

# SEQUENTIAL EXTRACTION PROCEDURE FOR DETERMINATION OF URANIUM, THORIUM, RADIUM, LEAD AND POLONIUM RADIONUCLIDES BY ALPHA SPECTROMETRY IN ENVIRONMENTAL SAMPLES

J. M. OLIVEIRA AND F. P. CARVALHO<sup>\*)</sup>

*Instituto Tecnológico e Nuclear  
Departamento de Protecção Radiológica e Segurança Nuclear  
E.N. 10, 2686-953 Sacavém, Portugal*

A sequential extraction technique was developed and tested for common naturally-occurring radionuclides. This technique allows the extraction and purification of uranium, thorium, radium, lead, and polonium radionuclides from the same sample. Environmental materials such as water, soil, and biological samples can be analyzed for those radionuclides without matrix interferences in the quality of radioelement purification and in the radiochemical yield. The use of isotopic tracers ( $^{232}\text{U}$ ,  $^{229}\text{Th}$ ,  $^{224}\text{Ra}$ ,  $^{209}\text{Po}$ , and stable lead carrier) added to the sample in the beginning of the chemical procedure, enables an accurate control of the radiochemical yield for each radioelement. The ion extraction procedure, applied after either complete dissolution of the solid sample with mineral acids or co-precipitation of dissolved radionuclide with  $\text{MnO}_2$  for aqueous samples, includes the use of commercially available pre-packed columns from Eichrom® and ion exchange columns packed with Bio-Rad resins, in altogether three chromatography columns. All radioactive elements but one are purified and electroplated on stainless steel discs. Polonium is spontaneously plated on a silver disc. The discs are measured using high resolution silicon surface barrier detectors.  $^{210}\text{Pb}$ , a beta emitter, can be measured either through the beta emission of  $^{210}\text{Bi}$ , or stored for a few months and determined by alpha spectrometry through the in-growth of  $^{210}\text{Po}$ . This sequential extraction chromatography technique was tested and validated with the analysis of certified reference materials from the IAEA. Reproducibility was tested through repeated analysis of the same homogeneous material (water sample).

## 1 Introduction

The analysis of alpha-emitting radionuclides in environmental materials is of the utmost interest in order to assess radiation exposure to the natural radioactive background and to technologically enhanced radioactive environments [1]. Several radiochemical analytical procedures have been developed based on extraction with liquid organic solvents, ion exchange column chromatography, and ready-to-use packed columns [2-4]. Most of these procedures are time consuming, generate high amounts of toxic waste, such as organic solvents, and do not always allow for high chemical recovery yields.

For many years we have been using column chromatography to extract and purify the radioactive elements of uranium and thorium decay series with good results [5-7]. As the main requirements of radiochemical procedures are reproducibility and reliability, high recovery yields, and low time demands, we tested several modifications to optimise the procedures and to incorporate ready-to-use packed columns.

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<sup>\*)</sup> E-mail: carvalho@itn.pt

This paper describes a sequential extraction technique, in two different versions, suitable for the analyses of naturally occurring alpha emitters at environmental levels in various sample matrices. Results of validation tests performed with certified reference materials are presented as well as the alpha spectra obtained for various radionuclides.

## **2 Materials and Methods**

Materials used include acids and reagents of analytical grade, Teflon beakers, glassware of Pyrex quality, and ion exchange resins of analytical grade. We combine the use of pre-packed ion exchange resins UTEVA (Eichrom®) and columns packed in the laboratory with Bio-Rad resins, namely the anion exchange AG1×8, 100-200 mesh, and the cation exchange AG 50W-×12, 200-400 mesh.

Polonium is spontaneously deposited onto silver foil 99.9% pure, cut in the laboratory with an extruder in 24 mm diameter discs. Discs are used once and discarded.

The electrodeposition of actinides is performed on the polished face of 19 mm diameter stainless steel discs. The deposition cells are of Teflon and use a 1 mm platinum wire as anode, with the disc as a cathode. The power source used allows setting the current intensity and voltage for a tandem of four deposition cells in a parallel array.

