

# The development of sequential separation methods for the analysis of actinides in sediments and biological materials using anion-exchange resins and extraction chromatography

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New, quantitative methods for the determination of actinides have been developed for application to marine environmental samples (e.g., sediment and fish). The procedures include aggressive dissolution, separation by anion-exchange resin, separation and purification by extraction chromatography (e.g., TRU, TEVA and UTEVA resins) with measurement of the radionuclides by semiconductor alpha-spectrometry (SAS). Anion-exchange has proved to be a strong tool to treat large volume samples, and extraction chromatography shows an excellent selectivity and reduction of the amounts of acids. The results of the analysis of uranium, thorium, plutonium and americium isotopes by this method in marine samples (IAEA-384, -385 and -414) provided excellent agreement with the recommended values with good chemical recoveries.

## Introduction

Isotopes of thorium, uranium, plutonium and americium are useful tracers for better understanding of biogeochemical processes and have attracted the public concern in the aspect of potential risks to human health in the marine environment. However, in general, the sampling of marine materials such as seawater, sediment, and biological material including sediment trap samples is difficult and expensive. Therefore, it is desirable to analyze as many radionuclides as possible on a minimum single sample aliquot. Numerous methods have been published for the determination of thorium, uranium, plutonium and americium in environmental samples, including precipitation methods,<sup>1–4</sup> use of ion-exchange resins,<sup>5–11</sup> extraction chromatography,<sup>12–19</sup> and liquid-liquid solvent extraction.<sup>20–23</sup> Radionuclide separation using liquid-liquid solvent extractions are time consuming and generate substantial volumes of organic wastes. One of the most popular methods, separation using ion-exchange resins, is effective for large samples and reasonable in cost relative to extraction chromatography resins such as TEVA, UTEVA, and TRU (EiChroM, Inc.). However, the process requires the use of many chemicals, time consuming and produces large amounts of chemical wastes. Extraction chromatography reduces the number of chemicals needed, as well as the processing time.<sup>12–14</sup> Nevertheless, large samples still need pre-concentration techniques such as co-precipitation to reduce the amount of matrix before extraction chromatography can be applied. On the basis of the advantages of anion-exchange resins and extraction chromatography methods, a sequential separation procedure has been developed by IAEA-MEL for marine environmental samples.

## Experimental

### *Dissolution by concentrated acids*

Several IAEA reference materials which were chosen for this study are representative of materials in the marine environment: IAEA-384 (Lagoon Sediment collected from the former nuclear bomb test site, Fangataufa atoll, in French territory) is mainly composed of calcareous material; IAEA-414 is a Fish Sample which is a mixture of those sampled in the Irish Sea and North Sea; and IAEA-385 is a Sediment which was collected in the Irish Sea.

A suitable quantity of a dry, ground solid sample is weighed into a porcelain crucible and ignited at 550 °C in an electric furnace. All or part of the remaining ash is transferred to a PTFE beaker and slurried with 2M HNO<sub>3</sub>. Known amounts (typically 10–20 mBq) of radiochemical yield determinants (<sup>229</sup>Th, <sup>232</sup>U or <sup>236</sup>U, <sup>236</sup>Pu or <sup>242</sup>Pu, <sup>243</sup>Am) are added to the suspension, which is heated for several hours to preclude possible vigorous reactions and evaporated to a conveniently small volume. Concentrated HF, HNO<sub>3</sub> and HCl are added successively to the paste.

