

# A sequential procedure for determining $^{238}\text{Pu}$ , $^{239+240}\text{Pu}$ , $^{241}\text{Am}$ , $^{90}\text{Sr}$ , U and Th activities in soils and peats from Spitsbergen

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**Abstract.** This paper presents results of application of a sequential radiochemical procedure for multi-elemental analyses for samples collected in the Arctic environment. The levels of activity of  $^{238}\text{Pu}$ ,  $^{239+240}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{90}\text{Sr}$  and the content of natural radioisotopes ( $^{238}\text{U}$ ,  $^{234}\text{U}$  and  $^{232}\text{Th}$ ,  $^{230}\text{Th}$ ) were investigated in soils and peats in the proglacial zone of the Werenskiöld glacier and on the strandflat in the vicinity of the glacier. Results on activity concentration shows general low level of radioactive contamination. Procedure was checked using reference materials. Reasonable recoveries were obtained for almost all analyzed radionuclides except for uranium. Further work is needed to improve this stage.

**Key words:** activity concentration • activity ratio  $^{238}\text{Pu}/^{239+240}\text{Pu}$  • radioactive contamination • sequential radiochemical procedure

## Introduction

Arctic ecosystems are particularly vulnerable to radioactive and other contamination because of such specific factors as the relatively short food chains, efficient transfer of contaminants along these food chains and the close relationship between marine and terrestrial ecosystems [1]. The Svalbard Archipelago lying close to the sites of previous atmospheric weapon tests (mainly at Novaja Zemlja) and in the path of atmospheric and marine transport from European sources of artificial radionuclides, remains vulnerable to radionuclide contamination ( $^{238}\text{Pu}$ ,  $^{239,240}\text{Pu}$ ,  $^{90}\text{Sr}$  and  $^{241}\text{Am}$ ). On the other hand, Svalbard is considered to be relatively unaffected by fallout from the Chernobyl accident in 1986 [2]. Radiation monitoring of the Arctic is important in order to obtain spatial and temporal information on radionuclide levels and to identify their major sources and pathways in this fragile environment.

Terrestrial radioactive elements like U and Th are a natural component of rock forming minerals. In soils, radionuclides of U and Th occur in their parent minerals or are adsorbed onto soil components (organic matter, clays, carbonates, Fe/Mn-oxides). Little is known about transfer of these radionuclides in the proglacial environment and how pedogenesis affects their depth distributions along soil profiles.

The main aim of this study is to test sequential radiochemical procedure for multi-elemental analyses. Validity of using this method is to investigate levels of activity of  $^{238}\text{Pu}$ ,  $^{239+240}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{90}\text{Sr}$  and analyse the content of natural radioisotopes ( $^{238}\text{U}$ ,  $^{234}\text{U}$  and  $^{232}\text{Th}$ ,  $^{230}\text{Th}$ ) in soils and peats in the proglacial zone of the

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Separation of strontium from the effluent from the Dowex 1  $\times$  8 column (8 M  $\text{HNO}_3$ ) took place on another column filled with Sr-Spec (Eichrom Ltd) [3, 8, 16]. The resin was loaded on a column of 6 mm in diameter and 10 cm in height. The column was conditioned with 50 ml of 8 M  $\text{HNO}_3$  and the sample was passed through the column. Strontium was eluted afterwards together with some possible traces of lead from the column by 50 ml of double distilled water (DDW). Strontium and lead were separated by precipitation of lead iodide [3]. Solution containing strontium was evaporated to dryness, dissolved in a mixture of 1.5 ml of 1 M  $\text{HNO}_3$  and 1.5 ml of DDW and then transferred to a 15 ml scintillator plastic vial. Those samples were analyzed on a HPGe low background gamma spectrometer to determine the recovery of  $^{85}\text{Sr}$ . This procedure is shown schematically in Scheme 1. Then, this solution was mixed with 10 ml of a liquid scintillation cocktail (HiSafe 3) and, after waiting two weeks for the equilibrium between  $^{90}\text{Sr}$  and its daughter,  $^{90}\text{Y}$  ( $T_{1/2} = 64$  h) was measured. The  $^{90}\text{Sr}$  activity was determined by a Wallac 1414-003 liquid scintillation spectrometer. Typical counting time was 30,000 s.

