

Sequential Determination of ^{241}Am , ^{237}Np , Pu Radioisotopes and ^{90}Sr in Soil and Sediment Samples

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Abstract

A sensitive and reliable method for the simultaneous determination of ^{241}Am , ^{237}Np , plutonium radioisotopes and ^{90}Sr in soil and sediment samples is described. Analysis involves leaching of the samples in conc. HNO_3 , followed by radiochemical separation and purification. The radiochemical procedure begins with separation of $^{241}\text{Am}/^{90}\text{Sr}$, plutonium radioisotopes and ^{237}Np by anion exchange chromatography. ^{241}Am and ^{90}Sr from the combined effluent are separated using TRU resin and Sr resin. Counting sources for alpha spectrometric measurements were prepared by the microcoprecipitation technique. Radiochemical yields were determined using ^{243}Am , ^{239}Np and ^{242}Pu tracers. Strontium recovery was determined gravimetrically and Sr counting sources were analysed by liquid scintillation counting. The method was successfully tested by analysis of six reference materials and on two sediment samples with high activities of the selected radionuclides. The results were compared with reference and literature values.

Key words: Actinides, strontium, extraction chromatography, microcoprecipitation technique, liquid scintillation counting.

Introduction

Radionuclide contamination resulting from global fallout and discharges from nuclear facilities includes the important man-made radionuclides ^{237}Np , ^{238}Pu , $^{239/240}\text{Pu}$, ^{241}Am and ^{90}Sr , so in environmental control attention has to be paid to the abundance and the behaviour of these radionuclides in various samples. The determination of critical man-made radionuclides in environmental samples is obviously important in view of the increasing energy production by nuclear reactors, the associated fuel cycle, reprocessing and waste disposal, the increased potential for environmental contamination and public concern over the potential hazards. Their determination is an important topic in relation to health, nuclear waste management from nuclear reactors, recycling and final storage of radioactive waste, control of illicit nuclear activities, etc. Methods for determination of radionuclides in a wide variety of environmental samples include non-destructive gamma spectrometry, alpha spectrometry, beta counting and scintillation techniques, as well as mass spectrometry and neutron activation analysis for some nuclides.^{1–3} Evaluation of the contamination source (nuclear power plant accidents, reprocessing plant discharges, nuclear weapon tests, etc.) requires accurate and precise isotopic analysis of actinides, especially uranium and plutonium. This can be achieved by alpha spectrometry^{4–12} or by inductively coupled plasma mass spectrometry after chemical separation. Alpha spectrometry has been widely used in our laboratory for many years^{11–17}

and since we have very positive experience with this technique, we decided to use it also in the present work. The radioactive characteristics of the radionuclides to be determined or were used as tracers are stated in Table 1.

Table 1. Radioactive characteristics of radionuclides of interest.¹⁸

Isotope	Alpha energy ^a (keV)	max. beta energy (keV)	Gamma energy ^a (keV)
^{239}Pu	5155 (73.3%)	–	–
	5143 (15.1%)		
^{240}Pu	5168 (73.5 %)	–	–
	5123 (26.4%)		
^{238}Pu	5499 (71.6%)	–	–
	5456 (28.3%)		
^{242}Pu	4900 (78.0%)	–	–
	4856 (22.4%)		
^{241}Am	5486 (85.2%)	–	59.5 (36.3%)
	5443 (12.8%)		
^{243}Am	5275 (87.9%)	–	74.7 (66%)
	5233 (10.6%)		
^{237}Np	4788 (47.0%)	–	–
	4771 (25.0%)		
^{239}Np	–	714	277.6 (14.1%)
	–		228.2 (10.7%)
^{90}Sr	–	546	–

^a two most abundant energies are stated for each isotope.

