

# Sequential determination of uranium and plutonium in soil and sediment samples by borate salts fusion

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## Abstract

This study describes a rapid method for sequential determination of uranium and plutonium isotopes in soil and sediment samples and its application to the study of Anthropocene sedimentary records. Different pretreatment methods have been tested (open-vessel digestion, borate salts fusion and NaOH salt fusion) achieving the complete dissolution of the sample in case of fusion methods.  $\text{LiBO}_2$  and  $\text{Li}_2\text{B}_4\text{O}_7$  (80/20) flux was finally selected because a higher amount of sample can be analyzed (up to 5 grams). Moreover, separation steps with extraction chromatographic resin UTEVA were optimized. Average recoveries obtained for uranium and plutonium were acceptable, 59 % and 72 % respectively, and relative bias were below  $\pm 15$  %. The time to complete the separation is approximately 11 hours without ashing the samples and, consequently, it can be used in emergencies.

## Keywords

Fusion pretreatment; uranium; plutonium; soil; sediment; borate salts

## 26 Introduction

27 Uranium and plutonium isotopes are mainly alpha emitters that can be present in the  
28 environment and are important to be controlled. Uranium isotopes are naturally found in  
29 the earth's crust in a mass proportion of 99.28 % for  $^{238}\text{U}$  ( $T_{1/2} = 4468 \cdot 10^6$  years), 0.72 %  
30 for  $^{235}\text{U}$  ( $T_{1/2} = 704 \cdot 10^6$  years) and 0.0057 % for  $^{234}\text{U}$  ( $T_{1/2} = 0.25 \cdot 10^6$  years) [1].  $^{238}\text{U}$  and  
31  $^{234}\text{U}$  are usually present in secular equilibrium in soils and sediments, with an average  
32 activity of  $30 \text{ Bq kg}^{-1}$  [2].  $^{235}\text{U}$  activity in nature is much smaller, but natural uranium can  
33 be enriched to 2 – 5 % of  $^{235}\text{U}$  to be used as nuclear fuel.

34 Plutonium alpha isotopes,  $^{240}\text{Pu}$  ( $T_{1/2} = 6,561$  years),  $^{239}\text{Pu}$  ( $T_{1/2} = 24,110$  years) and  $^{238}\text{Pu}$   
35 ( $T_{1/2} = 87.7$  years), are artificially produced and have long half-lives with high radiological  
36 toxicities. They appear in the environment as a result of global fallout from atmospheric  
37 nuclear weapons tests (1945-1980) [3], accidents of satellites such as SNAP-9A (1964),  
38 plane crashes like Palomares (1966) and Thule (1968), and fateful nuclear accidents like  
39 Chernobyl (1986) and Fukushima (2011) [4]. They are also produced in normal operation  
40 of nuclear installations as a waste in re-processing of nuclear fuels. Moreover, emerging  
41 risks, such as dirty bombs or improvised nuclear devices [5], could increase the presence  
42 of plutonium and uranium in rivers, oceans, soils, vegetation, etc.

43 For these reasons, the determination of the main isotopes of uranium and plutonium in soils  
44 and sediments is of great interest in studies of environmental radiological surveillance [6],  
45 in emergency situations due to nuclear or radiological accidents, or malevolent acts with  
46 radionuclides dispersion [5]. Moreover,  $^{239/240}\text{Pu}$  can be used as chronostratigraphic marker  
47 in studies of geological dating [7]. In particular, the Anthropocene is a new geological age  
48 proposed by experts that differs from Holocene due to the recent impact of human activity,  
49 and plutonium isotopes are considered to be the most useful indicator of this age among  
50 others (plastics, metal enrichments, pesticide residues, etc.) [8, 9].

51 Different methods for uranium and plutonium determination in environmental samples  
52 have been proposed in the literature [10]. Moreover, rapid and sequential methods for  
53 actinides determination in emergency response must be developed [11]. In particular, soils  
54 and sediments are complex matrices to be analyzed by radiochemical separation, being the  
55 complete dissolution of the sample the critical step of the procedure. Conventional leaching

56 methods with a mixture of acids ( $\text{HNO}_3/\text{HCl}/\text{H}_2\text{O}_2$ ) in an open-vessel or microwave  
57 digester have been used for soil and sediment dissolution [12]. However, these techniques  
58 may not be suitable for dissolution of refractory materials such as tetravalent oxides,  
59 silicates or hot particles [11]. In this case, total dissolution with a mixture of acids including  
60 HF produced good results for a small amount of sample ( $< 0.5$  g) [13], but HF must be  
61 removed by evaporation or  $\text{HBO}_3$  complexation and its use is restricted in some countries.  
62 Moreover, the sample could not completely dissolve, and the residue contains most of  
63 uranium and thorium radionuclides into the structure of insoluble minerals such as zircon,  
64 apatite, titanite, allanite, etc. [14].

65 According to the literature, fusion methods with an inorganic flux at high temperatures get  
66 to destroy the mineral structure of soils and sediments and dissolve completely the sample.  
67 The most commonly used fluxes are lithium borates [15–19], sodium hydroxides [20–22]  
68 combined with peroxides [23], sodium and potassium carbonates [14, 24] or sulfates [25]  
69 and mixtures of them [26]. The flux is mixed with 0.2 to 20 g of sample in proportions  
70 from 1:1 to 1:15. In addition, the material of the crucible and the melting temperature  
71 depend on the flux employed. Graphite, platinum or platinum with gold (95/5 %) crucibles  
72 are used for lithium borate and sodium or potassium carbonate fluxes with high  
73 temperatures (900 – 1200 °C). A less aggressive fusion is performed with NaOH in  
74 zirconium crucibles at approximately 600 °C. Recently, a low-temperature fusion method  
75 (250 °C) using  $\text{NH}_4\text{HSO}_4$  and  $\text{NH}_4\text{HF}_2$  was also proposed [27]. The fusion is used to carry  
76 out for 10 to 30 minutes in a muffle furnace or a fusion machine, which is usually used for  
77 X-ray fluorescence analysis [11].

