discussion

3.1 Results

The results of the alpha spectrometry analysis of the hair samples are listed in the following table. It is noted that the chemical recovery was between 59.6 and 70.6%, which can be characterized as satisfactory taking into account the complexity of the process and the nature of the samples. The detection limit was 0.035-0.19 mBq/g for ^{238}U and 0.048-0.19 mBq/g for ^{234}U.

Table 3.1 Alpha spectrometry analysis results

Sample	Gender	Country	^{238}U (mBq/g)	^{234}U (mBq/g)	$^{234}U/^{238}U$	^{238}U (ng/g)
S-1	F	B&H	0.160 ± 0.057	0.227 ± 0.073	1.42	12.9 ± 4.6
S-2	F	PT	0.394 ± 0.093	0.85 ± 0.14	2.16	31.7 ± 7.5
S-3	F	GR	0.133 ± 0.029	0.175 ± 0.033	1.31	10.7 ± 2.3
S-4	M	GR	0.115 ± 0.025	0.210 ± 0.036	1.83	9.2 ± 2.0
S-5	M	GR	0.895 ± 0.095	0.874 ± 0.097	0.98	71.9 ± 7.7
S-6	F	AUS	< LD*	0.466 ± 0.091	-	-
S-7	F	UK	0.465 ± 0.074	0.448 ± 0.078	0.96	37.4 ± 5.9

* Limit of Detection

Indicatively, in Figure 3.1 is illustrated the spectrum of sample 5 as exported from the alpha spectrometric analysis report.

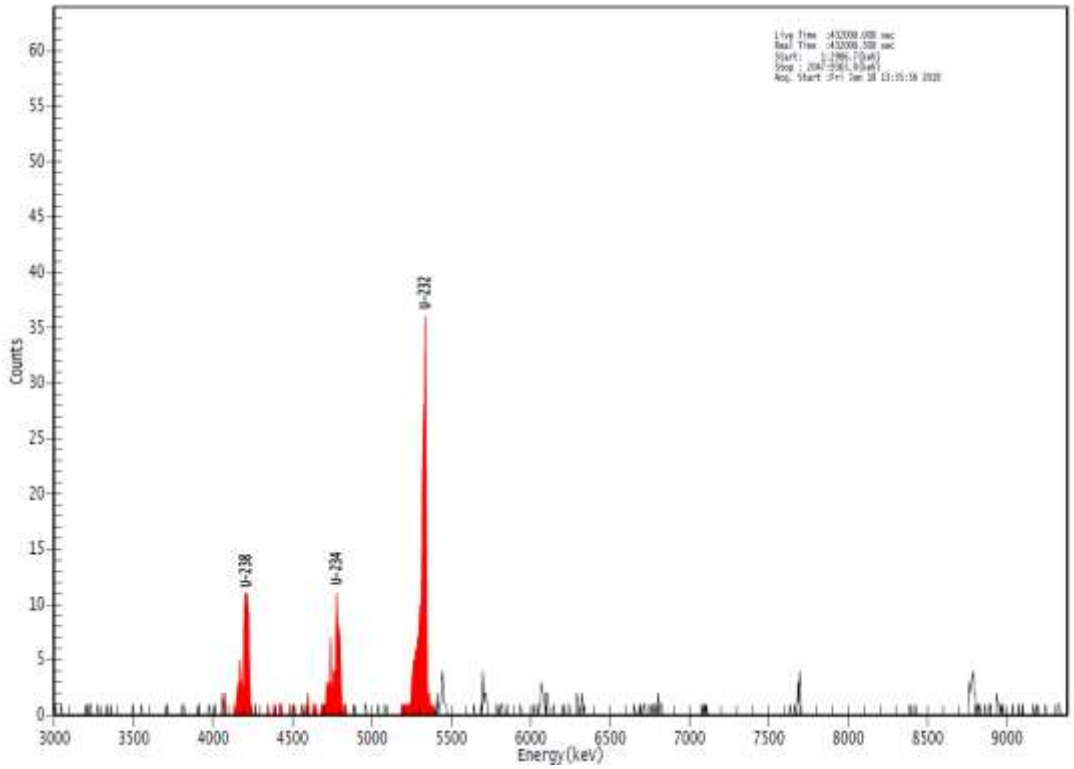

Figure 3.1: Alpha spectrometry spectrum after the analysis of sample 5. The peaks of ^{238}U, ^{234}Uand the tracer are clearly visible.

3.2 Discussion

The group of study comprises non-occupationally exposed individuals, residents of 5 different countries. The group is also heterogeneous regarding age. According to the alpha spectrometry results, the activity of ^{238}U ranged between 0.115-0.895 mBq/g with an average of 0.329 mBq/g and median of 0.160 mBq/g. The average and median mass was 29 and 23 ng/g respectively. The activity of ^{234}U varied between 0.175-0.874 mBq/g.