The aim of this study was to develop a rapid and sensitive analytical procedure for the sequential determination of critical man-made radioisotopes in environmental samples based on alpha spectrometry following radiochemical separation by ion exchange and extraction chromatography after leaching. Horwitz *et al.* described two extraction chromatographic materials commercially available as Sr and TRU resin from Eichrom Industries, USA. Sr resin is a strontium selective resin composed of bis-*t*-butyl-*cis*-dicyclohexano-18-crown-6 in 1-octanol as stationary phase immobilized on an inert polymeric support. Strontium is adsorbed on the column from nitrate media. TRU resin is a transuranium specific resin composed of octylphenyl-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) in tri-*n*-butyl phosphate (TBP) immobilized on an inert porous polymeric support. Extraction chromatography can be used for a number of analytical purposes, including the separation of actinides as a group from the matrix, separation of Sr from the matrix and sequential separation of individual actinides and Sr.^{4,11,19–31} These procedures represent a significant improvement over classical radiochemical separation methods. In this publication we used as a basis the method developed by Moreno *et al.*,³¹ which we further modified to fit our purpose. We used leaching with conc. nitric acid for sample preparation instead of destruction in a conventional microwave oven. We used 9M HCl for Th removal from anion exchange column instead 10M HCl and we found that we can use I⁻ ions in the form of KI or NH₄I and not just in a form of NH₄I. Neptunium determination was also included in the separation scheme. The microcoprecipitation sources were prepared differently from that described by Moreno *et al.*³¹ Our method for thin source preparation for alpha spectrometry measurements is described in detail below. The method was applied to reference materials and to sediments from the Cumbrian Coastline and from the river Ribble, Great Britain, which are contaminated by nuclear facilities.

Experimental

Samples

Reference materials IAEA-135 (Radionuclides in Sediment) and IAEA-368 (Pacific Ocean Sediment), SOIL 6 (Soil), IAEA-300 (Radionuclides in Baltic Sea Sediment), IAEA-375 (Soil), NIST-SRM 4350b (Columbia River Sediment) and two sediments which were collected in the vicinity of Sellafield and Springfields. Ribble Sediment, a sediment from the tidal zone of the river Ribble, Lancashire, UK, is influenced both by tidal borne radionuclides originating from Sellafield and by manufacture of fuel elements at Springfields upstream.

An intertidal Sediment from the Cumbrian Coastline was collected for an international characterisation in 1997 and the Jožef Stefan Institute participated in this comparative exercise.³²

Tracers

²⁴³Am and ²⁴²Pu tracers: calibrated solutions, with activities of 0.746 Bq/g and 0.83 Bq/g, respectively were purchased from the National Physical Laboratory, Teddington Middlesex, United Kingdom.

²³⁹Np tracer: This was prepared by irradiation of µg quantities of a solution of uranium in the Institute's TRIGA Mark II research reactor.

Sample preparation

Up to 10 g of sample was leached with up to 200 mL of conc. HNO₃ on a hot plate at 50–80 °C overnight in the presence of ²⁴³Am, ²⁴²Pu and ²³⁹Np tracers and 30 mg of strontium carrier. Leaching was performed in a covered beaker on a hot plate with magnetic stirring. The leachant and the residue were separated by filtration. The solution was evaporated and the residue dissolved in 1M HNO₃.

Analytical procedure

Oxidation state adjustment is very important for the separation of plutonium and neptunium radioisotopes. To assure as low losses of radionuclides as possible, plutonium must be present in solution for absorption on the anion exchange column as Pu(IV) and neptunium as Np(IV). During separation Pu is selectively reduced to Pu(III) with ammonium iodide, while Np remains as Np(IV). To the 1M HNO₃ solution about 1 g of hydroxylamine hydrochloride was added and the solution was warmed gently for about 15 min to ensure that plutonium was present as Pu(III) and neptunium as Np(III). After cooling the sample 2–3 g of sodium nitrite were added to ensure conversion of Pu(III) to Pu(IV) and Np(III) to Np(IV). The solution was then converted to 8M using conc. HNO₃.

This 8M HNO₃ solution was passed through an anion exchange column (Dowex 1X8, mesh 100–200) and washed with 100 mL 8M HNO₃. The 8M HNO₃ effluent was used for analysis of americium and strontium radionuclides. The column was washed with 100 mL 9M HCl to elute thorium. Pu was eluted with 100 mL of 0.1M I⁻/9M HCl solution. Iodide ions selectively reduce Pu(IV) to Pu(III). Pu(III) is not adsorbed on the column under these conditions and elutes. Iodide can be added in the form of KI or NH₄I. Neptunium remain on the column in Np(IV) form and it was later stripped with 100 mL of 4M HCl solution.

