Alpha spectrometry in radiochemical analysis and its environmental applications

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Alpha spectrometry is a highly sensitive and modern measurement technique which can be used to radiochemical and radiological studies of the natural environment. In the paper were presented the results on application of alpha spectrometry in the study on determination of natural (^{210}Po, ^{210}Pb, ^{234}U, ^{238}U) and artificial (^{238}Pu, $^{239+240}$Pu and ^{241}Pu) alpha and beta radionuclides in environment of Poland and Baltic Sea. Amongst the radionuclides, alpha particle emitters play the most important role as they are highly radiotoxic to organisms. The concentrations of alpha radionuclides in the environmental samples of Poland were characterized based on the environmental samples collected between 1998 and 2009. Biogeochemistry of polonium, uranium and plutonium in the southern Baltic Sea ecosystem combined with the use of radioactive disequilibrium ^{210}Po/^{210}Pb, ^{234}U/^{238}U and ^{238}Pu/$^{239+240}$Pu and ^{241}Pu/$^{239+240}$Pu allowed to identify the sources of these radionuclides in natural ecosystems, as well as to determine their circulation in the environment (e. g. to assess the impact of the Chernobyl nuclear accident on the radioactive contamination of Poland).

1. INTRODUCTION

Alpha spectrometry is one of the most important radiometric techniques used for the measuring of alpha particles emitted by natural and artificial radionuclides. The alpha spectrometer consists of a low-level semi-conducting detector usually with an active surface of 100-600 mm^2 placed in a vacuum chamber, connected to a 1024 multichannel analyzer. Detectors used are silicon diodes with a thin gold layer (so called Surface-Barrier detector) or, most often used, implanted and passivated (Planar Implanted Passivated Surface detector). The efficiency of such detectors is between 25% to 40% (in 2π geometry), but the resolution lies in the range of 20 keV up to 35 keV, depending on source quality. Alpha spectrometer measures alpha particles of energy 3–8 MeV and enables the determination of most alpha radionuclides occurring in the natural environment [1, 2]. Considering a small penetration range of alpha particles the use of alpha spectrometry should precede a labor-intensive radiochemical separation of analyzed radionuclides.

Taking into account their half-life time, type of decay and strong radiotoxicity, the most important alpha and also beta radionuclides in the natural environment are: ^{210}Po, ^{210}Pb, ^{222}Rn, ^{226}Ra, ^{234}U, ^{235}U and ^{238}U, and the artificial ones are: ^{238}Pu, ^{239}Pu, ^{240}Pu and ^{241}Pu. In the natural environment these radionuclides occur in trace quantities [1, 3, 4]. A number of natural and artificial radionuclides are, or could be used as indicators for studying geochemical and biological processes in the natural environment.

Polonium is present in the natural environment, especially in uranium and thorium ores. Amongst seven natural radionuclides ^{210}Po is the most important, it is an alpha emitter with energy 5.305 MeV and halt-life 138.376 days [5]. Polonium is a very radiotoxic element and undergoes strong bioaccumulation in land and aquatic organisms [1].

Naturally occurring uranium contains three alpha emitting radionuclides: ^{238}U (99.2745%), ^{235}U (0.7200%) and ^{234}U (0.0055%). They are long-lived radioisotopes: $2.455 \cdot 10^5$ years for ^{234}U, $7.037 \cdot 10^8$ years for ^{235}U and $4.468 \cdot 10^9$ years for ^{238}U. The alpha emitting energy for uranium isotopes lies between 4.040 to 4.776 MeV [5] and 1 Bq ^{238}U is equal to 81,6 μg total U in environmental samples. Moreover, ^{235}U is used as nuclear fuel in nuclear reactors [1].

Plutonium   is an artificial element   and three alpha emitting radionuclides: ^{238}Pu, ^{239}Pu, ^{240}Pu and beta ^{241}Pu are important from the radiological point of view due to their high radiotoxicity, long physical half-life, high chemical reactivity and long residence in the environment. The values of half-life are: 87.7 years for ^{238}Pu, 2.411·10^9 years for ^{239}Pu, 6583 years for ^{240}Pu and 14.2 years for ^{241}Pu [5]. The alpha energy for these plutonium isotopes lies between 4.755 and 5.499 MeV [5]. Among plutonium radionuclides ^{239}Pu isotope is the most important as it is fissile and used to produce nuclear weapon. The principal source of plutonium in the environment (about 5 tons totally) was atmospheric fallout from nuclear weapon tests [1]. Radiochemical determination of plutonium isotopes in environmental samples can be done by alpha spectrometry [6–8].