78 After sample dissolution, polyethylene glycol (PEG) is added to remove silica and boric  
79 acid present in the matrix and the flux after borates fusion [15, 16, 19]. Then, actinides are  
80 pre-concentrated from the rest of the interfering elements of the matrix. Iron hydroxide or  
81 calcium and lanthanum fluorides are usually used for coprecipitation, and sodium nitrite  
82 adjusts  $\text{Pu}^{+3}$  to  $\text{Pu}^{+4}$  to be retained in the extraction chromatographic column [15, 18, 20,  
83 22]. Then, actinides are usually separated with extraction chromatographic resins to  
84 determine individually their activity. In emergency situations some of them are sequentially  
85 determined to reduce time [15, 18, 20, 22].

86 This paper shows a comparison between different dissolution methods of soil and sediment  
87 samples for uranium and plutonium determination (open-vessel digestion, borates fusion  
88 and sodium hydroxide fusion). In addition, the steps for sequential separation of uranium  
89 and plutonium isotopes with extraction chromatographic resin UTEVA were optimized.  
90 The method with better results was validated with the analysis of a reference material and  
91 an intercomparison soil sample. The final method was tested with the analysis of estuarine  
92 sediments from the Cantabrian coast (North of Spain), and plutonium and uranium profiles  
93 of two cores were determined for the study of Anthropocene records.

## 94 **Experimental**

### 95 *Reagents and materials*

96 All the chemicals used were of analytical or reagent grade. Standard solutions of  $^{242}\text{Pu}$  (9.9  
97  $(0.2) \text{ Bq g}^{-1}$ ) and  $^{232}\text{U}$  ( $17.9(0.5) \text{ Bq ml}^{-1}$ ) supplied by AEA Technology (Harwell, UK) and  
98 CIEMAT (Madrid, Spain) respectively were used as tracers. Standard solution of  $^{243}\text{Am}$   
99 ( $286(1) \text{ Bq g}^{-1}$ ) supplied by CIEMAT was used as an interference in the separation. They  
100 were diluted to the appropriate activity.

101 Pt-Au crucibles (95/5 %) of 100 ml were supplied by 8853 S.p.A. (Milan, Italy) and Zr  
102 crucibles of 100 ml with lid were supplied by J.P. Selecta (Barcelona, Spain). The  
103 extraction chromatography resins employed in this work were UTEVA resin in columns  
104 ( $100\text{-}150 \mu\text{m}$  particle size) and the separation was performed in a 12 position vacuum box,  
105 both available by Triskem International (Bruz, France). Stainless steel disks of 25 mm  
106 diameter available from Tecnasa S.L. (Madrid, Spain) were used for electrodeposition.

### 107 *Soil and sediment samples*

108 Two natural soil samples from the Valencian Community (Spain) and a sediment sample  
109 from the Júcar river (Spain) were used to test the different methods. The method selected  
110 was validated with the reference material IAEA-326 (natural soil) and an agricultural  
111 natural soil spiked with artificial gamma emitters (Sample 04, IAEA-TEL-2018) in the  
112 Intercomparison IAEA 2018.

113 In addition, the method was applied to two cores of estuarine sediments from the  
114 Cantabrian coast of Spain, Core 1 (Mape) from the Urdaibai estuary [28] and Core 2  
115 (Miengo-2) from Suances estuary.

## 116 *Equipment*

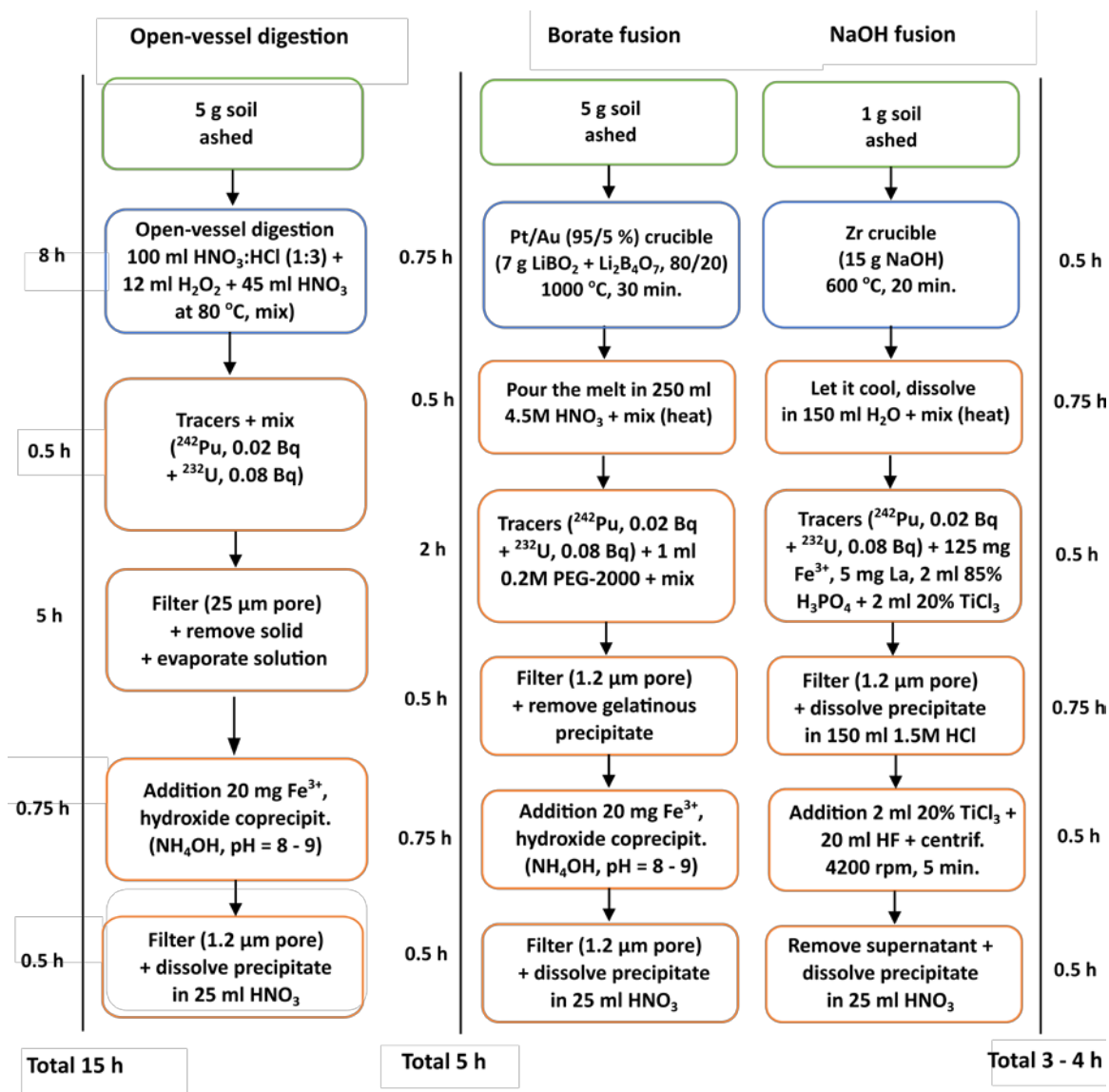
117 A muffle furnace LKN 85 (Nannetti) was used for the calcination of the soil and sediment  
118 samples and a muffle furnace R-3L (J.P. Selecta) was used for the fusion of the calcined  
119 samples. A centrifuge Mixtasel BLT (J.P. Selecta) was used to centrifuge 50 mL  
120 polyethylene falcon tubes. The samples were measured in EG&G ORTEC 576A Dual  
121 Alpha spectrometers, using surface barrier detectors of 450 mm<sup>2</sup> active area (BR-SNA-  
122 450-100).