After a successful dissolution (in the analyst's opinion) of a large insoluble residue, the resulting solution is in 100 ml of 1M HNO<sub>3</sub>. For biological samples or sediment samples containing no iron, 10–20 mg of Fe(III) as nitrate are added, but with sediment samples already containing considerable iron, no additional iron is added. To the hot solution, 1–4 ml of 25% hydrazinium hydroxide (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O) reducing agent are added slowly with vigorous stirring. All Pu species (IV, V and VI) and Fe(III) are reduced to Pu(III) if a substantial fraction of the Fe(III) is reduced to

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Fe(II). After the presence of a significant Fe(II) concentration is established by means of a spot test with 2,2'-bipyridine, 30 ml of conc. HNO<sub>3</sub> are added and the solution is heated to destroy the excess of hydrazinium hydroxide. After cooling to room temperature, 5 g of NaNO<sub>2</sub> are added to convert any remaining Pu(III) to Pu(IV) and to stabilize the Pu(IV), and then the solutions are gently boiled to destroy excess HNO<sub>2</sub>. Once again the solutions are cooled and 70 ml of cold 65–70% HNO<sub>3</sub> are added to produce a final 7–8M HNO<sub>3</sub> solution containing Pu(IV) as the anionic hexanitrate complex. These sample solutions are now ready for the purification procedure with anion exchange column chromatography.<sup>19,24</sup>

#### *Separation of americium and uranium from plutonium and thorium fractions*

The filtered sample solutions (7–8M HNO<sub>3</sub>) are passed through anion exchange resin (AG1-X8, 100–200 mesh, Cl<sup>-</sup>) columns (10 mm diameter × 120 mm long), which are pre-conditioned with 50 ml of 8M HNO<sub>3</sub>. The columns are washed with 100 ml of 8M HNO<sub>3</sub>. Americium(III) and uranium(VI) pass through the column, and these effluents are kept for americium and uranium analysis. Thorium is stripped with 100 ml of 10M HCl, which also converts the resin back into the chloride form. Plutonium(IV) converts to an anionic chloro-complex and is retained on the resin. Finally, plutonium is eluted with 100 ml of 0.1M NH<sub>4</sub>I–9M HCl solution, where the iodide reduces Pu(IV) to Pu(III). The eluates are evaporated to dryness.

#### *Purification of plutonium by TEVA column*

Four ml of conc. HNO<sub>3</sub> and a few drops of H<sub>2</sub>O<sub>2</sub> are added to the Pu fraction and evaporated. H<sub>2</sub>O<sub>2</sub> reduces iodate (formed by oxidation with conc. HNO<sub>3</sub>) to iodine (I<sub>2</sub>), which is vaporized. This process is repeated until no further violet fumes of iodine appear upon H<sub>2</sub>O<sub>2</sub> addition. The clear solution is evaporated. Samples are dissolved in 10 ml of 2.5M HNO<sub>3</sub>, 100 mg of NaNO<sub>2</sub> are added to oxidize Pu(III) to Pu(IV), and the solution is heated gently. After cooling, each sample is loaded into a pre-conditioned TEVA column with 10 ml of 2.5M HNO<sub>3</sub>. The column is washed with an additional 10 ml of 2.5M HNO<sub>3</sub> and then 10ml of 9M HCl. Finally, plutonium is eluted with 20 ml of 0.05M HNO<sub>3</sub>–0.05M HF. The eluates are evaporated to dryness.

#### *Purification of thorium by anion exchange resin*

Anion-exchange columns (AG1-X8 (100–200 mesh, Cl<sup>-</sup> form, 10 mm dia. × 50 mm long) are pre-conditioned with 25 ml of 8M HNO<sub>3</sub> to prepare for the

further purification of thorium. Thorium fractions from the 10M HCl strips of the first anion exchange resin column are evaporated to dryness, dissolved in 20 ml of 8M HNO<sub>3</sub> and passed through the column. Thorium is retained as an anionic nitrate-complex. The columns are washed with 50 ml of 8M HNO<sub>3</sub>. Finally, thorium is eluted with 50 ml of 10M HCl. The eluates are evaporated to dryness.

#### *Separation of americium from uranium fraction*

Anion-exchange resin columns (AG 1-X8, 100–200 mesh, 10 mm diameter × 10 mm long) pre-conditioned with 50 ml of 10M HCl are prepared for the separation of americium from uranium. Americium/uranium fractions from the 8M HNO<sub>3</sub> eluate of the first anion exchange resin column are evaporated to dryness, dissolved in 50 ml of 10M HCl and passed through the column. The columns are washed with 50 ml of 10M HCl. Uranium is retained but Am(III) is not retained in 10M HCl. Uranium is then eluted with 100 ml of hot 0.01M HCl. The eluates are evaporated to dryness.