2. MATERIALS AND METHODS

The subject of this study were determination of polonium ^{210}Po, uranium isotopes ^{234}U and ^{238}U as well as plutonium isotopes ^{238}Pu, $^{239+240}$Pu and ^{241}Pu in samples of sediments, surface and bottom waters, which were collected in the years 1997 and 1998 in the southern Baltic. Totally there were collected 11 sediment cores: the one with the Gulf of Gdansk and Puck, 4 from the Gdańsk Deep basin, two from the Bornholm Deep basin, 2 from the Słupsk Bank basin and 1from the Słupsk Narrow. The samples of bottom sediments and water from different regions of the southern Baltic cruises were collected during a research of the Institute of Oceanology r/v "Oceania". Sediments were collected in May and August 1996, in April 1997 and September 1998, the water sample in April 1997 and May 1998. The sediments samples were collected by the Niemistö core sound, surface water by plastic buckets and bottom water by bathometer (Nansen bottle). In case of sea birds analyzed material consisted of dead sea birds which were found on the beach or were caught by fishermen in nets while fishing.
The radiochemical procedure for the simultaneous determination of natural (^{210}Po, ^{210}Pb, ^{234}U, ^{235}U and ^{238}U) and artificial (^{238}Pu, $^{239+240}$Pu and ^{241}Pu) isotopes in environmental samples is based on the following steps [1, 2]:

a) co-precipitation of radionuclides with manganese dioxide in natural water samples,
b) mineralization of sediment, soil and biota samples,

c) sequential separation and purification of radionuclides on anion exchange resins,

d) spontaneous deposition of polonium on silver discs as well as electrodeposition of uranium and plutonium on steel discs,

e) measurement of activities of polonium (^{210}Po), uranium (^{234}U and ^{238}U) as well as plutonium (^{238}Pu, $^{239+240}$Pu and ^{241}Pu) using alpha spectrometer.

Before radiochemical analysis recovery tracers were added to each sample: ^{209}Po, ^{232}U and ^{242}Pu (from 5 to 50 mBq) [2]. Polonium in analyzed samples, after co-precipitation and mineralization, was spontaneously electrodeposited for 4 h at 90°C in a 0.5 HCl solution on a silver disc [9]. The solution after polonium deposition was used to determine radiolead (^{210}Pb), uranium and plutonium. Direct activity measurement of ^{210}Pb in natural samples is difficult, considering the low energy of emitted beta particles. Therefore, the activity of ^{210}Pb was calculated basing on the measurement of ^{210}Po activity (a daugther isotope of ^{210}Pb, via ^{210}Bi) [2]. Plutonium(IV) in the acidic media (8 mol/dm^3 HNO$_3$ and 10 mol/dm^3 HCl) comprises the anion complexes [Pu(NO$_3$)$_6$]$^{2-}$ and [PuCl$_6$]$^{2-}$ which adsorb on an anion exchange resin (e.g. Dowex), whereas Pu(III) occurs as the Pu^{3+} cation [10]. The reduction of the adsorbed Pu(IV) anion complexes by iodide ions causes conversion to Pu(III). Neptunium and thorium in the 8 mol/dm^3 nitric acid solution also form the anion complexes [Th(NO$_3$)$_6$]$^{2-}$ and [Np(NO$_3$)$_6$]$^{2-}$ which adsorb on the resin but uranyl (UO$_2$$^{2+}$), polonium (Po^{4+}) and iron (Fe^{3+}) ions pass the column. On the other hand, in the 10 mol/dm^3 HCl solution uranium and iron exist in anion forms UO$_2$Cl$_4$$^{2-}$ and FeCl$_4$$^-$, but thorium, americium and actinium do not form anion complexes and are not adsorbed on the anion exchange resin. These characteristics allow the purification of plutonium from any other contaminated radioelements [1, 2].

Uranium U(VI) in 10 mol/dm^3 HCl solution is present in the form of the complex uranyl anion UO$_2$Cl$_4$$^{2-}$ which is adsorbed on the anion exchange resin [11, 12]. The separation and purification of uranium from other elements is possible in a sulfuric acid solution. When the H$_2$SO$_4$(aq) concentration exceeds 0.01 mol/dm^3, uranium exists in the anionic forms UO$_2$(SO$_4$)$_2$$^{2-}$ and UO$_2$(SO$_4$)$_3$$^{4-}$. In contrast, other elements (Fe, Co, Cu, Zn) do not form anionic complexes in the sulfuric acid solution [1, 2].