The effluent solution (8 M  $\text{HNO}_3$  which was passed through the Sr-resin column contains Am, U and RE) was evaporated to below 50 ml and then 150 ml double distilled water was added to it. Ammonia was added to precipitate iron hydroxides. The sediment was centrifuged and dissolved in 50 ml of concentrated HCl. This solution was evaporated and dissolved in 50 ml of 9 M HCl. The column containing the resin Dowex 1  $\times$  8 was washed with 50 ml of 9 M HCl to condition anion exchange column and the sample was passed through the column. Because of large amounts of iron present in the samples, it was necessary to wash the column with 30 ml of 8 M  $\text{HNO}_3$  to removed the adsorbed iron. Large amounts of iron caused sometimes break-through of the column. The uranium was eluted from the column using 50 ml of a mixture of 0.5 M HCl, hydroxylamine hydrochloride and double distilled water. Uranium was co-precipitated directly from this eluate using  $\text{NdF}_3$  and Mohr's salt (ammonium iron sulfate) to obtain

thin spectrometric source. The uranium activity was determined by an alpha spectrometer. This procedure is presented schematically in Scheme 1.

The effluent from U separation (9 M HCl) contains still some matrix elements, among them traces of rare earths and Am. These will be separated by ion exchange procedure using Dowex 1 and methanol-acid solutions [7]. The analyses are not yet finished, however some tests were already done and thus we know that the procedure works.

## Results and discussion

Table 1 shows the plutonium and strontium recoveries obtained for reference soil materials and for blank sample and the minimum and maximum activity in soils and peats. Recoveries of plutonium ranged for soil samples from  $44 \pm 2\%$  to  $95 \pm 3\%$  and for peat samples ranged from  $20 \pm 2\%$  to  $86 \pm 3\%$ . Chemical recovery for strontium varied between  $20 \pm 3\%$  and  $87 \pm 7\%$  for soils and between  $13 \pm 2\%$  and  $88 \pm 6\%$  for peats, respectively. The recoveries obtained for reference material and blank sample were similar to the maximum values for soil and peat samples. To assure analytical quality, the analysis of IAEA reference materials (soil 375 and soil 327) were performed using the same procedure as for each of the sample. The reference values are typed in bold and the most of these values were in agreement with the reference. In IAEA-375 soil, the activity of  $^{239+240}\text{Pu}$  ( $0.266 \pm 0.027$  Bq/kg) was within the range of certified values (0.26 to 0.34 Bq/kg) and the activity of  $^{238}\text{Pu}$  ( $0.055 \pm 0.004$  Bq/kg) was just on the edge of the certified value (0.056 to 0.085 Bq/kg). The activity of  $^{90}\text{Sr}$  ( $62.4 \pm 1.7$  Bq/kg) was less of about 10% than the mean values (69 to 78 Bq/kg). In IAEA-327 soil, the activity of  $^{239+240}\text{Pu}$  ( $0.590 \pm 0.049$  Bq/kg) and  $^{238}\text{Pu}$  ( $0.019 \pm 0.005$  Bq/kg) fits into the range of mean values (0.56 to 0.60 Bq/kg) and (0.017 to 0.215 Bq/kg), respectively. There is no data of  $^{90}\text{Sr}$  for IAEA-327 soil.

The minimum and maximum activities in 3 soil and 3 peat profiles for plutonium and strontium are pre-

**Table 1.** The plutonium and strontium recoveries obtained for reference soil materials and for blank sample and the minimum and maximum activity in soils and peats (Bq/kg)

		$^{239+240}\text{Pu}$		$^{238}\text{Pu}$	$^{90}\text{Sr}$
Soil	min	$0.022 \pm 0.007$		$0.004 \pm 0.004$	$2.77 \pm 0.34$
Recovery (%)			$44 \pm 2$		$20 \pm 3$
Soil	max	$3.89 \pm 0.28$		$0.351 \pm 0.034$	$16.1 \pm 2.5$
Recovery (%)			$95 \pm 3$		$87 \pm 7$
Peat	min	$0.003 \pm 0.001$		$0.003 \pm 0.005$	$2.12 \pm 0.44$
Recovery (%)			$20 \pm 2$		$13 \pm 2$
Peat	max	$9.27 \pm 0.95$		$0.304 \pm 0.075$	$21.6 \pm 1.7$
Recovery (%)			$86 \pm 3$		$88 \pm 6$
IAEA-375 soil		$0.266 \pm 0.027$		$0.055 \pm 0.004$	$62.4 \pm 1.7^*$
<b>Reference value</b>		<b>0.3 (0.26–0.34)</b>		<b>0.071 (0.056–0.085)</b>	<b>74 (69–78)*</b>
Recovery (%)			$74 \pm 3$		$87 \pm 2$
IAEA-327 soil		$0.590 \pm 0.049$		$0.019 \pm 0.005$	–
<b>Reference value</b>		<b>0.58 (0.56–0.60)</b>		<b>0.019 (0.0165–0.215)</b>	
Recovery (%)			$77 \pm 3$		
Blank		$0.003 \pm 0.002$		$< 2.12 \times 10^{-4}$	$< 0.008$
Recovery (%)			$69 \pm 5$		

\* calculated for 2008.