## 123 *Procedure*

124 Several pretreatment methods for soil and sediment dissolution and actinides  
125 preconcentration were tested to select the best option. In addition, the steps for the  
126 sequential separation of uranium and plutonium isotopes with extraction chromatographic  
127 resin UTEVA were optimized. After separation, each fraction was electrodeposited and  
128 measured by alpha spectrometry. The different options tested are shown in the following  
129 subsections.

### 130 *Sample pretreatment*

131 Among the dissolution techniques found in the literature, a conventional open-vessel  
132 digestion [29] and two fusion methods, one based on borates fusion [19] and the other  
133 based on NaOH fusion [20, 21] were tested. The timelines and steps of each method are  
134 shown in Fig. 1.



135

136 **Fig. 1** Timelines and steps of the different pretreatment methods (open-vessel digestion,  
 137 borate fusion and NaOH fusion) for uranium and plutonium determination in soil and  
 138 sediment samples.

139 In the open-vessel digestion, 5 g of ashed soil or sediment sample (at 525 °C, at least 2  
 140 hours) are mixed with concentrated HNO<sub>3</sub>, HCl and H<sub>2</sub>O<sub>2</sub> for 8 hours. The tracers are added  
 141 to calculate the recovery of the separation when all the elements of the sample should be  
 142 already in solution and the isotopic equilibrium with tracers can be reached. Then, the  
 143 sample is filtered to remove the residue with the refractory compounds that are difficult to  
 144 dissolve. After evaporation, the actinides are coprecipitated with iron hydroxides and  
 145 dissolved in 8 M HNO<sub>3</sub> to perform the column separation. The time needed to complete  
 146 the open-vessel pretreatment is 15 hours, which is not suitable in case of emergency.

147 In the borate fusion method, 5 g of ashed soil or sediment sample are fused in a Pt/Au (95/5  
148 %) crucible mixed with 7 g of a mixture of  $\text{LiBO}_2$  and  $\text{Li}_2\text{B}_4\text{O}_7$  (80/20) at 1000 °C. This  
149 flux permits the dissolution of alkaline or metallic oxides ( $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ , etc.) and  
150 acidic or non-metallic oxides such as silica ( $\text{SiO}_2$ ) and rutile ( $\text{TiO}_2$ ) [30]. Samples with a  
151 high carbonate content must be pretreated with concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  to avoid an  
152 aggressive reaction during fusion. The fused samples are dissolved in 4.5 M  $\text{HNO}_3$  after  
153 pouring the hot melt. After dissolution and addition of tracers, polyethyleneglycol (PEG-  
154 2000) is added to the solution to remove silica and boric acid in form of a gelatinous  
155 precipitate. After filtration, actinides are coprecipitated with iron hydroxides and dissolved  
156 in 8 M  $\text{HNO}_3$ . The time to complete this fusion method is 5 hours, which is suitable for  
157 rapid methods and emergencies.

158 Finally, in the sodium hydroxide fusion the melting temperature is lower (600 °C), and  
159 zirconium crucibles are less expensive than platinum crucibles. This is a widely used fusion  
160 for soil and sediment dissolution [20-22], but sometimes high refractory compounds can  
161 not be dissolved [11]. In this case, the ashed soil or sediment samples are mixed with 15 g  
162 of  $\text{NaOH}$  and the crucible is covered with a lid to avoid losses. After fusion, the melt cools  
163 and is dissolved in distilled water. Tracers and several carriers are added to coprecipitate  
164 actinides as proposed by Maxwell et al. [20]:  $\text{Fe}^{3+}$  to produce actinides coprecipitation,  
165  $\text{La}^{3+}$  and  $\text{PO}_4^{3-}$  to increase Am and U coprecipitation respectively, and  $\text{TiCl}_3$  to reduce  
166 soluble U(VI) to more insoluble U(IV). After filtering, the precipitate is dissolved in diluted  
167  $\text{HCl}$  and a following actinides coprecipitation is performed in form of  $\text{LaF}_3$  and  $\text{CaF}_3$  to  
168 remove interfering elements such as Si, Ti, Ca, Fe, etc. The precipitate is dissolved in 25  
169 ml of 8 M  $\text{HNO}_3$  to pass through the column. However, samples with high calcium content  
170 are difficult to dissolve in this small volume and we restricted the method to 1 g of sample.  
171 This fusion method is completed in 3 – 4 hours.