After the separation and purification, uranium and plutonium fractions were electroplated on polished stainless discs and then the activities are measured by alpha spectrometry. In some cases a resolution

of the detector (usually 17–20keV FWHM) is too low to differentiate peaks of alpha energy. Energy of $-^{239}$Pu and ^{240}Pu are so close (below 15keV) that detector is not able to measure them separately. Therefore, activities of these two nuclides are presented as summarized values [1, 2]. The ^{210}Pb activity was calculated on the basis of ^{210}Po ingrowth after the lead fraction has been purified and stored for several months (up to two years). The ^{210}Pb activity at the time of sample collection was calculated according to formula [1, 2]:

$$A_0\left(^{210}\text{Pb}\right)=\left[\frac{A_2\left(^{210}\text{Po}\right)}{1-\exp\left[-\lambda\left(t_2-t_1\right)\right]}\right] \tag{1}$$

where: $A_0(^{210}\text{Pb})$ is the activity of ^{210}Pb at the time of sample collection, $A_2(^{210}\text{Po})$ is the activity of ^{210}Po originating from ^{210}Pb decay, following the second electrodeposition, t_1 is the timespan between the sample collection and the first ^{210}Po counting, t_2 is the timespan between the sample collection and the second ^{210}Po counting, and λ is the ^{210}Po decay constant.

^{241}Pu is a low-energy electron emitter with E_{max} of 21 keV, and a half-life 14.2 years. ^{241}Pu can be determined directly by measurement with beta proportional counter or using liquid scintillation counter (for samples with a relatively high content of ^{241}Pu) [13–14], and indirectly by alpha spectrometry measurement of activity its daughter radionuclide ^{241}Am [15-16]. Determination is based on the ingrowth of ^{241}Am (at 5.49 MeV) and can be carried out only after a long period sample storage – between 4 to 20 years. Even after 4 years the activity ratio of ^{241}Am/^{241}Pu is only 1/166. Thus, the lower limit of detection for ^{241}Pu by direct measurement using a proportional counter is about 10 mBq, whereas via the ^{241}Am build-up about 200 mBq [17]. The ^{241}Pu activity can be calculated according to formula [15]:

$$1\,A_{\text{Pu}_0}=31.11\cdot\frac{A_{241_{\text{Am}}}\cdot e^{\lambda_{\text{Am}}\cdot t}}{\left(1-e^{-\lambda_{\text{Pu}}\cdot t}\right)} \tag{2}$$

where: A_{Pu_0} is the ^{241}Pu activity at the time of sampling, $A_{241_{\text{Am}}}$ is the ^{241}Am activity measured after particular period of time (years), λ_{Pu} is the decay constant of ^{241}Pu (0,050217 year^{-1}), λ_{Am} is the decay constant of ^{241}Am (0,001604 year^{-1}), 31.11 is the $\lambda_{\text{Pu}}/\lambda_{\text{Am}}$ ratio, and t is the time from sampling to the measurement of ^{241}Am. It is important to take into

account a possible presence of ^{238}Pu in the sample which alpha energy falls into the same region.