Technical procedures include the steps of addition of internal tracers to the sample, dissolution of solid samples in mineral acids or co-precipitation of radionuclides from aqueous matrices with MnO<sub>2</sub>, followed by chromatographic extraction of radioactive elements from the sample matrix and their purification using cationic and anionic exchange resin beds, followed by the electrodeposition of purified radionuclides onto stainless steel discs to obtain a thin layer alpha source, and, finally, the determination of radionuclides by alpha spectrometry.

Internal tracers added to the samples in the beginning of the procedure include the addition of: 0.120 Bq <sup>232</sup>U in radioactive equilibrium with its daughter radionuclides <sup>228</sup>Th and <sup>224</sup>Ra from a stock 1M HNO<sub>3</sub> solution; 0.017 Bq of <sup>229</sup>Th and 0.08 Bq of <sup>209</sup>Po in 1M HNO<sub>3</sub> solutions, and 10 mg of stable Pb from a Pb(NO<sub>3</sub>)<sub>2</sub> solution. These solutions of pure radionuclides are calibrated against certified alpha standards (electroplated sources) purchased from CEA and Amersham.

The initial step of dissolution of the sample has been applied to soils, sediments, air filters, foods, such as vegetables, fish, meat, and milk powder, and the co-precipitation method has been applied to liquid samples such as drinking water, sea water, wine and biological fluids such as urine.

Both techniques described below have in common the initial step of sample dissolution/precipitation, the deposition of polonium onto a silver disc and, at the end, the electrodeposition of purified radioactive elements followed with alpha spectrometry measurement. The two techniques are different in the sequence of the extraction and purification steps to obtain the various radioactive elements.

### 3 Experimental

*Sample preparation.* Solid samples such as soils (about 0.5 g) or freeze-dried foods (about 5 g) are weighted with an analytical balance. Isotopic tracers are pipetted onto the sample in a Teflon beaker and the sample covered with concentrated  $\text{HNO}_3$  and  $\text{HCl}$ . Wet ashing is performed with gentle heating on a hotplate. Small amounts of  $\text{HF}$  are added to dissolve the silica fraction. Occasionally, drops of  $\text{H}_2\text{O}_2$  are added to oxidize organic matter and to ensure conversion of oxidation state of tracers and radionuclides of the sample. After complete dissolution of the sample material, the solution is evaporated to dryness and the residue further treated with concentrated  $\text{HCl}$  to remove all traces of nitric acid.

Liquid samples such as water (3 – 5 L) are acidified at the collection point or immediately after filtration in order to avoid loss of radionuclides from the soluble phase onto the container walls. The isotopic tracers are added and the sample homogenized by vigorous stirring. At the moment of analyses,  $\text{MnCl}_2$  is added to the sample with  $\text{KMnO}_4$ , and air bubbled overnight to ensure thorough mixing. Ammonium hydroxide is used to raise the pH to 8-9 under continuous stirring and pH control with a pH electrode. Manganese precipitates at this pH as a brown flock. The precipitate is allowed to settle for several hours on the bottom of the beaker and the supernatant siphoned with a pump. The final volume is centrifuged in order to discard as much water as possible. The precipitate is dissolved directly in the centrifuge tubes with  $\text{HCl-H}_2\text{O}_2$  mixture, and transferred with washes into a Pyrex beaker. The sample solution is gently evaporated to dryness.

*Polonium deposition.* The beaker containing the dry residue obtained either from the solid sample wet ash or from the precipitate of aqueous sample will be used for polonium deposition. The sample residue is dissolved with 0.5M  $\text{HCl}$  and 200 mg of ascorbic acid is added. Polonium is spontaneously plated overnight onto a silver disc with magnetic stirring at room temperature.

In both cases after polonium deposition, the solution is recuperated, evaporated to dry residue and the residue treated with  $\text{HNO}_3$  to destroy the ascorbic acid. From this point onwards, the sample is dissolved in a different solution according to the chromatographic separation schema to be adopted.

If  $^{226}\text{Ra}$  determination is wanted, the formation of radioactive equilibrium between the  $^{228}\text{Th}$  of the sample and its  $^{224}\text{Ra}$  daughter should be ensured. For this purpose the sample should be stored for at least 15 days from the collection date to the chromatographic separation. However, sample preparation and polonium deposition can be performed during these 15 days.