#### *Purification of uranium by U/TEVA column*

Evaporated uranium fractions are dissolved in 10 ml of 2.5M HNO<sub>3</sub>+0.5M Al(NO<sub>3</sub>)<sub>3</sub>. 2 ml of 0.6M Fe-sulfamate and 200 mg of ascorbic acid are added, and the solution is set aside for 30 minutes. The samples are loaded into pre-conditioned UTEVA 2-ml columns with 10 ml of 2.5M HNO<sub>3</sub>. 15 ml of 2.5M HNO<sub>3</sub> are added to rinse out ferrous sulfamate and ascorbic acid. Under these conditions, Pu is reduced to Pu(III) and passes through the UTEVA. 15 ml of 6M HCl are added to the columns to strip any Th(IV). Finally, uranium is eluted with 20 ml of 0.01M HCl. The uranium eluates are evaporated to dryness.

#### *Pre-concentration of americium by Ca-oxalate precipitation*

Am effluents (10M HCl fraction) are evaporated to 20 ml, and 100 ml of de-ionized water and 100 mg of Ca in the form of CaCl<sub>2</sub> are added. 20 g of oxalic acid are added to the solution and heated on a hot plate until dissolved. Concentrated NH<sub>4</sub>OH is added to pH 2 to form the Ca-oxalate precipitates and gently boiled. Centrifuge the solution to separate the precipitates at 3000 rpm for 15 minutes. Supernatants are acidified to pH 1 with 10M HCl. 100 mg of Ca are added to the solutions and the oxalate precipitation is repeated. The solutions are centrifuged using the same tubes and washed with D.I water. Finally, Ca-oxalate precipitates are destroyed by 50 ml of conc. HNO<sub>3</sub> on the hot plate and evaporated to dryness.

*Purification of americium by TRU column*

Samples are dissolved in 10 ml of 2.5M HNO<sub>3</sub>+0.5M Al(NO<sub>3</sub>)<sub>3</sub>. 1.0 g of ascorbic acid is added to the solution to convert Fe(III) to Fe(II). The samples are loaded into pre-conditioned TRU columns with 15 ml of 2.5M HNO<sub>3</sub>. The columns are washed with 15 ml of 2.5M HNO<sub>3</sub> and 3 ml of 9M HCl. Americium is eluted with 20 ml of 4M HCl. The eluates are evaporated to dryness.

*Separation of americium from rare earths*

The samples (taken up by 0.5 cm<sup>3</sup> of AG1-X4 (100–200 mesh, Cl<sup>-</sup>) anion exchange resin in 10 ml of 1M HNO<sub>3</sub>–93% CH<sub>3</sub>OH) are passed through anion-exchange columns (10 mm diameter × 50 mm long) pre-conditioned with 1M HNO<sub>3</sub>–93% CH<sub>3</sub>OH. The columns are washed with 50 ml of 1M HNO<sub>3</sub>–93% CH<sub>3</sub>OH, and then 50 ml of 0.1M HCl–0.5M NH<sub>4</sub>SCN–80% CH<sub>3</sub>OH are passed to elute rare earths. The columns are then washed again with 30 ml of 1M HNO<sub>3</sub>–93% CH<sub>3</sub>OH. Americium is eluted with 50 ml of 1.5M HCl–86% CH<sub>3</sub>OH. The eluates are evaporated to dryness. The samples were then electrodeposited using the procedure described in Reference 25.