Fig. 1 shows the aggregated spectrum, resulting from the imposition of spectra of measured isotopes of polonium (^{209}Po – tracer, ^{210}Po), uranium (^{232}U – tracer, ^{234}U, ^{235}U, ^{238}U) and plutonium (^{238}Pu, $^{239+240}$Pu, ^{242}Pu – tracer). In Fig. 1 are also shows energy of alpha particles emitted by isotopes of thorium (^{228}Th, ^{230}Th and ^{232}Th), radium (^{226}Ra), neptunium and americium (^{237}Np and ^{241}Am) has been indicated.
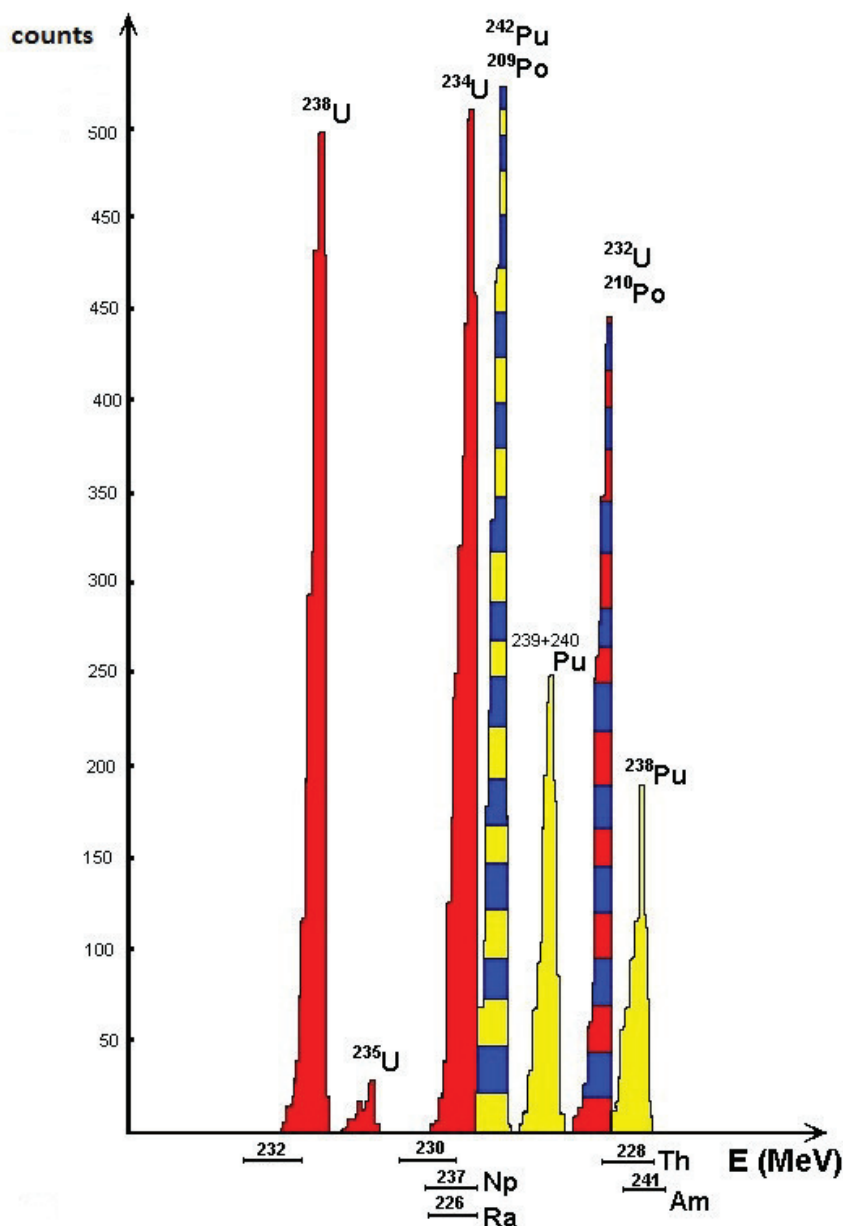
3. RESULTS AND DISCUSSION

3.1. Polonium ^{210}Po and radiolead ^{210}Pb

The study performed for Baltic Sea indicated that the average concentration of ^{210}Po in the waters of the southern Baltic Sea is 0.59 Bq/m^3. The concentration of ^{210}Po in the Baltic suspension is 74 Bq/kg d.m., and the value of distribution coefficient (DC) of this radionuclide for the suspended solids is $2 \cdot 10^5$. Polonium is sorbed on the suspended particles and the intensity of this process depends on the contents of organic matter present in the suspended solids [18–20]. In the Baltic Sea bottom sediments, the concentration of ^{210}Po in the upper layer (0–1 cm) is: 224 Bq/kg (Gdańsk Basin) and 209 Bq/kg (Arkona Basin), whereas in layers deeper than 10 cm, decreases below 100 Bq/kg [18]. This drop is justified, since under conditions of the radioactive equilibrium, the activity of ^{210}Po, being in equilibrium with ^{210}Pb, depends on the content of ^{238}U, or rather of ^{226}Ra, which is the longest-living preceding nuclide in the natural uranium-radium decay series. In the sediments separated from outer effects, activity equilibrium is reached after about 200 years. Recent sediments generally contain excess of ^{210}Pb with reference to ^{226}Ra being in equilibrium. This excess comes from decay of ^{222}Rn contained in the atmosphere and water. Determination of the excess ^{210}Pb activity enables us to calculate the settlement rate of the sediments. This method is particularly useful for relatively fast sedimentation (from 1 to 3 mm per year) [21]. Polonium ^{210}Po is highly accumulated in the organisms of the southern Baltic Sea and the mean values of the bioconcentration factor (BCF) lie in the range: $1.5 \cdot 10^3$–$3.2 \cdot 10^4$. In the case of plankton, the values of the BCF factor increase in the series: phytoplankton < macrozooplankton < mezozoo-plankton, whereas in the representatives of the Baltic zoobenthos these values increase in the series: priapulid worms < polychaetes < crustaceans < clams (soft tissue) [18, 19, 22, 23]). In analyzed Baltic crustaceans and clams, the concentration of ^{210}Po decreases in the series hepatopancreas > gills > muscles. In the fish of the southern Baltic Sea, higher polonium concentrations occur in visceras (intestine, liver, pyloric caeca, spleen), and lower in the muscles. The contribution of the viscera organs in accumulating polonium in fish depends not only on species but also on a type and quantity of ingesta (chyme). Moreover, ^{210}Po and ^{210}Pb in Baltic organisms are not in a radioactive equilibrium: the activity ratio of ^{210}Po/^{210}Pb reach 70, and lower values were found in the hard tissues of