Fe(III) that may be present in the samples interfere in separation of americium on the TRU resin

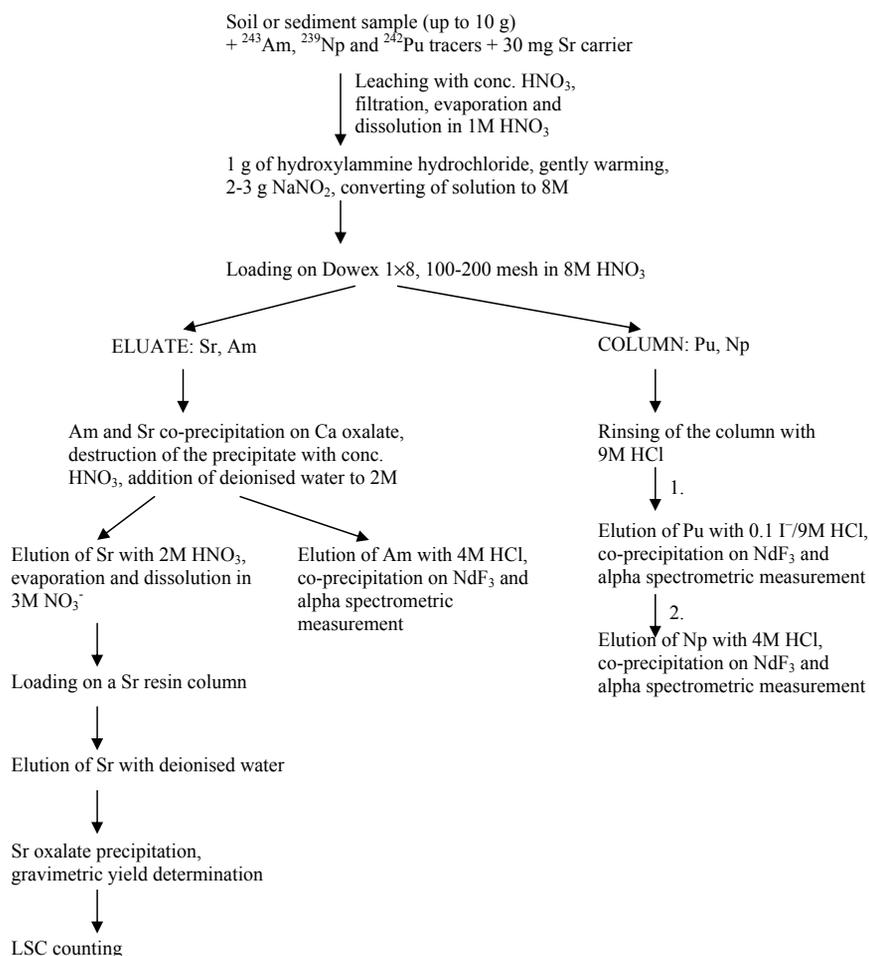


Figure 1. Analytical procedure for the simultaneous determination of plutonium, neptunium, americium, and strontium in soil and sediment samples.

column. To the Am/Sr effluent about 10 g of oxalic acid were added and the pH was adjusted to 5.5–6.0 with ammonia solution. If no precipitate was formed, up to 500 mg of calcium nitrate was added. Both americium and strontium co-precipitated with calcium oxalate. Iron, both 2+ and 3+, forms soluble complexes and remains in the solution. The precipitate was centrifuged and washed with deionised water. The oxalate precipitate was destroyed with conc. HNO_3 and the residue was taken up in 2M HNO_3 .

Separation of americium was performed using a TRU resin column. 2M HNO_3 was tested for Fe(III) using NH_4SCN solution. If the test was positive up to 300 mg of ascorbic acid was added to the solution to reduce Fe(III) to Fe(II). 3 g TRU resin was mixed with deionised water and used to fill a column 15 cm long and 1 cm in diameter. The sample was loaded onto the column and washed with 100 mL 2M HNO_3 . Strontium was not retained on the column and elutes in the

2M HNO_3 fraction. Americium was stripped with 100 mL 4M HCl solution.