**Results and discussion***Comparison of total dissolution method with acid leaching method*

The samples were ashed at a temperature below 550 °C to avoid refractory plutonium compounds (e.g., PuO<sub>2</sub>) forming at higher temperature.<sup>26</sup> Either an acid leaching method (8M HNO<sub>3</sub>) or an aggressive dissolution method (using conc. HNO<sub>3</sub>, HCl, and HF) can usually achieve the extraction of actinides from the samples. Especially, the acid leaching method for anthropogenic radionuclides (e.g., Pu, Am, Cs and Sr) have been widely adopted by a number of laboratories to accommodate large sample sizes.<sup>4</sup> However, it has been shown that leaching is not appropriate for soils contaminated with refractory PuO<sub>2</sub> (for example, certain soil samples collected from near Sellafield and Chernobyl).<sup>27,28</sup> Moreover, this method is generally not suitable for naturally occurring uranium or thorium. As an alternative, the aggressive dissolution method using a combination of HNO<sub>3</sub>, HCl, and HF or a high temperature, molten salt fusion method can replace the acid leaching method. However, these “total dissolution” methods can be more time-consuming, costly (in terms of amounts of reagents and equipment such as Pt crucibles) and hazardous.<sup>29</sup> We have conducted two methods on the sea sediment (IAEA 384 and IAEA 385) and on the biological material (IAEA

414), focusing on the fallout-derived radionuclides (i.e., Pu and Am). As shown in Table 1, no remarkable differences were found between the acid leaching (8M HNO<sub>3</sub>) and total dissolution method using the combination of HNO<sub>3</sub>, HCl, and HF. Similar results have been reported by the other investigators as well.<sup>30</sup> This suggests that the leaching method is generally acceptable to analyze the fallout-derived radionuclides in the marine environmental samples.

*Sequential separation of actinides by anion-exchange resin*

The separations of actinides could be carried out on the basis of their different sorption characteristics on anion-exchangers in HNO<sub>3</sub> or HCl.<sup>31</sup> While Pu(IV) is strongly retained in 8M HNO<sub>3</sub> and 10M HCl, U(IV) is only moderately sorbed in 8M HNO<sub>3</sub> but strongly sorbed in 10M HCl. Am(III) has no affinity for an anion-exchanger in either medium. On the other hand, Th(IV) is strongly sorbed in 8M HNO<sub>3</sub> and desorbed in 10M HCl. Accordingly, several selective reagents were used for the stripping of radionuclides from the anion resin, i.e., 8M HNO<sub>3</sub> for americium and uranium, 10M HCl for thorium and 0.1M NH<sub>4</sub>I–9M HCl for plutonium. The uranium isotopes may be difficult to remove completely from the anion resin at a concentration of 7–8M HNO<sub>3</sub> due to a significant affinity ( $K_d$  distribution coefficient is around 10–15).<sup>32</sup> To overcome this problem, we approached the other method using same type of anion-exchange resin but pre-conditioned with 10M HCl, not with 8M HNO<sub>3</sub>. Also samples were prepared in 10M HCl solution. In this condition, while americium and thorium are not retained, uranium and plutonium are strongly retained, but they could be stripped with 0.01M HCl due to a much lower affinity with the resin in this condition. After further purification steps, this procedure provided consistently higher chemical recoveries for americium, thorium and uranium. However, the chemical recoveries of plutonium by this procedure were inconsistent and varied significantly between trials (i.e., ranged from 20 to 85%), and Pu was often found to be missing in the usual 0.1M NH<sub>4</sub>I–9M HCl stripping solution. The cause of this variation is not well understood. In general, plutonium is removed from the resin by reduction to the Pu(III) using iodide in strong HCl or by using the complexation with fluoride ion at low overall acid concentration. A low acidity of stripped solution (0.01M HCl) in the absence of complexing agents can cause hydrolysis, polymerization, conversion of plutonium into a colloidal form,<sup>31</sup> and slow desorption kinetics from the resin, any of which may contribute to the lower Pu chemical recovery. Therefore, if target elements in the sample are only uranium and thorium, the adoption of this method might be useful.