fish, and higher in the inner organs of fish and mussels [18, 22, 23]. Baltic fish are a main source of polonium for Poland's inhabitants [21]. Also marine birds that live on the southern Baltic Sea coast accumulate polonium that gets into their bodies as a result of eating marine organisms, mainly small fish and molluscs [24]. In the biocenosis of the southern Baltic Sea, the content of ^{210}Po in organisms living in the marine environment increase in the series: marine birds < fish < zooplankton < phytoplankton < phytobenthos < crustacean < clams.

In the sea bottom sediments, the concentration of polonium depends to a considerable degree on the contents of detritus formed mostly from the settled dead cells of phytoplankton and excrements of both zooplankton and fish. In this way they contribute to fast removing of polonium from the marine waters. Through eating the formed detritus and filtering sea bottom and pore waters, the zoobenthos contribute to concentrating polonium. In turn, fish that feed with crustaceans and clams accumulate ^{210}Po earlier settled on the sea sediments. Therefore, the migration of polonium in the southern Baltic Sea ecosystem is to some extent consistent with the organic matter cycle in the individual links of the food chain [18].

Alpha spectrometry technique was also used for polonium determination in the Vistula and Oder rivers. The highest concentrations of ^{210}Po in the Vistula waters were found in Dęblin town, whereas the lowest – in Sandomierz town. Amongst the Vistula tributaries, the highest concentration of the radionuclide occured in the Bzura, the lowest in the Drwęca. The annual flow of ^{210}Po in both branches of the Vistula (the Leniwka and the Nogat) is 71.6 GBq in Kiezmark town and 2.1 GBq in Malbork town. Amongst the tributaries of the Vistula, the Narew was marked by the largest runoff of ^{210}Po (11.32 GBq). Mean yearly runoffs of ^{210}Po from the drainage basin of the Vistula were the highest in the upland tributary of the Dunajec (1720 kBq/km^2 for ^{210}Po), whereas the lowest ones were observed in the lowland tributary of the Narew (150 kBq/km^2 for ^{210}Po) [25]. The most important sources of polonium in the upland tributaries of the Vistula basin were the erosion and leaching of rock material as well as wet and dry atmospheric fallout [21]. Along the Oder, the highest concentrations of ^{210}Po occured in Słubice town, the lowest in Głogów town. Amongst the Oder tributaries, maximal concentrations of ^{210}Po were observed in the Nysa Łużycka, the Bystrzyca, the Mała Panew, and the Barycz. On the basis of water flows in the Oder and its tributaries, the annual flow of polonium could be estimated in the drainage basin of the Oder. The yearly runoff of ^{210}Po

with waters of the Oder river was maximal in Gozdowice town, whereas minimal in Chałupki town. Among the Oder tributaries, the Warta river was marked by the highest polonium runoff. Yearly surface flows for [210]Po were highest in the Oder upland tributaries: the Nysa Łużycka (245 kBq/km^2) and the Nysa Kłodzka (229 kBq/km^2), and the lowest in the Barycz (8 kBq/km^2). The annual runoffs on the discussed radionuclide from the Pomeranian rivers (Rega, Parsęta, and Słupia rivers) ranged from 0.72 to 3.48 GBq [26].