*Chromatographic separation – Technique 1.* The sample residue is dissolved in a small volume of 3M  $\text{HNO}_3$  – 1M  $\text{Al}(\text{NO}_3)_3$ , 10 mL or 15 mL as needed. Add 2 mL or 3 mL of ferrous sulphamate and swirl. Add 200 mg of ascorbic acid and mix [8]. This solution is transferred to a UTEVA column (column I) preconditioned with 3M  $\text{HNO}_3$  (Fig. 1). The sample volume plus washes until a total of 20 ml are collected in a first eluate fraction. This fraction contains Ra and Pb still mixed with other elements such as Fe, Mn, Pu and Am and it is saved to be purified in column II. Take a note of date and hour of this separation of  $^{224}\text{Ra}$  from  $^{228}\text{Th}$  for correction of  $^{224}\text{Ra}$  decay. Further work on column I

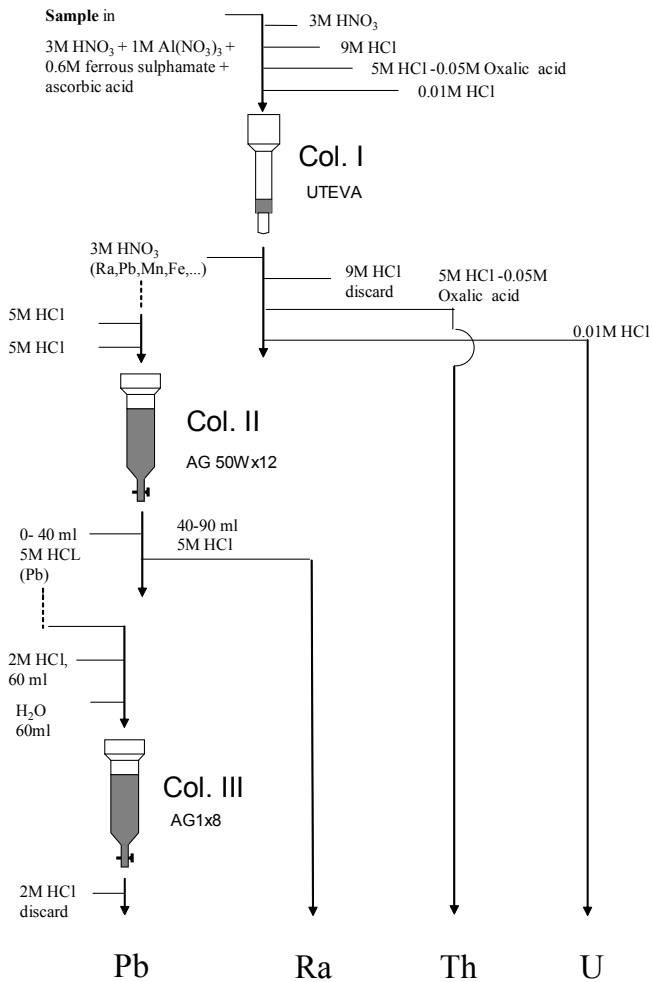


Fig. 1. Flow diagram of the sequential extraction and purification of radionuclides after polonium deposition (Technique 1).

includes the elution with 5 mL of 9M HCl to convert column to chloride system (discard) and elution with 20 mL of the mixture 5M HCl-0.05M oxalic acid. The eluate of this fraction contains thorium sufficiently purified to be electroplated. In samples from some locations neptunium may occur and will be co-eluted with thorium. However, this is not the case in most of the current environmental materials analyzed. Further elution of column I with 15 mL of 0.01M HCl, removes uranium from the resin bed, ready for the electrodeposition step.

The first fraction obtained, containing Ra and Pb, is slowly evaporated to dryness and the residue treated with small volumes of concentrate HCl to convert salts into chlorides. The residue is dissolved with 6 mL of 5M HCl and fed onto a cation exchange column AG 50W×12, with 4 mL resin bed previously equilibrated with this acid. The first fraction of eluate, 40 mL corresponding to the sample volume plus washes with 5M HCl, contain lead and it is saved for further purification. Continuing the column elution with 5M HCl, the eluate from 40 mL to 90 mL will contain radium. The radium solution is saved for the electrodeposition step.