### 172 *Sample separation and measurement*

173 Sequential separation of uranium and plutonium after sample pretreatment was performed  
174 with the extraction chromatographic resin UTEVA. According to the technical  
175 specifications of the resin, different solutions were tested to optimize the separation.  
176 Eighteen tests were carried out with samples of 20 ml 8 M  $\text{HNO}_3$ - $\text{NaNO}_2$  spiked with  $^{232}\text{U}$   
177 (0.06 Bq),  $^{242}\text{Pu}$  (0.02 Bq) and  $^{243}\text{Am}$  (0.02 Bq) to calculate the chemical yield in the

178 separation and to detect the presence of interferences in each fraction.  $\text{Fe}^{3+}$  (20 mg) were  
179 also added to simulate the sample obtained after pretreatment. Sample solution and thorium  
180 elution were the same in all tests, but uranium and plutonium elutions were optimized.

181 After separation, each fraction was electrodeposited with the method proposed by  
182 Hallstadius [31], and uranium and plutonium were measured by alpha spectrometry.

## 183 **Results and Discussion**

184 In the following section, the study of the separation steps with UTEVA for sequential  
185 separation of uranium and plutonium isotopes is presented. After the selection of the  
186 separation method, the different pretreatment options of soil and sediment samples were  
187 tested and the recoveries and activities obtained are shown. The final method was tested  
188 with sediment samples and validated with intercomparison soil samples. Moreover,  
189 plutonium and uranium in two cores of estuarine sediments from the Cantabrian coast of  
190 Spain were analyzed.

### 191 *UTEVA separation optimization*

192 Uranium and plutonium separation was performed with UTEVA column. After loading the  
193 sample (20 ml 8 M  $\text{HNO}_3$ - $\text{NaNO}_2$ ) through the column, plutonium (IV), uranium and  
194 thorium are retained in the resin, and it is washed with 10 ml 8 M  $\text{HNO}_3$  to remove iron  
195 and americium isotopes. Thorium is removed with 4 ml 9 M HCl and 20 mL 5 M HCl.  
196 Then, different options for uranium and plutonium elution were tested to improve chemical  
197 yields (R) and avoid the presence of interferences. They were selected taking into account  
198 the UTEVA specification sheet supplied by Triskem. Each of the eluted solutions with the  
199 uranium and plutonium fractions were electrodeposited according to Hallstadius [31] and  
200 measured by alpha spectrometry.

201 Among the different options, plutonium isotopes can be eluted by changing their oxidation  
202 state.  $\text{Pu}^{4+}$  can be reduced in the resin to  $\text{Pu}^{3+}$  with a reducing agent, such as hydroxylamine,  
203 *rongalite* (sodium hydroxymethanesulphinate),  $\text{TiCl}_3$ , etc. With this valence, plutonium  
204 behaves similarly to  $\text{Am}^{3+}$  and can be eluted from the resin. Other option is the addition of



205 oxalic acid to form a complex with plutonium. If Pu<sup>4+</sup> is considered to behave similarly to  
 206 Np<sup>4+</sup>, oxalic acid can be used to separate uranium from plutonium. According to the  
 207 UTEVA specification sheet, Np/Pu can be eluted from the resin with HCl containing 0.05  
 208 M oxalic acid, while U is retained.

209 Uranium and plutonium recoveries of the different tests and the presence of interferences  
 210 are shown in Table 1. Between one to six replicates of each type of separation were tested.

211 **Table 1** Different tests (number of replicates in brackets) for plutonium and uranium  
 212 elution steps with UTEVA and their corresponding recoveries (R (%)). RSD: Relative  
 213 standard deviation.

Test	Elution	Steps	R (%) (RSD)	Interferences (R (%))
P1 [x3]	Pu	15 mL 4 M HCl-0.05 M oxalic acid	73.5 (7 %)	U (1.5 %)
	U	10 mL 0.01 M HCl	76.6	No
P2 [x1]	Cleaning	5 mL 8 M HNO <sub>3</sub>	-	-
	U	15 mL 0.1 M HNO <sub>3</sub>	84.7	Pu (15 %)
	Pu	15 mL 0.1 M HNO <sub>3</sub> -0.3 M NH <sub>2</sub> OH·HCl	74.5	U (1.5 %)
P3 [x4]	Cleaning	5 mL 8 M HNO <sub>3</sub>	-	-
	Pu	15 mL 2 M HNO <sub>3</sub> -0.05 M oxalic acid	94.7 (4 %)	Th (5 %)
	U	15 mL 0.01 M HNO <sub>3</sub>	86.3 (4 %)	Th (2 %)
P4 [x4]	Cleaning	5 mL 8 M HNO <sub>3</sub>	-	-
	Pu	15 mL 2 M HNO <sub>3</sub> -0.3 M NH <sub>2</sub> OH·HCl	62.5 (44 %)	No
	U	15 mL 0.01 M HNO <sub>3</sub>	81.9 (3 %)	Pu (30 %)
P5 [x6]	Cleaning	5 mL 8 M HNO <sub>3</sub>	-	-
	Pu	20 mL 2 M HNO <sub>3</sub> - 0.04 M rongalite	92.7 (6 %)	No
	U	20 mL 0.01 M HNO <sub>3</sub>	48.7 (34 %)	No

214 Plutonium elution with oxalic acid in hydrochloric media before uranium elution (P1)  
 215 produced good chemical yields for both isotopes (approximately 75 %) but some <sup>232</sup>U  
 216 appeared in the plutonium fraction. For this reason, separation steps of P2 were proposed,  
 217 where plutonium (Pu<sup>3+</sup>) was eluted after uranium by reduction to Pu<sup>3+</sup> with hydroxylamine.  
 218 Both recoveries obtained were acceptable, but plutonium activity appeared in uranium  
 219 fraction (15 % approximately). In test P3, plutonium was eluted with oxalic acid in nitric

220 media. However,  $^{228}\text{Th}$  from  $^{232}\text{U}$  chain was observed in both fractions and this option was  
 221 discarded. Finally, hydroxylamine and *rongalite* (sodium hydroxymethanesulfinate) were  
 222 selected as reductant agents in tests P4 and P5, respectively. Plutonium was not completely  
 223 eluted with hydroxylamine and part of it was obtained in the uranium fraction (P4).  
 224 Therefore, *Rongalite* was tested, obtaining high recoveries (> 90 %) for plutonium, and  
 225 acceptable recoveries (50 % approximately) for uranium. This method (P5) was finally  
 226 selected due to the acceptable uranium and plutonium recoveries and mainly because no  
 227 interferences were observed in both fractions, unlike in the other tests (P1-P4).