The strontium fraction was evaporated to dryness and the residue was dissolved in 3M NO_3^- . This can be done using 3M HNO_3 or 1M $\text{Al}(\text{NO}_3)_3$. $\text{Al}(\text{NO}_3)_3$ prevents destruction of bis-*t*-butyl-*cis*-dicyclohexano-18-crown-6, which is the extractant of the Sr resin column. To use this column repeatedly, then $\text{Al}(\text{NO}_3)_3$ should be used instead of 3M HNO_3 . Column capacity decreases up to 5-times slower when using $\text{Al}(\text{NO}_3)_3$ instead of nitric acid. However, both of these possible-loading solutions perform the separation in the same way with the same selectivity. The strontium fraction was loaded onto a Sr resin column and washed with 100 mL 3M NO_3^- . If using $\text{Al}(\text{NO}_3)_3$ then the washing of the column was followed by elution with 20 mL 3M HNO_3 which eliminates aluminium from the column (that can otherwise interfere with LSC counting). Strontium was eluted from the column with 100 mL deionised water.

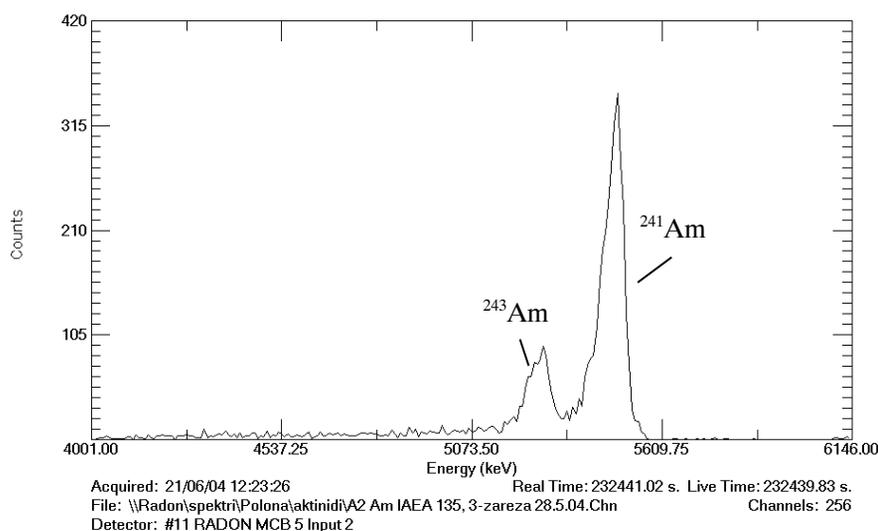


Figure 2. Alpha spectrum of americium radioisotopes isolated from IAEA-135 reference material.

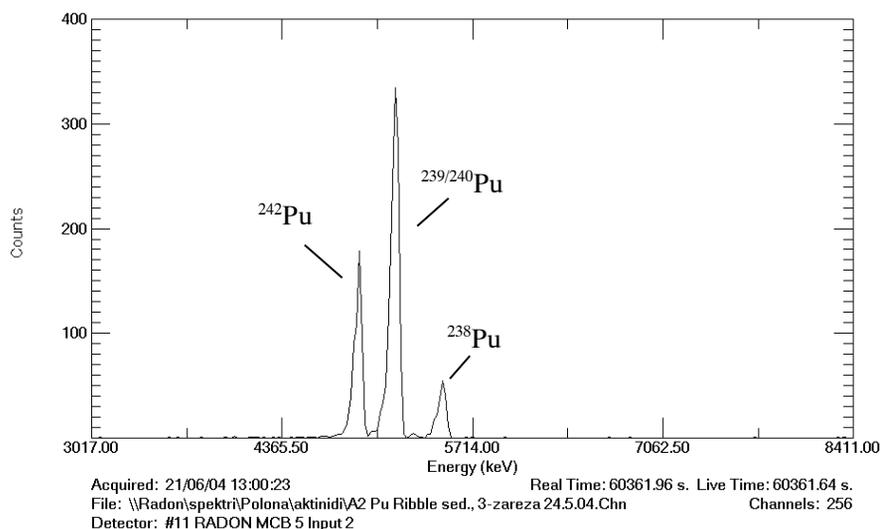


Figure 3. Alpha spectrum of plutonium radioisotopes isolated from Ribble sediment.

About 300 mg of oxalic acid were added to the strontium effluent and strontium oxalate precipitated from pH 9 to 10, adjusting the pH with ammonia solution. The precipitate was centrifuged, plated on a measuring planchet, dried and weighed for recovery calculation. The precipitate was then dissolved in 2 mL 1M HNO₃ and mixed with 14 mL Ultima Gold XR scintillation cocktail.