The fraction containing lead is taken to dryness and the residue dissolved in a small volume of 2M HCl. This lead solution is fed onto column III, an anion exchange resin AG1×8, with 10 mL resin bed previously equilibrated with 2M HCl. The first 60 mL of eluate corresponding to the sample volume and washes are discarded. Elution with 60 mL of distilled water will strip lead from the column. Lead solution is saved for co-precipitation of  $^{210}\text{Pb}$  as lead chromate.

*Technique 2.* After polonium plating, the sample solution is evaporated to residue and dissolved with 6 mL of 5M HCl (Fig. 2). This solution is fed into a column with 4 mL AG 50W×12 resin bed pre-equilibrated with 5M HCl (column I). The sample solution plus washes with 5M HCl until 40 mL of eluate volume, will drain the U and Pb through the column. This fraction is saved for further purification.

Continuing the elution of the column I with 5M HCl, radium is eluted in the fraction from 40 to 90 mL, sufficiently purified to be electroplated. Take a note of date and hour of radium elution for correction of  $^{224}\text{Ra}$  radioactive decay. Further elution of the column with 40 mL of 0.5M oxalic acid will remove thorium, purified for electrodeposition.

The first eluate fraction of column I, containing U and Pb, is taken to dryness and the residue dissolved in a small volume, 10 mL (or 15 mL if residue is abundant) of 3M  $\text{HNO}_3$  – 1M  $\text{Al}(\text{NO}_3)_3$ . Add 2 mL (or 3 mL) of ferrous sulphamate and swirl. Add 200 mg of ascorbic acid and mix. This solution is fed in to a UTEVA column (column II) pre conditioned with 3M  $\text{HNO}_3$ .

The sample volume plus two washes of the beaker and column, 5 mL of 3M  $\text{HNO}_3$  each, are recuperated as a first eluate fraction. This fraction contains Pb but still requires further purification. Continuing elution of column II with 5 mL of 9M HCl will convert column to chloride system. Elution with 20 mL of 5M HCl-0.05M oxalic acid will clean up the column and will remove traces of thorium and iron that later could interfere with the electrodeposition. Elution with 15 mL of HCl 0.01M strips uranium from the column, ready to go for electrodeposition.

The first eluate fraction, containing lead, is slowly evaporated and the residue recuperated in concentrated HCl, dried again to remove nitric acid and redissolved in a small volume of 2M HCl. This solution is passed through an AG1×8 column, pre-equilibrated with 2M HCl, followed by 60 mL 2M HCl washes. Lead is then removed from the column with 60 mL of distilled  $\text{H}_2\text{O}$  and saved for precipitation as lead chromate.

*Electrodeposition.* Electrodeposition of uranium and thorium is performed on the polished surface of stainless steel discs, in Teflon cells with a platinum wire as anode, inspired on the design proposed by Talvatie [9]. The eluate fraction containing uranium or thorium for electrodeposition, are evaporated to dryness and the residue treated with a