Table 1. Comparison between total dissolution and leaching method in the marine samples using IAEA reference materials (weighted means)

IAEA reference materials	Sample types*	Total dissolution		Leaching	
		<sup>239,240</sup> Pu, Bq kg <sup>-1</sup>	<sup>241</sup> Am, Bq kg <sup>-1</sup>	<sup>239,240</sup> Pu, Bq kg <sup>-1</sup>	<sup>241</sup> Am, Bq kg <sup>-1</sup>
IAEA 384	Lagoon sediment N	110 ± 6 4	6.8 ± 0.5 4	111 ± 5 5	6.5 ± 0.4 5
IAEA 385	Sediment (Irish Sea) N	2.90 ± 0.01 5	3.8 ± 0.1 5	3.0 ± 0.2 5	3.9 ± 0.1 5
IAEA 414	Fish N	0.115 ± 0.003 5	0.190 ± 0.004 5	0.125 ± 0.004 5	0.200 ± 0.007 5

\*N: Tested sample numbers.

As a consequence, to complete the stripping of uranium with 8M HNO<sub>3</sub> in the anion exchange resin preconditioned with 8M HNO<sub>3</sub>, it is recommended to use a large volume of 8M HNO<sub>3</sub>. In this study, 10 free column volumes (100 ml) in addition to the original sample volume were enough to strip the uranium from the resin.

#### *Purification of plutonium and uranium by extraction chromatography (TEVA and UTEVA)*

The TEVA resin was used for the purification of plutonium because it has a strong preference for tetravalent actinides, and is simple and effective to use with small volumes. However, in general, there were no differences in the plutonium chemical recovery between the TEVA method and conventional anion-exchange method. The UTEVA column with reducing conditions is a very effective method to separate uranium from the americium and trace plutonium, where uranium is sorbed and americium(III) and plutonium (III) are washed through with a small volume of 2.5M HNO<sub>3</sub>–0.05M ferrous sulfamate. However, the 8M HNO<sub>3</sub> fractions containing americium and uranium isotopes separated from the 1st anion-exchange column work produce the significant amounts of residues after evaporation. As a result, it may need large volumes of 2.5M HNO<sub>3</sub> to re-dissolve the residues, and this is not suitable for a small UTEVA column. Therefore, AG1-X8 (100–200 mesh, Cl<sup>-</sup> form) anion-exchange columns preconditioned with 10M HCl were prepared for the separation of americium from uranium, which allows a large volume of sample. This step also helps to separate americium from polonium that may be found in the final fraction of americium. After the purification process using UTEVA, alpha-spectrometry displayed the highly purified peaks of uranium as well as the excellent chemical recovery (Table 2).

#### *Americium purification by combined method*

To carry out the TRU column procedure for americium, a pre-concentration method is necessary to separate the americium from bulk salts contained in the 10M HCl fraction from the anion exchange resin column. For this purpose, Ca oxalate precipitation was used, where americium was co-precipitated with CaC<sub>2</sub>O<sub>4</sub> around pH 2. After this step, Am was purified by either a conventional method, liquid-liquid solvent extraction with DDCP (dibutyl-N, N-diethyl carbamyl phosphonate), or TRU extraction column chromatography. The TRU procedure was chosen due to several advantages: (1) reduction of the amount of liquid waste generated, (2) no organic solvent waste generated, and (3) reduction of the analyst's time required.<sup>33</sup> Although most of the Fe was removed during the previous anion-exchange step, the addition of ascorbic acid into the sample solution (2.5M HNO<sub>3</sub>) may be necessary to reduce any remaining Fe(III) to Fe(II). While Fe(III) has an affinity for the TRU resin that is strongly dependent on the nitrate ion concentration, it is well known that Fe (II) is not retained on the TRU and Am(III) is still retained strongly under these conditions. Although the former several purification steps, i.e., anion-exchange column chromatography, Ca oxalate co-precipitation and TRU column could remove most elements, the rare earth elements (REEs) may still exist in the americium fraction due to their similarity of chemical behavior. More than a few tens of micrograms of REEs may cause a serious degradation of resolution in the americium alpha-spectrum, and these elements must be separated from the Am prior to electrodeposition. AG1X4 anion-exchange resin in 1M HNO<sub>3</sub>–93% CH<sub>3</sub>OH was used for this purpose. 1M HNO<sub>3</sub>–93% CH<sub>3</sub>OH treatment could remove heavy REEs and beryllium from the resin whereas americium is retained. 0.1M HCl–0.5M NH<sub>4</sub>SCN–80% CH<sub>3</sub>OH elutes the remaining light REEs.<sup>34,35</sup>