**Table 2.** The thorium and uranium recoveries obtained for reference soil materials and for blank sample and the minimum and maximum activity in soils and peats (Bq/kg)

		$^{232}\text{Th}$	$^{230}\text{Th}$	$^{234}\text{U}$	$^{238}\text{U}$
Soil	min	$9.93 \pm 0.78$	$3.55 \pm 0.49$	$8.95 \pm 0.65$	$9.83 \pm 0.92$
Recovery (%)			$9 \pm 3$	$4 \pm 1$ (pH < 9)	
Soil	max	$44.4 \pm 2.4$	$27.8 \pm 1.7$	$16.9 \pm 1.6$	$16.5 \pm 1.1$
Recovery (%)			$64 \pm 3$	$24 \pm 1$	
Peat	min	$1.06 \pm 0.22$	$0.025 \pm 0.004$		
Recovery (%)			$30 \pm 1$		
Peat	max	$2.01 \pm 0.15$	$0.034 \pm 0.002$		
Recovery (%)			$52 \pm 2$		
IAEA-375 soil		$20.3 \pm 2.1$	$27.4 \pm 2.8$	$25.2 \pm 1.6$	$24.7 \pm 1.6$
<b>Reference value</b>		<b>20.5 (19.2–21.9)</b>	<b>no data</b>	<b>25 (17–32)</b>	<b>24.4 (19–29.8)</b>
Recovery (%)			$42 \pm 4$	$26 \pm 7$	
IAEA-327 soil		$33.4 \pm 2.7$	$27.3 \pm 2.5$		
<b>Reference value</b>		<b>37.6 (35.5–39.7)</b>	<b>33.4 (31.3–35.5)</b>		
Recovery (%)			$6 \pm 4$		
Blank		$0.0081 \pm 0.013$	$0.0100 \pm 0.0001$	$0.76 \pm 0.14$	$0.18 \pm 0.07$
Recovery (%)			$100 \pm 5$	$14 \pm 4$	

sented in Table 1. The lowest activities determined in this study for  $^{239+240}\text{Pu}$  in soils are  $0.022 \pm 0.007$  Bq/kg and only  $0.003 \pm 0.001$  Bq/kg in peats. The maximum measured value is  $3.89 \pm 0.28$  Bq/kg in soils and  $9.27 \pm 0.95$  Bq/kg in peats. The minimum  $^{238}\text{Pu}$  activities in soils and peats are similar ( $0.004 \pm 0.004$  and  $0.003 \pm 0.005$  Bq/kg) as well as the maximum activities, which range from  $0.351 \pm 0.034$  to  $0.304 \pm 0.075$  Bq/kg, respectively. The  $^{90}\text{Sr}$  activity varies from  $2.77 \pm 0.34$  Bq/kg to  $16.1 \pm 2.5$  Bq/kg for soils and varies from  $2.12 \pm 0.44$  to  $21.6 \pm 1.7$  Bq/kg for peats.

Table 2 shows the thorium and uranium recoveries obtained for reference soil materials and for blank sample and the minimum and maximum activity in soils and peats. Recoveries of thorium ranged for soil samples from  $9 \pm 3\%$  to  $64 \pm 3\%$  and for peat ranged from  $30 \pm 1\%$  to  $52 \pm 2\%$ . The lowest recovery was attained for uranium. The recovery for soils varied between  $4 \pm 1\%$  and  $24 \pm 1\%$ . The lowest recoveries were obtained when pH of the solution from which uranium was precipitated was below 4. The recoveries obtained for reference material and blank sample for thorium in IAEA-327 soil was very low ( $6 \pm 4\%$ ) and for uranium in blank sample the recovery was  $14 \pm 4\%$ . The result obtained for IAEA-375 soil agrees with the reference value for  $^{232}\text{Th}$ ,  $^{234}\text{U}$  and  $^{238}\text{U}$ . There is no reference data for  $^{230}\text{Th}$ . In IAEA-327, the soil activity of  $^{232}\text{Th}$  and  $^{230}\text{Th}$  was less of about 6% than the mean values ( $35.5\text{--}39.7$  Bq/kg) and less of about 13% for  $^{230}\text{Th}$  activity ( $31.3\text{--}35.5$ ).