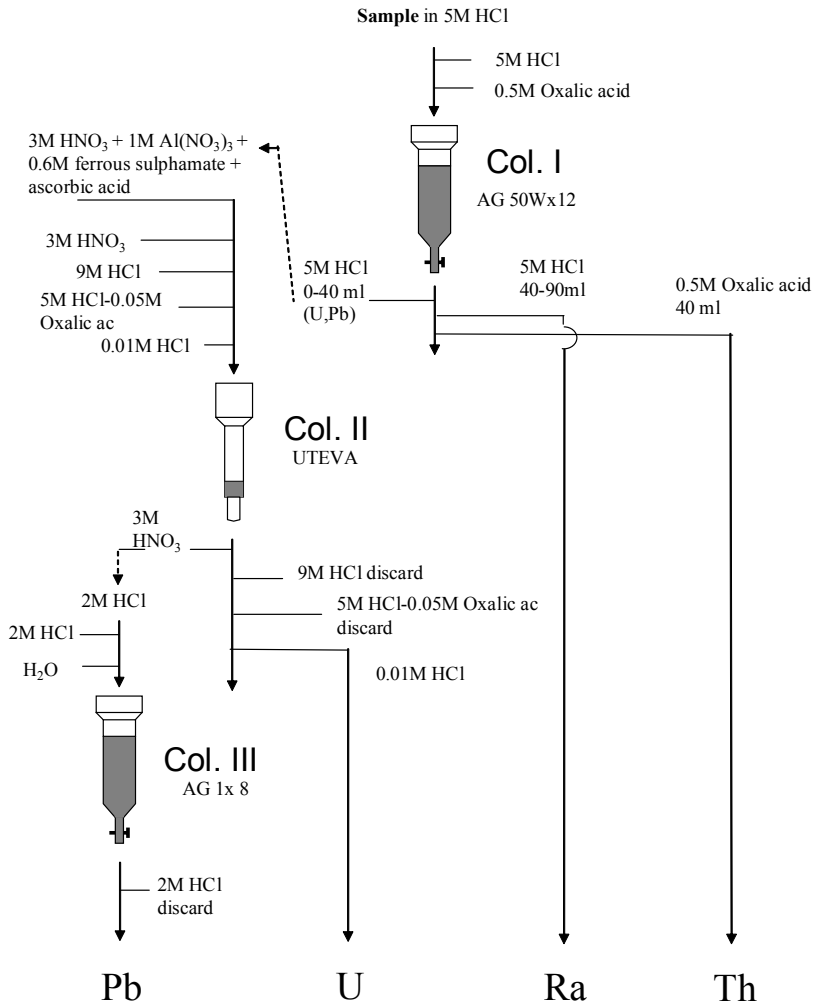


Fig. 2. Flow diagram of the sequential extraction and purification of radionuclides after polonium deposition (Technique 2)

few drops of HNO<sub>3</sub> to convert salts. The dry residue is dissolved with 10 mL of ammonium solution (100g L<sup>-1</sup> of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) at pH 2 adjusted with H<sub>2</sub>SO<sub>4</sub> and transferred to the electrode position cell with rinses with ammonium solution [2]. The electrodeposition is made during 1 hour with the electric current of 1A. The disc surface is than rinsed with distilled water and ethanol and strongly heated on the hotplate. Usually, a blue-like colour taints the stainless steel surface and no deposit is visible.

Radium is electrodeposited following a different procedure. The solution purified above (radium fraction for electrodeposition) is gently evaporated to dryness. The residue is dissolved with 0.35M ammonium acetate – 0.1M HNO<sub>3</sub> and the solution transferred with washes to the deposition cell [10]. Electrodeposition on a stainless steel disc is performed during 3 hours with a electric current of 600 mA. At the end, the disc surface is clear and no deposit should be visible.

Alternatively, radium can be electroplated from a solution of 1 mL of 0.1M HNO<sub>3</sub> + 9 mL of ethanol, during 30 min with 70 mA electric current [2,11]. However, this method has no advantage over the one described above.

Lead is recuperated from the purified solution obtained as described in section above, according to the following procedure. The solution is slowly evaporated to dryness and the residue dissolved with a few drops of HNO<sub>3</sub>. Evaporate again and dissolve the residue with 30 mL of distilled water and 1mL of acetate buffer solution. Bring solution to boiling and, always on the hotplate, add 1 mL of 10% Na<sub>2</sub>CrO<sub>4</sub> solution [2]. A yellow precipitate of PbCrO<sub>4</sub> is formed. Maintain the heating for 30 min. Allow to cool and recuperate the precipitate by filtration. Determine the radiochemical yield by the gravimetric method and store the filter with the precipitate for several months (4-6). Then dissolve the filter and precipitate in the presence of a new amount of the tracer <sup>209</sup>Po and proceed with the deposition of polonium to determine <sup>210</sup>Pb through the in-growth of <sup>210</sup>Po since the date of precipitation. Alternatively, the filter with lead chromate may be mounted on a sample holder and counted with a low background beta counter using the beta radiation emitted by <sup>210</sup>Bi and after formation of the radioactive equilibrium of <sup>210</sup>Bi with <sup>210</sup>Pb. However, the determination of <sup>210</sup>Pb through the <sup>210</sup>Po in growth is much more sensitive and accurate.

*Alpha measurements.* The measurement of radionuclides is performed using silicon surface barrier detectors R-Type, 100 μm depletion depth, and ion implanted detectors ULTRA-AS (Ortec). The ion implanted detectors, 450 mm<sup>2</sup> active surface, are assembled in groups of 8 in OCTETE Plus (EG&G). Counting time is adjusted to the activity in the sample discs in order to obtain a counting statistics better than 5% relative uncertainty.