Since uranium is a naturally occurring element is abundant in our food and water. Thus, differences in dietary habits and the origin of drinking water may account for significant variations of uranium concentration in hair [25]. In our group of study, the activities of uranium can be characterized as homogeneous among the individuals, except for the individual no 5, who appears to have higher activity (0.895 mBq/g) comparing to the rest. According to the information provided, the sample group abstains from the consumption of large quantities of meat. The diet of individual no 5 includes a lot of nuts and fresh vegetables and the water he consumes is filtered tap water. Also, he is of

the highest age among the group. It could be assumed that the age of the individual plays a role to the increased levels of uranium in his hair, due to the fact that uranium reflects chronic accumulation in hair follicles. Individuals 1, 2 and 3 consume tap water, whereas individual 6, whose activity of ^{238}U was below the detection limit, consumes mineral water.

For reasons of comparison, in Table 3.2 the results of previous studies regarding uranium hair analysis in non-occupationally exposed people from different countries are listed.

Table 3.2: Studies on uranium concentration in hair of non-occupationally exposed people

Country (Year)	**U (ng/g) (mean value)**	**Reference**
Slovenia (1991)	2.3-33 (13.6)	[26]
Sweden (2000)	6-436 (0.057)	[27]
Balkan area (2012)	0.9-449	[28]
Serbia (2015)	0.25-77 (16)	[29]
Greece (2010)	12-170	[21]
Brazil (2007)	2.1-49 (15)	[30]
Finland (2007)	18,000-821,000	[25]
Finland (2005)	6.5-250,000	[31]
Balkan region (2014)	11-54	[32]
Several regions	**9.2-71.9**	**Our study**

From the results of the above table it is observed that the uranium concentration in hair varies between individuals according to the geographical area. It is possible that these variations are due to differences in the geochemical environment, since all results regard non-occupationally exposed people. Exceptionally, the two studies in Finland report significantly high levels of uranium (up to 821,000 ng/g). These studies regard individuals who drink water from private drilled wells with high uranium concentration. Notably, these levels are higher than those regarding occupationally exposed workers (workers in uranium mining, milling and yellowcake production), which were between 34 and 34,000 ng/g [26]. The results of the uranium concentration in our study vary between 9.2 and 71.9 ng/g, thus appear to be generally in accordance with all other the listed studies. In addition, the ICRP in publication 23 reports a concentration of uranium in hair of 130 ng/g and none of our samples exceeds this value [15].

Regarding the activity ratio $^{234}U/^{238}U$, in the present study the range is between 0.96 and 2.16. Theoretically, the ratio of the two isotopes equals to unity, since ^{234}U exists in

equilibrium with its much more long lived parent ^{238}U. It is reported that the activity of ^{234}U is often higher than that of ^{238}U due to physical and chemical processes, especially in groundwater and bedrock well water [8, 33]. In a study in Sweden is reported an activity ratio range of 1.2-5.6 in human hair. The aforesaid study regards individuals who were drinking water from drilled bedrock wells. Because the activity ratio was found in accordance with the ratios found in water analysis in the same study, the authors assume that hair could be used as a useful bioindicator of chronic exposure to uranium [33].

4. Conclusions

The aim of the present project work was the analysis of uranium in hair of a non-occupationally exposed group by alpha spectrometry. The chemical recovery of the process ranged between 59.6 and 70.6. The recovery can be characterized as satisfactory taking into account the complexity of the radiochemical procedures that are followed in hair. Our results vary between 9.2 to 71.9 ng/g, which is in accordance with reported values in hair of non-occupationally exposed people. In addition, none of our concentrations exceed the value of 130 ng/g reported in the ICRP (Publication 23). Moreover, the values of our study appear lower than those of people that consume water of high uranium background. The highest value that was found in our samples is 0.895 mBq/g or 71.9 ng/g. It could be assumed that the dietary habits or the age of the individual plays a role, due to the fact that uranium reflects chronic accumulation in hair follicles. However, further experiments and epidemiological studies are needed for clearer conclusions. Finally, the ratios of $^{234}U/^{238}U$ were found in accordance with other studies.

5. References

[1] J. J. Katz, L. R. Morss, N. M. Edelstein *et al.*, *The Chemistry of the Actinide and Transactinide elements*, 4th ed. The Netherlands: Springer, 2010.

[2] "Royal Society of Chemistry," 2019. [Online]. Available: http://www.rsc.org/periodic-table/element/92/uranium.

[3] M. Bé, V. Chisté and C. Dulieu, *Table of Radionuclides*, vol. 3. Bureau International Des Poids Et Mesures, 2006.

[4] M. Bé, V. Chisté, C. Dulieu *et al.*, *Table of Radionuclides*, vol. 5. Bureau International Des Poids Et Mesures, 2010.

[5] W. Bo, L. Æ. Paul, R. Æ. Wolfgang *et al.*, "Biokinetic modeling of uranium in man after injection and ingestion," *Radiation and Environmental Biophysics*, no. June, 2005.

[6] "Radiation Safety-International Atomic Energy Agency." [Online]. Available: https://www.iaea.org/topics/radiation-safety-norm.

[7] *Toxicological profile for uranium*. U.S. Department of Health and Human Services. Agency for Toxic Substances and Disease Registry, 2013.

[8] *Environmental radiation data. Report 132*. U.S. Environmental Protection Agency, 2007.