Table 2 shows the minimum and maximum activities in soil and peat for  $^{232}\text{Th}$ ,  $^{230}\text{Th}$ ,  $^{234}\text{U}$  and  $^{238}\text{U}$ . The thorium activities ( $^{232}\text{Th}$ ) in soils are higher than in peats and ranged from  $9.93 \pm 0.78$  Bq/kg to  $44.4 \pm 2.4$  Bq/kg and from  $1.06 \pm 0.22$  to  $2.01 \pm 0.15$ , respectively. Similarly, the  $^{230}\text{Th}$  activities in soils are higher than in peats and varied from  $3.55 \pm 0.49$  to  $27.8 \pm 1.7$  Bq/kg and  $0.025 \pm 0.004$  to  $0.034 \pm 0.002$  Bq/kg, respectively. The activity of  $^{238}\text{Th}$  cannot be measured with any reasonable accuracy due to the presence of this isotope in the added  $^{232}\text{U}$  tracer. Differences of thorium activities between soil and peat reflect natural content of these nuclides in the mineral layer. There is no data for uranium in peats, because of problems which appeared with low recovery (few percent) in some cases. At this moment, it

is checked if the problems are with final co-precipitation with  $\text{NdF}_3$  (this can happen if U is not reduced to  $\text{U}^{4+}$ ) or in other stages of the procedure, for example, due to the break-through of the column by iron. In terrestrial environment of the Svalbard area, typical activity concentrations of natural radionuclides  $^{238}\text{U}$  (17 to 72 Bq/kg),  $^{232}\text{Th}$  (10 to 57 Bq/kg) were similar to global averages [4]. Each of these natural radionuclides showed little variation in activity concentration with soil depth. This may indicate that the processes, which normally govern vertical redistribution of these radionuclides have been diminished or retarded by the influence of the cold climate in the area. In the analyzed soil samples there were lower  $^{238}\text{U}$  activities were observed, but the activities of  $^{232}\text{Th}$  were similar to the typical activity concentration in the northern part of Svalbard. This indicates that geology and lithology can be responsible for this situation.

Activity concentrations of  $^{238}\text{Pu}$  and  $^{239+240}\text{Pu}$  in the analyzed soil and peat samples were higher than in a typical Kongsfiorden peat soil (Svalbard) ( $0.20 \pm 0.03$  to  $6.9 \pm 0.2$  Bq/kg for  $^{239+240}\text{Pu}$  and  $0.01 \pm 0.01$  to  $0.25 \pm 0.02$  Bq/kg for  $^{238}\text{Pu}$ ) [4], but despite these value, the average  $^{238}\text{Pu}/^{239+240}\text{Pu}$  activity ratios are similar to the global fallout ratios for Svalbard of 0.025 [5, 6]. In the case of analyzed soil samples, the average global fallout ratio of  $^{238}\text{Pu}/^{239+240}\text{Pu}$  were often higher than 0.025, and ranged from  $0.018 \pm 0.011$  to  $0.087 \pm 0.011$ . This paper presents preliminary results of research. Based on these values it is difficult to identify other sources of radionuclide contamination. Average plutonium ratios in this paper show that this region was unaffected by fallout from the Chernobyl accident.

## Conclusions

The method described in this work is valid for the determination of levels of environmental contamination due to especially anthropogenic radionuclides (plutonium, strontium and americium) in the presence of higher levels of natural alpha emitters (uranium, thorium isotopes). The described above sequential procedure was

used for the first time by us in the analyses of Arctic soil matrix. The proposed sequential radiochemical procedure, combined with the known procedures used in our laboratory [11–14], seems to be a reasonable choice for multi-elemental analyses since it saves a lot of laboratory labour for early stages of sample preparation. Namely, the whole mineralization is done only once for each sample. Some disadvantages of such approach may appear due to the interference of used tracers (and their decay products) with analyzed radionuclides (case of  $^{228}\text{Th}$ , for instance) as well as some unwanted losses of analyzed radionuclides during long course of several steps analyses. Moreover, some improvements still need to be made, especially since the recoveries of uranium seems to be too low to make us satisfied.

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