The performance of purification and electrodeposition steps is crucial to obtain alpha sources of good quality. Typically in our sources the energy resolution measured on the <sup>210</sup>Po peak is 45-50 keV with surface barrier detectors and 20 keV with ion implanted detectors. Fig. 3 shows typical spectra of environmental samples.

The average recovery yields obtained are reported in Table 1 based on analytical results of a large number of environmental samples with different matrices. In general the yields are consistently high and similar for both techniques.

*Validation and Testing.* Validation of the procedures was made for reproducibility and accuracy using certified reference materials from the IAEA in the available matrices.

The IAEA-385 reference material, sediment from the Irish Sea, was analysed by both techniques described above. Table 2 shows the results, as well as the IAEA recommended concentration values for this material. There is, in general, a good agreement between the results obtained by each technique used by us, and also between the results of our determinations and the IAEA values.

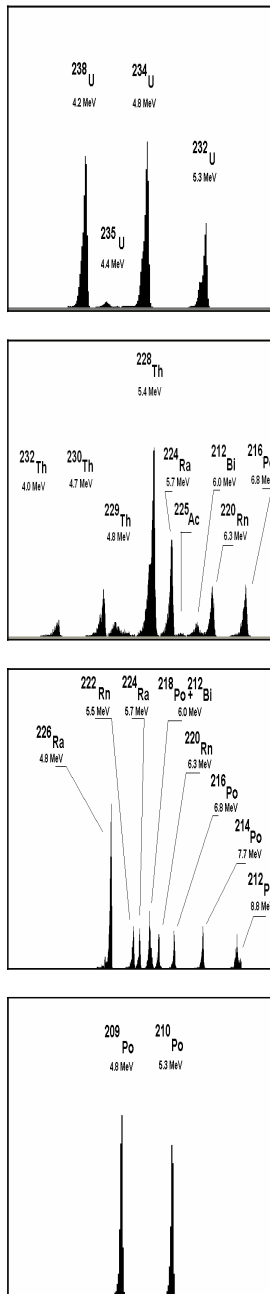


Fig. 3. Alpha spectrogram of sources prepared using the techniques described herein. From top to bottom: uranium, thorium, radium and polonium spectra. The main energies are indicated for each radionuclide.



Table 1. Recovery yields (mean  $\pm 1\sigma$ ) of the radiochemical separation procedures applied in the analyses of  $n$  independent environmental samples, determined with the internal isotopic tracers added to the sample

Sample matrix	Separation technique	$n$	U	Th	Ra	Po	Pb
Water	2	16	$0.71 \pm 0.10$	$0.37 \pm 0.10$	$0.16 \pm 0.09$	$0.86 \pm 0.09$	$0.47 \pm 0.20$
	1	23	$0.58 \pm 0.17$	$0.51 \pm 0.18$	$0.27 \pm 0.20$	$0.86 \pm 0.09$	$0.47 \pm 0.16$
Suspended matter	1	21	$0.83 \pm 0.09$	$0.59 \pm 0.17$	$0.31 \pm 0.11$	$0.84 \pm 0.11$	$0.48 \pm 0.10$
Biota	1	19	$0.88 \pm 0.12$	$0.47 \pm 0.18$	$0.22 \pm 0.12$	$0.80 \pm 0.08$	$0.28 \pm 0.24$
Sediments	1	17	$0.83 \pm 0.06$	$0.73 \pm 0.14$	$0.09 \pm 0.02$	$0.88 \pm 0.09$	--

Table 2. Analytical results for reference material IAEA-385, marine sediment from the Irish Sea ( $\text{Bq kg}^{-1}$  dry weight)