[9] *Exposures from the uranium series with emphasis on radon and its daughter. NCRP Report No 77.* National Council on Radiation Protection and Measurements, 1984.

[10] M. Sheppard, T. Vandergraaf and D. Thibault, "Technetium and uranium: Sorption by and plant uptake from peat and sand," *Health Physics*, vol. 44, pp. 635–644, 1983.

[11] *Uranium in Drinking-water*. World Health Organisation, 2012.

[12] *Age-dependent doses to members of the public from intake of radionuclides: Part 4, Inhalation dose coefficients. ICRP Publication 71*. International Commission for Radiation Protection, 1996.

[13] M. Wrenn, P. Durbin, B. Howard *et al.*, "Metabolism of ingested U and Ra," *Health Physics*, vol. 48, pp. 601–633, 1985.

[14] *Age-dependent doses to members of the public from intake of radionuclides: Part 3, Ingestion dose coefficients.ICRP Publication 69*. International Commission for Radiation Protection, 1995.

[15] *Report of the Task Group on Reference Man. ICRP Publication 23*. International Commission for Radiation Protection, 1975.

[16] *Ionizing radiation: Sources and biological effects. 1982 Report to the General Assembly*. United Nations Scientific Committee on the Effects of Atomic Radiation, 1982.

[17] A. Tannenbaum, H. Silverstone and J. Koziol, "Tracer studies of the distribution and excretion of uranium in mice, rats, and dogs," in *Toxicology of uranium compounds*, New York: McGraw-Hill, 1951.

[18] *Guidlines for Drinking-water quality*, 4th ed. World Health Organisation, 2017.

[19] V. Valkovic, *Human hair. Volume I: Funtamentals and Methods for Measurement of Elemental Composition*. CRC Press, 1988.

[20] Z. Karpas, "Uranium Bioassay-Beyond urinalysis," *Health Physics*, vol. 84, no. 4, 2001.

[21] K. Kehagia, S. Bratakos, M. Kolovou *et al.*, "Hair analysis as an indicator of exposure to uranium," *Radiation ProtectionDosimetry*, pp. 1–4, 2010.

[22] W. B. Li, Z. Karpas, L. Salonen *et al.*, "A compartmental model of uranium in human hair for protracted ingestion of natural uranium in drinking water," *Health Physics*, vol. 96, pp. 636–645, 2009.

[23] G. Olszewski, A. Boryło, B. Skwarzec *et al.*, "Is human hair a proper 210 Po and 210 Pb monitor of their increased activity in the human body ?," *Journal of Radioanalytical and*

Nuclear Chemistry, vol. 319, no. 3, pp. 953–963, 2019.
[24] "The Idle man." [Online]. Available: https://theidleman.com/blogs/grooming/stimulate-hair-follicles.
[25] M. Muikku, T. Heikkinen, M. Puhakainen *et al.*, "Assessment of occupational exposure to uranium by indirect methods need information on natural background variations," *Radiation Protection Dosimetry*, vol. 125, pp. 492–495, 2007.
[26] A. R. Byrne and L. Benedik, "Uranium content of blood,urine and hair of exposed and non-exposed persons determined by radiochemical neutron activation analysis, with emphasis on quality control," *The Science of Total Environment*, vol. 107, pp. 143–157, 1991.
[27] I. Rodushkin and M. Axelsson, "Application of double focusing sector field ICP-MS for multielemental characterization of human hair and nails. Part II. A study of the inhabitants of northern Sweden," *The Science of Total Environment*, vol. 262, pp. 21–36, 2000.
[28] Z. S. Zunic, S. Tokonami, S. Mishra *et al.*, "Distribution of uranium and some selected trace metals in human scalp hair from balkans," *Radiation Protection Dosimetry*, vol. 152, pp. 220–223, 2012.
[29] S. K. Sahoo and Z. S. Zuni, "Distribution of uranium, thorium and some stable trace and toxic elements in human hair and nails in Ni ska Banja Town, a high natural background radiation area of Serbia (Balkan Region, South-East Europe)," *Journal of Environmental Radioactivity*, vol. 145, pp. 66–77, 2015.
[30] A. U. Akamine, M. A. D. Silva, M. Saiki *et al.*, "Determination of uranium in human head hair of a Brazilian populational group by epithermal neutron activation analysis," *Journal of Radioanalytical and Nuclear Chemistry*, vol. 271, no. 3, pp. 607–609, 2007.
[31] Z. Karpas, O. Paz-Tal, A. Lorber *et al.*, "Urine, hair and nails as indicators for ingestion of uranium in drinking water," *Health Physics Society2*, vol. 88, no. 3, pp. 229–242, 2005.
[32] B. Seslak, "Urine and hair analysis as an indicator of exposure to uranium," *PGEC*, 2014.
[33] A. Israelsson and H. Pettersson, "Measurements of ^{234}U and ^{238}U in hair, urine and drinking water among drilled bedrockwell water users for the evaluation of hair as a biomonitor of uranium intake," *Health Physics Society*, vol. 107, no. 2, 2014.