### 228 *Pretreatment optimization*

229 After optimization of UTEVA separation, the different pretreatment methods were tested.  
 230 Table 2 shows uranium and plutonium recoveries for two soil samples (S1 and S3) and a  
 231 sediment sample (S2) from the Valencian Community (Spain). They were analyzed with  
 232 the complete method (pretreatment, UTEVA separation, electrodeposition and alpha  
 233 spectrometry), but considering different pretreatment options: open-vessel digestion  
 234 method, borate fusion method and NaOH fusion method. Only uranium isotopes were  
 235 calculated because samples were not contaminated with plutonium isotopes. Between one  
 236 to three replicates of the samples were analyzed with each type of pretreatment. Relative  
 237 standard deviation between replicates are shown in parentheses in Table 2.

238 **Table 2** Uranium and plutonium recoveries and uranium activities for the different  
 239 pretreatment methods. Relative standard deviations are shown in parentheses.

Method	Sample	R (%) U	A (Bq kg <sup>-1</sup> ) $^{238}\text{U}$	A (Bq kg <sup>-1</sup> ) $^{234}\text{U}$	A (Bq kg <sup>-1</sup> ) $^{235}\text{U}$	R (%) Pu
Open-vessel digestion	S1	87.7 (10 %)	6.4 (2 %)	7.1 (1 %)	0.2 (33 %)	92.5 (7 %)
	S2	40.0 (79 %)	6.8 (2 %)	8.3 (2 %)	0.3 (65 %)	68.0 (25 %)
	S3	91.6 (8 %)	2.8 (3 %)	2.7 (1 %)	0.1 (28 %)	83.0 (8 %)
Borate fusion	S1	29.7	18.9	18.6	0.5	21.7
	S2	60.1 (24 %)	20.3 (1 %)	20.4 (1 %)	0.9 (27 %)	67.1 (5 %)
	S3	56.3	27.5	26.4	0.8	63.9
NaOH fusion	S1	59.3 (7 %)	20.4 (1 %)	18.8 (2 %)	0.8 (2 %)	29.6 (1 %)
	S2	65.1 (6 %)	18.3 (20 %)	19.3 (11 %)	0.8 (57 %)	30.7 (18 %)

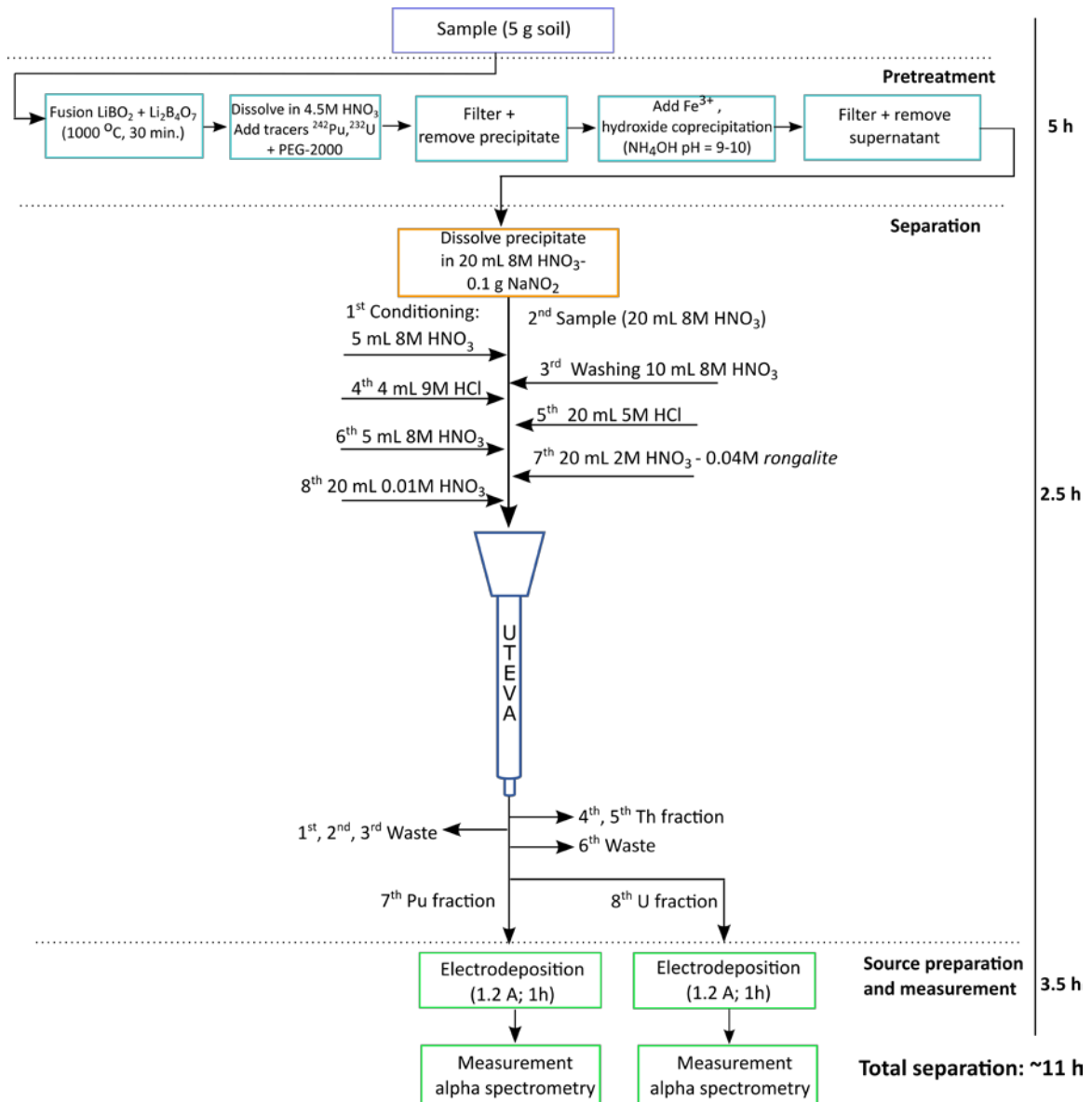
	S3	60.0 (3 %)	18.8 (5 %)	18.0 (16 % )	1.3 (21 %)	75.3 (17 %)
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240 As can be seen in Table 2, average recoveries obtained for uranium and plutonium were  
 241 higher in case of the open-vessel digestion method. However, these samples were also  
 242 analyzed by gamma spectrometry through  $^{214}\text{Pb}$  peak (351.92 keV) and assuming secular  
 243 equilibrium in  $^{238}\text{U}$  chain. The average activities obtained for  $^{238}\text{U}$  and  $^{234}\text{U}$  were 20 Bq kg<sup>-1</sup>  
 244 approximately. Therefore, these recoveries are not correct and lower activities were  
 245 obtained, because the open-vessel digestion method without HF can not extract completely  
 246 uranium isotopes from the matrix.