	$^{238}\text{U}$	$^{235}\text{U}$	$^{234}\text{U}$	$^{232}\text{Th}$	$^{230}\text{Th}$	$^{226}\text{Ra}$	$^{210}\text{Po}$ (= $^{210}\text{Pb}$ )
IAEA-385 Recommended values	29.4	1.36	27.2	33.8	31.8	22.7	35.5
Mean and range	28.0-30.5	1.24-1.51	25.8-28.6	32.6-34.5	30.0-34.9	21.8-24.0	31.2-38.9
Technique 1 Mean $\pm 1\sigma$ of the mean ( $n=3$ )	$31.4 \pm 0.8$	$1.44 \pm 0.01$	$31.3 \pm 1.2$	$33.3 \pm 0.8$	$31.6 \pm 1.3$	$25.0 \pm 4.2$	$36.9 \pm 0.8$
Technique 2 Mean $\pm 1\sigma$ of the mean ( $n=4$ )	$31.7 \pm 1.0$	$1.36 \pm 0.08$	$30.3 \pm 0.7$	$29.3 \pm 1.1$	$32.0 \pm 2.7$	$22.0 \pm 1.6$	$36.9 \pm 0.8$

The IAEA-414 reference material, mixed fish sample from the Irish Sea, was analyzed as an example of organic matrix with high fat content. Our results are comparable to the IAEA values and show that a consistent analytical performance is obtained in this matrix also (Table 3).

No liquid sample is available as a reference material. We tested reproducibility of our procedure in a water sample from the tap. A 30 L sample was split into 3 portions of equal volume, acidified and then the subsamples were analyzed in parallel following the procedure outlined above as technique 1. Results are in the confidence interval of the mean  $\pm 1$  standard deviation, indicating high reproducibility (Table 4).

Robustness of the performance when the technique is applied to samples with different matrix was tested analyzing cabbage, potatoes, fish filet, meat, water, urine, soils and sediments with high yield of recovery and complete separation of radioactive elements. Precision was tested also through participation in analytical inter-laboratory worldwide comparisons analysing blind samples (round robin tests) organized by IAEA and WHO, with good results.[12-14] Table 5 shows the results of the intercomparison exercise for uranium isotopes in a urine sample.

Table 3. Analytical results for the certified reference material IAEA-414, mixed with fish muscle from the Irish Sea

	$^{238}\text{U}$	$^{235}\text{U}$	$^{234}\text{U}$	$^{226}\text{Ra}$	$^{210}\text{Po}$ (= $^{210}\text{Pb}$ )
IAEA-414 Recommended values Mean and range	1.11 (1.06-1.117)	0.050 (0.045-0.058)	1.22 (1.14-1.27)	1.40 (0.59-1.76)	2.22 (1.55-2.60)
Mean $\pm$ 1 $\sigma$ of the mean (n=3) Technique 1	1.08 $\pm$ 0.08	0.064 $\pm$ 0.012	1.38 $\pm$ 0.09	1.10 $\pm$ 0.02	1.96 $\pm$ 0.03

Table 4. Analytical results (Bq m<sup>-3</sup>) of three replicate water sub samples

Sub sample	$^{238}\text{U}$	$^{235}\text{U}$	$^{234}\text{U}$	$^{232}\text{Th}$	$^{230}\text{Th}$	$^{226}\text{Ra}$	$^{210}\text{Po}$
a	24.9 $\pm$ 0.9	1.2 $\pm$ 0.1	27.3 $\pm$ 0.9	0.16 $\pm$ 0.07	0.96 $\pm$ 0.13	17.0 $\pm$ 1.3	4.3 $\pm$ 0.2
b	24.2 $\pm$ 0.8	1.1 $\pm$ 0.1	27.6 $\pm$ 0.9	0.09 $\pm$ 0.03	0.79 $\pm$ 0.09	17.4 $\pm$ 1.3	4.5 $\pm$ 0.2
c	24.2 $\pm$ 0.8	1.2 $\pm$ 0.1	25.9 $\pm$ 0.9	0.15 $\pm$ 0.05	0.93 $\pm$ 0.12	18.5 $\pm$ 1.7	4.4 $\pm$ 0.2
Mean $\pm$ 1 $\sigma$ of the mean	24.4 $\pm$ 0.2	1.2 $\pm$ 0.03	26.9 $\pm$ 0.5	0.13 $\pm$ 0.02	0.93 $\pm$ 0.08	17.6 $\pm$ 0.4	4.4 $\pm$ 0.06

Table 5. IAEA interlaboratory analytical comparison results (mBq in sample  $\pm$  2 $\sigma$ ) in a urine sample organized by the IAEA [12]