Table 2. Results of plutonium, americium, uranium and thorium obtained by this sequential procedure in the IAEA reference materials (weighted means, in Bq kg<sup>-1</sup>)

IAEA reference materials	<sup>238</sup> Pu	<sup>239,240</sup> Pu	<sup>241</sup> Am	<sup>234</sup> U	<sup>235</sup> U	<sup>238</sup> U	<sup>230</sup> Th	<sup>232</sup> Th
IAEA 384	41 ± 1 38.1-40.1*	110 ± 1 105-110*	6.9 ± 0.2 6.7-7.6*	43 ± 1 35.2-43.0*	1.7 ± 0.1 1.69-2.00*	37 ± 1 33.4-37.3*	2.5 ± 0.1 2.4-2.7*	— 0.008-0.024*
IAEA 385	0.448 ± 0.027	2.81 ± 0.11	3.75 ± 0.16	27.3 ± 0.4	1.15 ± 0.04	29 ± 1	27 ± 1	32 ± 1
IAEA 414	0.022 ± 0.003 0.022-0.023*	0.115 ± 0.003 0.114-0.125*	0.190 ± 0.004 0.193-0.225*	1.24 ± 0.05 1.14-1.28*	0.052 ± 0.001 0.045-0.058*	1.11 ± 0.02 1.065-1.190*	0.0420 ± 0.005 0.039-0.054*	0.038 ± 0.007 0.029-0.031*
Chemical recovery, %:	74-95	74-95	67-92	85-100	85-100	85-100	90-100	90-100

\* Confidence interval (IAEA384 and 414).

Note: IAEA-385 is being processed as new reference material and certified value for all isotopes have not been established yet.

Further washing with 1M HNO<sub>3</sub>-93% CH<sub>3</sub>OH helps to remove traces of NH<sub>4</sub>SCN as well as Fe. Even though trace REEs are still found in the final effluent of americium in the 1.5M HCl-86% CH<sub>3</sub>OH, the alpha-spectra show well-resolved, purified Am peaks and also give higher chemical recoveries.

#### *Purification of thorium by anion-exchange resin*

For the purification of thorium, either the anion exchange resin method or EIChrom extraction chromatography resins such as UTEVA, TEVA and TRU could be applied. In this study, the anion exchange method was employed to purify the thorium. For most of the samples, this step is enough to get sufficiently pure thorium fractions that are ready for electrodeposition.

Using this procedure, the overall chemical recoveries are high.

#### *Source preparation for alpha-spectrometry*

Rare earth (neodymium) fluoride co-precipitation and electrodeposition are the two most commonly used methods of source preparation for alpha-spectrometry. Compared with fluoride co-precipitation, the electrodeposition technique is very simple and gives a very thin and even deposit, which is essential for a high resolution of the peaks<sup>25</sup> (Fig. 1). In simple trials with spikes and no chemical processing, the electrodeposition method, in general, produced 90–100% chemical yields for plutonium, americium, uranium and thorium.