The microcoprecipitation method for thin source preparation for alpha spectrometry was performed for all solutions of americium, plutonium, and neptunium radionuclides isolated from soil or sediment samples. Solutions of the isolated radionuclides were evaporated and dissolved in 1–2 mL 1M HCl. About 100 µL 0.5 mg mL⁻¹ of Nd carrier were added and shaken about one

minute on a mini shaker. About 0.5 mL of conc. HF was added, the solutions shaken again and left on ice for half an hour. In the meantime a filter for microcoprecipitation (Supor-100 membrane filter, 25mm, 0.1µm) was prepared.

Through this filter were first passed 5 mL 80% ethanol, then 5 mL solution containing 50 µg of freshly precipitated NdF₃ and then the sample fraction in the form of the NdF₃ suspension. The filter was washed twice with 2 mL 0.58M HF, twice with deionized water and twice with 80% ethanol. The filter was then dried, glued on an Al planched and measured on an alpha spectrometer. Analytical procedure is schematically presented in Figure 1.

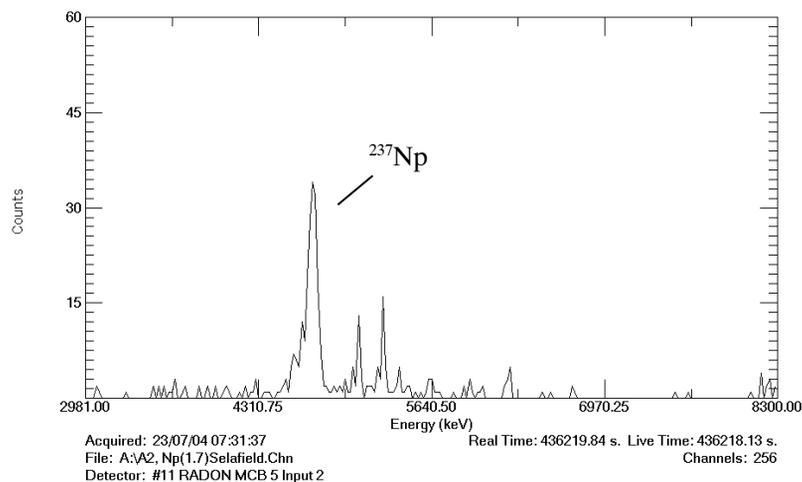


Figure 4. Alpha spectrum of ^{237}Np isolated from Cumbrian sediment.

Table 2. Activities of $^{239/240}\text{Pu}$, ^{238}Pu , ^{241}Am and ^{237}Np in some reference materials and samples of sediments collected in the vicinity of Sellafield and Springfields.

Sample	Nuclide	Activity concentration (Bqkg^{-1})	
		<i>This work</i>	<i>Ref. or lit. value</i>
IAEA 300	$^{239/240}\text{Pu}$	3.49 ± 0.23	3.55
	^{238}Pu	< 0.2	0.15
	^{241}Am	1.21 ± 0.18	1.38
	^{237}Np	< 0.05	–
IAEA 375	$^{239/240}\text{Pu}$	0.34 ± 0.06	0.3 ± 0.04
	^{238}Pu	0.08 ± 0.03	0.071 ± 0.014
	^{241}Am	0.15 ± 0.03	0.13 ± 0.02
	^{237}Np	< 0.2	–
IAEA 368	$^{239/240}\text{Pu}$	31 ± 5	31 ± 2
	^{238}Pu	8.2 ± 1.0	8.5 ± 0.9
	^{241}Am	1.35 ± 0.19	1.3
	^{237}Np	0.20 ± 0.08	0.25^{12}
IAEA 135	$^{239/240}\text{Pu}$	217 ± 12	213
	^{238}Pu	46 ± 4	43
	^{241}Am	313 ± 14	318
	^{237}Np	0.80 ± 0.28	0.87^{12}
SOIL-6	$^{239/240}\text{Pu}$	1.03 ± 0.16	1.04 ± 0.07
	^{238}Pu	< 0.2	< 0.036
	^{241}Am	0.39 ± 0.08	0.39–0.45
	^{237}Np	< 0.1	–
SRM-4350b	$^{239/240}\text{Pu}$	0.56 ± 0.07	0.508 ± 0.030
	^{238}Pu	< 0.02	0.013 ± 0.002
	^{241}Am	< 0.2	0.15 ± 0.03
	^{237}Np	< 0.2	–
Ribble sediment	$^{239/240}\text{Pu}$	187 ± 10	161 ± 8^{11}
	^{238}Pu	32 ± 3	33 ± 5^{11}
	^{241}Am	288 ± 23	320 ± 18^{11}
	^{237}Np	1.72 ± 0.14	$1.66\text{--}1.83^{12}$
Cumbrian sediment	$^{239/240}\text{Pu}$	960 ± 74	995 ± 19^{20}
	^{238}Pu	193 ± 19	211 ± 4^{20}
	^{241}Am	1508 ± 99	1590 ± 13^{20}
	^{237}Np	6.45 ± 0.14	6.33 ± 0.53^{20}