3.2. Uranium ^{234}U and ^{238}U

Alpha spectrometry has been used in studies of the marine environment of the southern Baltic and it was shown that the uranium isotope concentrations (^{234}U, ^{235}U, ^{238}U) differed in a large extend. Uranium isotopes ^{234}U and ^{238}U in the environment are not in radioactive equilibrium. The concentration of uranium in sediments increased with depth of the sediment core, indicating the vertical diffusion processes of uranium from sediments to the bottom water through the intersticial water, and diagenetic changes occurring in the sediment material. The intersticial water plays very important role in the uranium migration because it penetrates the upper layers of sediment and increases values of the activity ratio $^{234}U/^{238}U$, as well as causes leaching of uranium from the sediment into the sea water. Such specific effect of the intersticial water was clearly visible in the sediments from the Słupsk Bank [27]. The small differences in the uranium content of the southern Baltic Sea bottom waters were observed. The uranium concentrations varied between 1.81 and 3.81 µg·dm^{-3}, while the values of the activity ratio $^{234}U/^{238}U$ were comparable for all the analyzed basins and ranged from 1.16 to 1.19 [27]. The values of the $^{234}U/^{238}U$ ratio in the analyzed samples of interstitial water from the southern Baltic sediments ranged from 1.17 to 1.18 and were consistent with the value recorded for the Baltic waters. This does not mean that the uranium presence is of hydrogenic origin, because its concentration in the interstitial water is significantly higher than in the bottom water. Uranium transfer to the interstitial water is possible due to the processes taking place in diaganetic sediment material, due to the release of adsorbed uranium by organic matter.

The sea water is the source of uranium in the Baltic plants and animals The values of the bioaccumulation factor (BCF) in the southern Baltic organisms ranged from 0.4 in the muscle of fish to 120 or 130 in clams (*Bivalvia*) and crustaceans, respectively [28]. The concentration of ^{238}U in the analyzed Baltic organisms ranged widely from 0.0112 Bq/kg

d.m. in the muscle of fish to 5.5 Bq/kg d.m. in phytoplankton [29]. In the case of ^{238}U concentration in southern Baltic zoobenthos large differences were observed which can be the result of the eating habits of the tested organisms. The uranium concentrations in phytoplankton were about 4 times higher than in zooplankton what indicates that uranium is easier and more eagerly accumulated by the phytoplankton. The values of the activity ratio ^{234}U/^{238}U in the representatives of the phytoplankton and zooplankton from the southern Baltic (from 1.13 to 1.16) are very similar to the values in ocean water and Baltic water (1.14 and 1.17, respectively) [30].

  The average values of the activity ratio ^{234}U/^{238}U in marine birds from southern Baltic Sea oscillate around 1.00 and are in the range from 0.75 to 1.12. The obtained results were slightly lower than that for marine organisms inhabiting the southern part of the Baltic Sea. The values of uranium participation factor (PF) (the quotient of the percentage precipitation of activity radionuclide in a particular organ or tissue and the percentage precipitation of organ or tissue mass in the total mass of the analyzed organism) suggest that the uranium in the links: seabird → fish is accumulated (PF > 2), but in the trophic links: seabirds → crustaceans and bivalves PF the values are much smaller than 1.00 [31]. The results of uranium concentration in sea birds are similar to those obtained for deer-like animals of northern Poland, where the ratio ^{234}U/^{238}U ranged from 0.61 to 1.42 and did not depend on the type of analyzed tissues nor on the age and sex of the animals [32].

  It was found that ^{234}U and ^{238}U are not in radioactive equilibrium in the Vistula river water and ranged between 1.00 and 2.14 [33]. The highest annual runoff of uranium from the Vistula to the southern Baltic Sea was observed in Kiezmark (230.6 GBq of ^{238}U and 276.8 GBq of ^{234}U). The largest amounts of uranium were transported yearly from the Dunajec catchment (3140 kBq/year·km^2 for ^{234}U, 2330 kBq/year·km^2 for ^{238}U and totally 190 g/year·km^2 for uranium), the smallest amounts of ^{234}U and ^{238}U were transported to the Vistula from the Brda catchment (700 kBq/year·km^2 for ^{234}U and 670 kBq/year·km^2 for ^{238}U) and total uranium from the Narew catchment (30 g/year·km^2). Mountain tributaries the Dunajec and the San were characterized by the largest flow of uranium, respectively 2330 GBq/year·km^2 and 1590 GBq/year·km^2, the lowest values revealed the Narew (430 GBq·year^{-1}·km^{-2}) and the Wieprz (630 GBq/year·km^2) tributories. Obtained results of uranium concentrations in waters of the Oder river were comparable to the results obtained from waters of the Vistula river. Within one year the highest values of surface runoff of ^{234}U, ^{238}U and total uranium flow from the