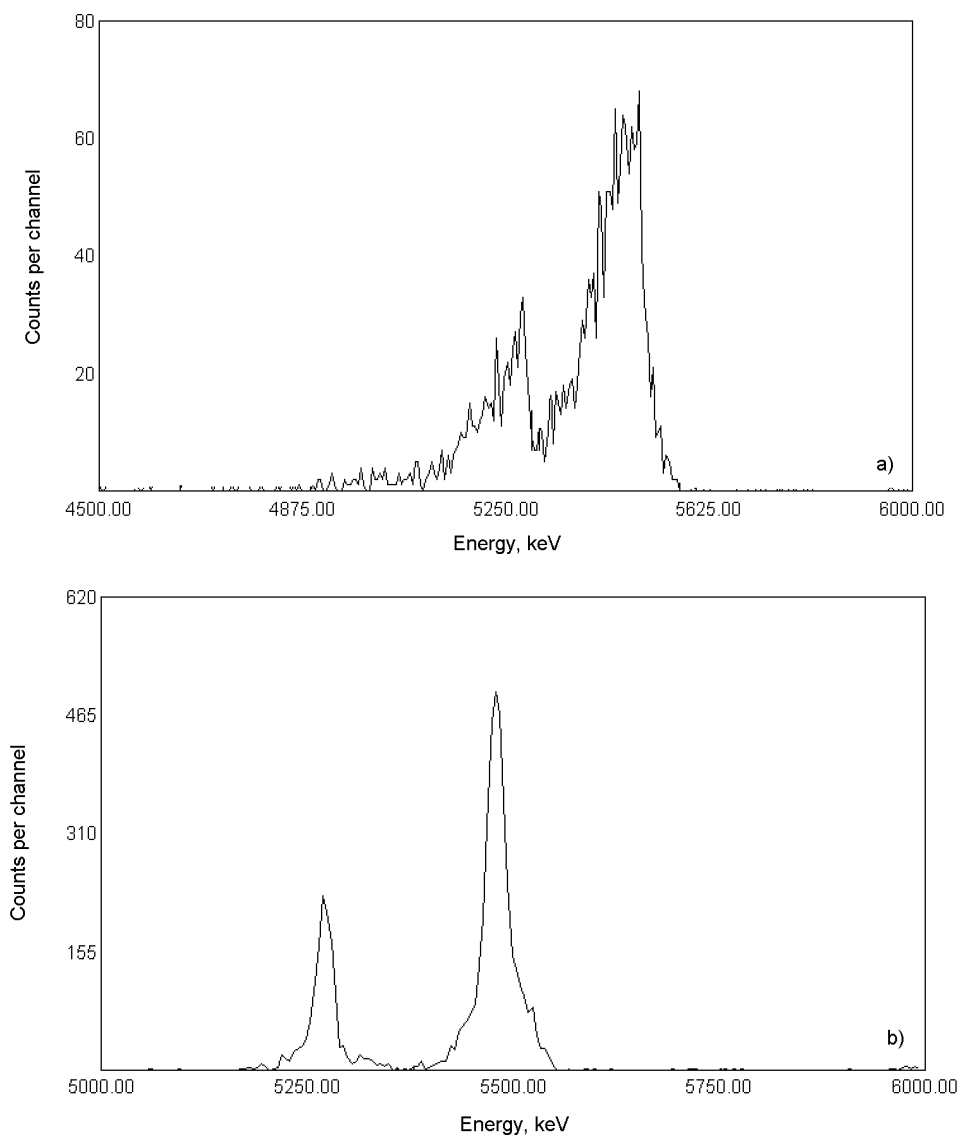


Fig. 1. Comparison of spectra obtained by using NdF<sub>3</sub> co-precipitation method (a) and electrodeposition method (b); <sup>241</sup>Am ( $E_{\alpha}$  = 5.48 MeV) and <sup>243</sup>Am ( $E_{\alpha}$  = 5.28 MeV)

## Conclusions

The sequential method based on the advantages of anion-exchange resin and extraction chromatography was developed for marine samples. The leaching method is generally acceptable to analyze plutonium and americium in marine samples, however, for the measurement of uranium and thorium, it is recommended to use a total dissolution method. The combined procedure using anion-exchange resin and extraction chromatography allows the treatment of large sample sizes and provides excellent selectivity, high chemical recoveries as well as reduction of the amounts of acids. The alpha-spectra of uranium, thorium, plutonium and americium isotopes obtained by this procedure have shown clear peaks.

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