Table 3. Activities of ^{90}Sr in sediment and soil samples obtained by liquid scintillation counting.

Sample	^{90}Sr (Bq/kg)	
	<i>This work</i>	<i>Ref. or lit. value</i>
IAEA 300	11.4 ± 2.7	10.8
IAEA 375	114.0 ± 2.4	108 ± 6
IAEA 368	< 6.5	1.8
IAEA 135	58 ± 41	64.5
SOIL-6	28.1 ± 1.4	30.3 ± 3.6
SRM-4350b	< 9.9	5.3
Ribble sediment	18 ± 10	22 ± 3^{11}
Cumbrian sediment	194 ± 97	234 ± 12^{20}

Results and discussion

The results obtained by this method for simultaneous determination of americium, neptunium, plutonium and strontium radionuclides are shown in Tables 2–3. Spectra are presented in Figures 2–4.

The results obtained with above-mentioned method are in good agreement with reference, information or literature values. Average chemical recoveries for plutonium, americium and neptunium were 61%, 66% and 40%, respectively. Overall recoveries for neptunium were generally lower than for the other radionuclides. This is due to loss of neptunium because of inappropriate oxidation state adjustment. Some of the neptunium remains in the Np(V or VI) state which are poorly retained by the column and wash out with 8M HNO_3 . In addition, some impurities of ^{242}Pu at 4900 keV and $^{239/240}\text{Pu}$ at approx. 5155 keV can be observed in the alpha spectrum, but they usually do not interfere with the ^{237}Np peak. If however the tails of Pu radio-

isotopes do interfere, further purification or repeated analysis is necessary.

Average chemical recovery for ^{90}Sr was 67%. Lower activities of ^{90}Sr are difficult to measure because of the high background and the small amounts of sample taken for the analysis. This is especially seen in results for IAEA 135, Ribble and Cumbrian sediments where we took a very small amount of sample (0.5–1g) and due to high background the results have high measurement uncertainty. The average background of the beta counter was 33 cpm. The limit of detection was calculated for each sample separately taking mass and recovery into consideration.

Conclusions

The radiochemical procedure described here was found to be reliable and accurate. In addition, the advantage of this method is the determination of the most critical alpha activation products and ^{90}Sr simultaneously thus saving time and the amount of sample needed for analysis. The main disadvantage is its higher detection limit for determination of ^{90}Sr by liquid scintillation counting due to the high background of the counter. This problem can be avoided using more sensitive beta proportional counting but the time for the analysis is then extended due to time needed for ^{90}Y ingrowth. A beta proportional counter has very low efficiency for low the beta energies of ^{90}Sr (17%).

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Povzetek

Razvili smo zanesljivo in občutljivo metodo za istočasno določanje ^{241}Am , ^{237}Np , Pu radioizotopov in ^{90}Sr v vzorcih sedimentov in prsti.

Ločitev radionuklidov sem izvedla z anionsko izmenjevalno kolono, kjer sta se selektivno ločila Pu in Np. Za ločitev Am in Sr sem uporabila ekstrakcijsko kromatografijo z uporabo TRU in Sr kolon. Tanke merilne vire za alfa spektrometrično detekcijo smo pripravili z mikroobarjanjem in mikrofiltracijo. Izkoristke radiokemičnega postopka smo določili z uporabo radioaktivnih sledilcev ^{243}Am , ^{239}Np in ^{242}Pu . Za stroncij smo izkoristek določili gravimetrično s tehtanjem oborine stroncijevega oksalata, merilni vir pa smo izmerili s tekočinsko-scintilacijskim števcem.

Metodo smo testirali z analizo referenčnih vzorcev sedimentov ter zemelj. Rezultate smo primerjali z referenčnimi ali literaturnimi vrednostmi in ugotovili dobro ujemanje.