Oder river drainage area were observed in Słubice (119 g/year·km^2), the smallest in Gozdowice (75 g/year·km^2). Among the Oder river tributaries the highest surface runoff of uranium was noticed for the Bystrzyca drainage (5244 kBq/year·km^2 for ^{238}U, 428 g/year·km^2 for total uranium), and the lowest for the Mała Panew drainage (126 kBq/year·km^2 for ^{238}U and 10 g/year·km^2 for total uranium). The high concentration of uranium in the water of the Bystrzyca was the result of discharge of saline mine waters, the use of phosphate fertilizers in agriculture, increased the surface and underground runoff and increased soil erosion. The drainage basins of the Vistula, the Oder and the Pomeranian rivers are the main sources of uranium in the southern Baltic Sea. Every year about 750 GBq of $^{234+238}$U flows from these rivers to the southern Baltic [34].

Alpha spectrometry was also used to determine the concentrations of uranium and polonium in the environment of the phosphogypsum stockpile in Wiślinka village near Gdańsk agglomeration. The largest ^{210}Po, ^{234}U and ^{238}U concentration in analyzed water samples taken in the vicinity of the phosphogypsum waste heap indicated that these radionuclides were lixiviated from phosphogypsum waste dump to the retention reservoir and pumping station. The lower concentration of these radionuclides in surface water samples taken from the Martwa Wisła river shows that the migration and distribution of polonium and uranium radionuclides from the phosphogypsum waste heap to the Martwa Wisła river was rather slow [35]. The maximum polonium and uranium concentration in the analyzed water samples was observed in the pumping station and retention reservoir [36–40]. In the analyzed flora organisms from Wiślinka area the highest amount of polonium and uranium was found in ruderal plant samples. The concentrations of ^{210}Po, ^{234}U and ^{238}U in the analyzed plants were higher in roots of plants than in green parts of plants. The highest uranium and polonium concentrations were observed for plants which are covered with tomentose [36–38].

Another example of the use of alpha spectrometry in the study of the natural environment is the determination of radionuclides in drinking water from Gdańsk agglomeration. The research show that analyzed waters are safe from the radiological protection point of view because, according to the World Health Organization (WHO) recommendation water can be useful to drink if its total α activity is below 0.1 Bq/dm^3 and the overall activity of β emitters is less than 0.1 Bq/ dm^3 (all the water samples from Wiślinka area were characterized by a lower content of ^{238}U, ^{234}U and ^{210}Po and the values of the activity ratio ^{234}U/^{238}U were closed to values obtained for typical groundwater) [41].

3.3. Plutonium ^{238}Pu, ^{239}Pu, ^{240}Pu and ^{241}Pu

In the case of ^{238}Pu and $^{239+240}$Pu activity determination, alpha spectrometry is an irreplaceable measurement technique. The activity of plutonium isotopes in the environment is much lower than ^{210}Po and ^{238}U [18]. Studies done in 1998–2003 on southern Baltic Sea showed that the highest activity of $^{239+240}$Pu was found in water collected in the Pomeranian Bay, the lowest in the water from the Gulf of Gdańsk. Significant amount of plutonium found in the Pomeranian Bay was caused by its inflow with waters enriched in $^{239+240}$Pu from the Skagerrak and the Kattegat that comes from the nuclear fuel reprocessing facilities in Sellafield and Cap de la Hague [42]. Further research and ^{241}Pu activity measurements in the southern Baltic showed significant increase of its concentration within 15 years. The activity of ^{241}Pu in water samples from the Gulf of Gdańsk and the Gdańsk Basin increased 10 times [43]. In the marine environment only a few percent of plutonium was found in water, more than 95% was deposited in sediments. Majority of plutonium in the Baltic Sea was moved quite quickly from water to sediments and this process was dependent on the depth, water circulation and physiochemical conditions [18]. Plutonium was concentrated in organisms due to processes of selective natural accumulation. This property leads to self-cleaning of the marine environment but causes the increase of plutonium activity in marine flora and fauna [44]. Especially, benthic organisms are exposed on higher plutonium concentrations due to its deposition in sediments. Some marine plants and animals are extremely able to high plutonium accumulation [18, 16]. The data showed that the benthic animals accumulate more $^{239+240}$Pu than phytobenthos which comes indirectly from the sediments, while plants adsorb plutonium from seawater [16, 45]. The accumulation of plutonium in fish depends on the sampling site, fish age and species. The analysis of six most important Baltic fish species showed the highest $^{239+240}$Pu activities in benthic fish and concluded non-uniformly plutonium distribution in their tissues and organs [43, 46]. Seabirds are typical double habitat (land and water) organisms, characterized by high body temperature and fast metabolism. Studies on $^{239+240}$Pu concentration in southern Baltic sea seabirds showed that plutonium content was significantly differentiated among species, their tissues and organs [47, 48]. The results of plutonium determination in marine organisms indicate its increase in the sequence as follows: seabirds < fish < zooplankton < phytoplankton < zoobenthos < phytobenthos. The values of plutonium concentration in southern Baltic ecosystem components were used to estimate the $^{239+240}$Pu inventory in