	$^{238}\text{U}$	$^{235}\text{U}$	$^{234}\text{U}$
IAEA Reference value	21.5 $\pm$ 0.25	0.99 $\pm$ 0.012	20.7 $\pm$ 0.406
Our determination	20.4 $\pm$ 1.01	1.20 $\pm$ 0.205	19.6 $\pm$ 0.977

The comparison with other sequential extraction techniques used before, show that the current technique has the advantages of separating a large set of radioactive elements in less time (about half of the time required before), with similar high performance, less chromatography columns, less manipulation, and generating a lower volume of acid waste. The disadvantage is the relatively higher cost of each analysis with the purchase of ready-to-use chromatography columns although this becomes compensated by the lower technical time needed in the analytical work.

#### 4 Final considerations

This radiochemical procedure, in comparison with procedures used before, allows for obtaining results faster. In three days, either by technique 1 or technique 2, samples are completely analyzed from the polonium deposition to the completion of electrodeposition of all other radionuclides on discs.

Both procedures outlined in this paper conduce to comparable results in the sample matrices tested. Actually, the main difference is the sequence of radionuclide extraction and purification. Nevertheless, technique 1 has the relative disadvantage that will not remove neptunium from the thorium fraction, although this is not a problem in most of the samples currently analyzed. Technique 2 eliminates neptunium more efficiently and allows to obtaining purified radium earlier than technique 1, which may be of interest in some cases.

Both versions allow for a comparable accuracy in the final results. The reproducibility and identical performance of each technique was shown in the analyses of environmental samples and intercomparison analytical exercises.

### References

- [1] UNSCEAR (2000). Sources and Effects of Ionizing Radiation. United Nations Scientific Committee on the Effects of Atomic Radiation. UNSCEAR 2000 Report to the General Assembly, Vol. I. United Nations, New York.
- [2] Bojanowski R., Fukai R., Balestra S., and Asari H.: *In: Proceed. of the 4<sup>th</sup> Symposium on the Determination of Radionuclides in Environmental and Biological Materials*. Laboratory of the Government Chemist, London, Paper No. 9 (1983).
- [3] Holm E.: *Int. J. Appl. Radiat. Isot.* 35 (1984) 285]
- [4] Horwitz E. P., Dietz M. L., Chiarizia, R., and Diamond, H.: *Analytica Chimica Acta* 266 (1992) 25.
- [5] Carvalho F. P.: *The Science of the Total Environment* 196 (1997) 151.
- [6] Carvalho F. P. et al.: *In: Proceed. of an International Workshop on Environmental Contamination from Uranium Production Facilities and Remediation Measures*, Lisbon 11-13 Feb. 2004, p.41. International Atomic Energy Agency, Vienna, 2005.
- [7] Carvalho F.P., et al.: *In: Uranium in the Environment: Mining Impacts and Consequences*. B. J. Merkel and A. Hasche-Berger Eds., p. 691. Springer-Verlag Berlin Heidelberg Publ. (2006).
- [8] Eichrom: Analytical procedure for the determination of Americium, Plutonium and Uranium in Water. Eichrom Industries Inc., Analytical Procedures, UK, Ref. ACW03 Rev 1.5, (1995).
- [9] Talvitie N.A.: *Analytical Chemistry* 44 (1972) 280.
- [10] Roman D.: *Int. J. Appl. Isot.* 35 (1984) 990.
- [11] Hancock G. J. and Martin P.: *Appl. Radiat. Isot.* 42 (1991) 63.
- [12] Results of the 2001/02 Intercomparison Exercise on Determination of the Quantity Activity of Alpha Emitters in Urine Samples. IAEA Division of Radiation and Waste Safety, Radiation Monitoring and Protection Services Section, Report on Exercise PROCOSTAT 2000. International Atomic Energy Agency, Vienna, 2003.
- [13] Pham M., La Rosa J., Lee S.H. and Povinec P.: IAEA-414, Radionuclides in Mixed Fish from Irish Sea and the North Sea. International Atomic Energy Agency, Monaco Report IAEA/MEL/73 (2004).
- [14] Pham M. K., Sanchez Cabeza, J. A. and Povinec, P. P.: IAEA-385, Radionuclides in Irish Sea Sediment. International Atomic Energy Agency, Monaco Report IAEA/MEL/76 (2005).