247 Uranium activities calculated with borate fusion and NaOH fusion methods were close to  
 248 the values obtained by gamma spectrometry, despite the lower recoveries obtained in some  
 249 cases and the high relative standard deviation obtained for  $^{235}\text{U}$  due to their low activities.  
 250 Secular equilibrium was confirmed with  $^{234}\text{U}/^{238}\text{U}$  ratios close to 1 in all cases. For these  
 251 reasons, fusion methods were faster and more suitable than open-vessel digestion method  
 252 to pretreat soil and sediment samples for analyzing uranium and plutonium isotopes.  
 253 Among fusion methods, borate fusion was selected despite the cost of platinum crucibles  
 254 for two reasons: a higher amount of sample could be analyzed (up to 5 grams) to permit  
 255 the analysis of low contaminated samples and the following steps of the separation are  
 256 simpler.

### 257 *Validation of the final method*

258 The final method selected was based on borate fusion pretreatment, UTEVA separation,  
 259 electrodeposition and measurement by alpha spectrometry. The time needed to complete  
 260 the separation is approximately 11 hours without ashing the samples, as can be seen in Fig.  
 261 2.



263

264 **Fig. 2** Diagram of the final method for sequential determination of uranium and plutonium  
 265 isotopes in soil and sediment samples.

266 The method was validated with the analysis of the reference material (RM) IAEA-326, a  
 267 natural soil sample with 29.4  $\text{Bq kg}^{-1}$  and 27.9  $\text{Bq kg}^{-1}$  of  $^{238}\text{U}$  and  $^{234}\text{U}$  respectively, and  
 268 0.5  $\text{Bq kg}^{-1}$  and 0.02  $\text{Bq kg}^{-1}$  of  $^{239/240}\text{Pu}$  and  $^{238}\text{Pu}$  respectively. Table 3 shows the results  
 269 obtained for three replicates analyzed with the sequential method based on borate fusion.  
 270 Uranium and plutonium recoveries were high for both elements and the activities of each  
 271 isotope were calculated, obtaining relative bias below  $\pm 13\%$  in all cases.  $^{238}\text{Pu}$  relative  
 272 bias were not calculated because limits of detection (LD) of  $^{238}\text{Pu}$  for 5 grams of sample

273 and 300,000 seconds of measurement were approximately 0.03 Bq kg<sup>-1</sup> [32]. Relative  
 274 standard deviation of the activities between the replicates were 4 % and 8 % for uranium  
 275 and plutonium isotopes respectively. In addition, dispersion between recoveries was low,  
 276 17 % for uranium and 13 % for plutonium. Therefore, the reproducibility and accuracy of  
 277 the method was validated.

278 **Table 3** Results obtained for the reference material IAEA-326: recoveries of uranium and  
 279 plutonium, and activities, limits of detection (LD) and relative bias obtained for each  
 280 isotope. Uncertainties calculated for k = 2.

Sample	R (%) U	A (Bq kg <sup>-1</sup> ) <sup>238</sup> U	LD (Bq kg <sup>-1</sup> ) <sup>238</sup> U	A (Bq kg <sup>-1</sup> ) <sup>234</sup> U	LD (Bq kg <sup>-1</sup> ) <sup>234</sup> U	Rel. Bias <sup>238</sup> U	Rel. Bias <sup>234</sup> U
RM-1	70.2 ± 5.5	28.3 ± 2.3	0.06	26.1 ± 2.1	0.09	-3.7 %	-6.6 %
RM-2	64.4 ± 5.0	29.9 ± 2.4	0.07	28.0 ± 2.3	0.10	1.5 %	0.3 %
RM-3	49.6 ± 4.0	27.6 ± 2.3	0.04	26.7 ± 2.3	0.06	-6.1 %	-4.4 %
Sample	R (%) Pu	A (Bq kg <sup>-1</sup> ) <sup>239/240</sup> Pu	LD (Bq kg <sup>-1</sup> ) <sup>239/240</sup> Pu	A (Bq kg <sup>-1</sup> ) <sup>238</sup> Pu	LD (Bq kg <sup>-1</sup> ) <sup>238</sup> Pu	Rel. Bias <sup>239/240</sup> Pu	Rel. Bias <sup>238</sup> Pu
RM-1	89.5 ± 4.9	0.43 ± 0.08	0.06	< LD	0.03	-13.0 %	-
RM-2	83.1 ± 4.7	0.50 ± 0.09	0.06	< LD	0.03	0.7 %	-
RM-3	68.7 ± 4.3	0.48 ± 0.09	0.06	< LD	0.03	-4.7 %	-