the Gulf of Gdańsk and the Gdańsk Basin. The studies showed that the main source (about 80 %) of plutonium in the above regions was run-off river water. The total amount of $^{239+240}$Pu in the Gulf of Gdańsk was calculated at 1.18 TBq, while in the Gdańsk Basin at 3.77 TBq and almost all plutonium load (over 99%) was deposited in sediments. In the water of the Gulf of Gdańsk contains about 3.70 GBq $^{239+240}$Pu and 40.8% of $^{239+240}$Pu is connected to suspended matter. The water of the Gdańsk Basin contains 9.92 GBq $^{239+240}$Pu and in this case 56% is connected to suspended matter. Marine organisms living in the Gulf of Gdańsk basin accumulated 3.81 MBq $^{239+240}$Pu and 7.45 MBq of $^{239+240}$Pu [49]. Study about sources of plutonium origin can be estimated on the basis values of activity ratio: ^{238}Pu/$^{239+240}$Pu and ^{241}Pu/$^{239+240}$Pu. Obtained results of ^{241}Pu measurements in air particles collected over Gdynia in 1986 strictly indicated plutonium from the Chernobyl accident because the analyzed values of ^{241}Pu/$^{239+240}$Pu activity ratio increased from 0.23 in February to 0.47 in April 1986 [45]. Analysis values of ^{238}Pu/$^{239+240}$Pu and ^{241}Pu/$^{239+240}$Pu activity ratio showed that the global atmospheric fallout and the Chernobyl accident were the main sources of plutonium in the southern Baltic Sea. Also higher values of ^{238}Pu/$^{239+240}$Pu and ^{241}Pu/$^{239+240}$Pu activity ratios in east tributaries of the Vistula river (Bug and Narew tributaries) and Oder river (Mała Panew and Warta tributaries) indicated the Chernobyl accident is the main source of plutonium. However, analysis of the values of ^{238}Pu/$^{239+240}$Pu activity ratio in their north-western tributaries indicated the presence of both global and Chernobyl fallouts [45, 47, 50–53].

Moreover, obtained results showed variations in ^{238}Pu, $^{239+240}$Pu and ^{241}Pu activities depending on season, atmospheric conditions, geological structure and sampling site location. On the basis of $^{239+240}$Pu and ^{241}Pu activity concentration determined in analyzed river water samples, it was calculated that the Vistula river enriched the Baltic Sea in 89 MBq of $^{239+240}$Pu and 1650 MBq of ^{241}Pu annually. On the other hand, the Oder river enriched the Baltic Sea in 45.86 MBq of $^{239+240}$Pu and 616 MBq of ^{241}Pu annually [47, 45, 49, 50, 52]. These data indicated, that more than 10% of the total plutonium in the Baltic Sea originate from the Vistula and Oder rivers.

4. CONCLUSIONS

Alpha spectrometry is a very good and efficient technique for determination of natural and artificial emitting radionuclides in environmental samples. It can be successfully applied to a number of scientific research in chemistry, biology, ecology, medicine, agriculture and environmental protection. Alpha spectrometry can also be used for indirect measurement of beta radionuclides activities as ^{210}Pb (via ^{210}Po determination) or ^{241}Pu (via ^{241}Am determination). Additionally alpha spectrometry is also used in radiological studies of the effects of consuming and inhalation, as well as human excretion processes of highly radiotoxic alpha radionuclides, especially plutonium ^{210}Po and plutonium ^{238}Pu, $^{239+240}$Pu and ^{241}Pu.

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