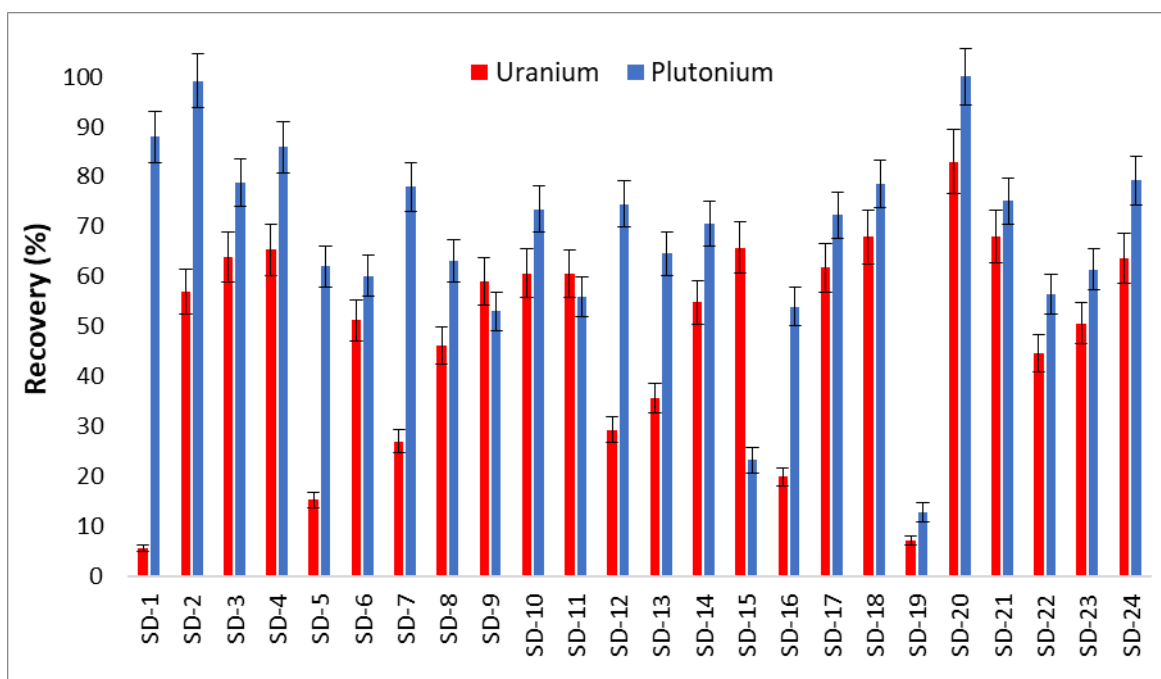
281 In addition, our laboratory participated in the intercomparison exercise IAEA-TEL-2018  
 282 with the analysis of an agricultural natural soil (Sample 04) spiked with artificial gamma  
 283 emitters. Activities of <sup>238</sup>U, <sup>235</sup>U and <sup>234</sup>U calculated are shown in Table 4. Relative bias  
 284 for all uranium isotopes were below ± 10 % and the results were accepted for being below  
 285 ± 20 % for <sup>238</sup>U and <sup>234</sup>U, and ± 30 % for <sup>235</sup>U. However, it is important to highlight that  
 286 the number of laboratories taking part in this international intercomparison exercise with  
 287 the analysis of uranium isotopes in the soil sample was very low. Only between 15 to 27  
 288 % of 267 laboratories reported results for uranium isotopes, and between 6 to 11 % obtained  
 289 acceptable results. This demonstrates the complexity of uranium determination in soil  
 290 samples and the validation of the method proposed in this work.

291 **Table 4** Results obtained for the intercomparison sample (Sample 04) of the IAEA-TEL-  
 292 2018: uranium recovery, and activities, limits of detection and relative bias obtained for  
 293 each isotope. Uncertainties calculated for k = 2.

Sample	R (%) U	Isotope	A (Bq kg <sup>-1</sup> )	LD (Bq kg <sup>-1</sup> )	Rel. Bias
IAEA 2018	41.2 ± 3.5	<sup>238</sup> U	26.6 ± 2.4	0.11	6.4 %
		<sup>235</sup> U	0.93 ± 0.19	0.08	-7.0 %
		<sup>234</sup> U	25.9 ± 2.3	0.13	3.6 %

294 *Estuarine sediments*

295 The method was also tested with the analysis of 24 estuarine sediment samples (SD) with  
 296 an average organic matter content of 7.5 %, ranging from 4 to 14 %. Plutonium and uranium  
 297 recoveries are shown in Fig. 3.



298

299 **Fig. 3** Uranium and plutonium recoveries for different estuarine sediment samples (SD).  
 300 Uncertainties calculated for  $k = 2$ .

301 Uranium recoveries of 18 samples (out of 24) were higher than 30 % with an average  
 302 recovery of 59 %, ranging from 36 to 83 % and a relative standard deviation (RSD) of 18  
 303 %. LD for uranium isotopes ranged from 0.03 to 1 Bq kg<sup>-1</sup> depending on the recoveries.  
 304 Therefore, these recoveries were suitable to determine uranium isotopes in normal soil and

305 sediment samples with good uncertainties and limits of detection due to their range of  
306 activities.

307 In case of plutonium recovery, 22 samples (out of 24) obtained values higher than 30 %.  
308 The average value was 72 %, ranging from 53 to 100 %, and a RSD of 19 %. These high  
309 and reproducible recoveries permitted the quantification of plutonium isotopes, usually  
310 with lower activities than uranium. Their limits of detection range from 0.01 to 0.14 Bq kg<sup>-1</sup>  
311 <sup>1</sup> depending on the recoveries.

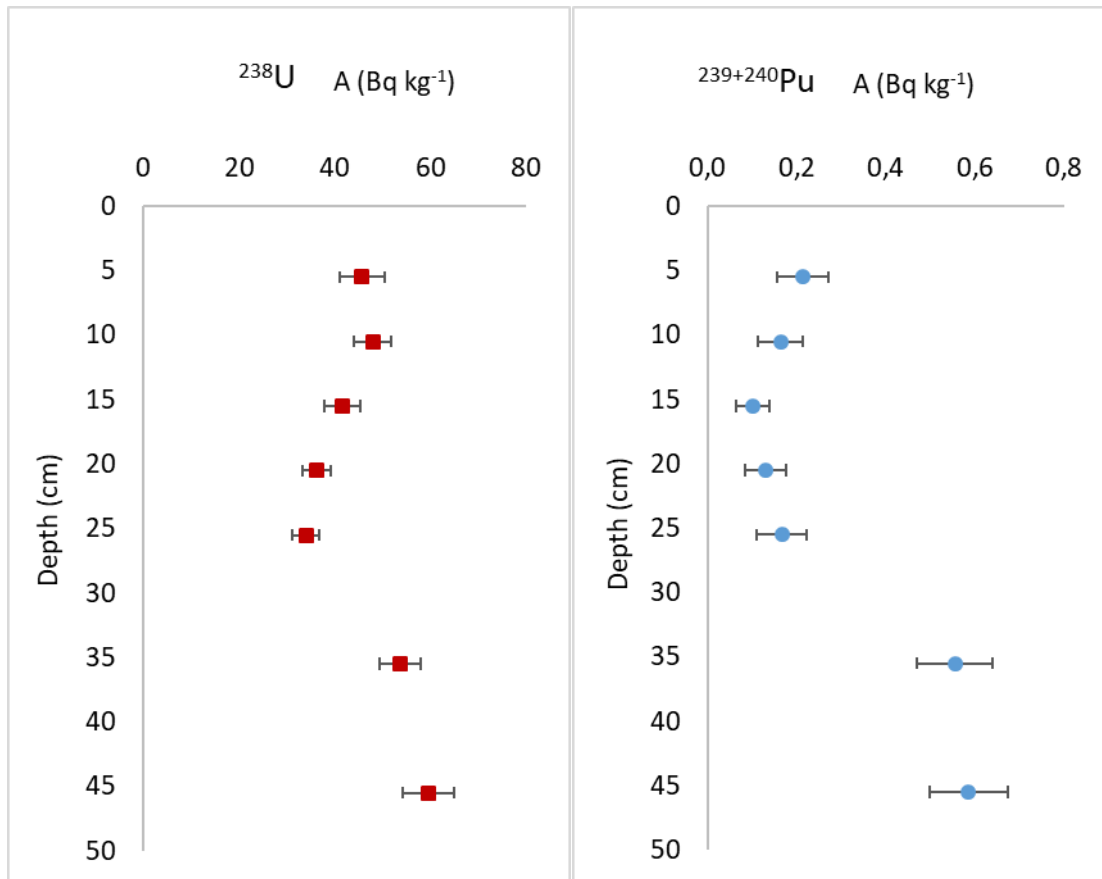
312 These estuarine sediments correspond to two cores collected for different unpublished  
313 studies of Anthropocene records in coastal areas perturbed by human activities. In order to  
314 verify the possibility of using Pu-activity concentrations (and the reference dates they  
315 provide) to validate sediment dating with <sup>210</sup>Pb<sub>excess</sub>, Core 1 (Mape, 46-cm long) from the  
316 Urdaibai estuary was retrieved in September 2007 whereas Core 2 (Miengo-2, 40-cm long)  
317 from the Suances estuary was obtained in May 2016, both in the Cantabrian coast of Spain.  
318 Plutonium and uranium isotopes were determined for each 1-cm layer sampled at 5-cm  
319 intervals approximately, from 5 cm to 45 cm depth (except samples 30 and 40 cm depth  
320 that were not analyzed) in Core 1 and from top core to 40 cm depth in Core 2.

321 All samples presented <sup>238</sup>U and <sup>234</sup>U activities between 35 and 65 Bq kg<sup>-1</sup>, with average  
322 <sup>234</sup>U/<sup>238</sup>U ratios of 0.98 (RSD: 2 %), and between 1 to 3 Bq kg<sup>-1</sup> for <sup>235</sup>U. Plutonium  
323 activities in the samples ranged from 0.1 to 1.5 Bq kg<sup>-1</sup> for <sup>239+240</sup>Pu, and up to 0.08 Bq kg<sup>-1</sup>  
324 <sup>1</sup> for <sup>238</sup>Pu although most of them were below the limits of detection for <sup>238</sup>Pu (0.007 to  
325 0.05 Bq kg<sup>-1</sup>, depending on the recovery).

326 Results of <sup>238</sup>U and <sup>239+240</sup>Pu for Core 1 and Core 2 are shown in Fig. 4 and Fig. 5  
327 respectively. As it can be seen, <sup>238</sup>U activity in both cores is always above 30 Bq kg<sup>-1</sup> and  
328 it does not show a high variation with depth due to its natural origin. However, its  
329 maximum values appear at the same depths as plutonium. <sup>239+240</sup>Pu activity in the top  
330 sample is practically negligible and increases to a maximum value depending on the depth.  
331 For Core 1 it appears between 35 – 36 cm and 45 – 46 cm layers, although it could still be  
332 increasing below 46 cm depth. For Core 2 a peak between 22 – 23 and 24 – 25 cm layers  
333 is observed. The contrasting behavior between Core 1 and Core 2 may be due to their  
334 different geographical location (Urbaidai estuary and Suances estuary, respectively) and  
335 sampling dates (2007 and 2016, respectively). Moreover, the sedimentary materials and

336 processes in each estuary are not the same. However, due to the artificial origin of  $^{239+240}\text{Pu}$ ,  
337 its presence and abundance in these particular layers will be a very useful marker to identify  
338 Anthropocene sediments in the future.

339

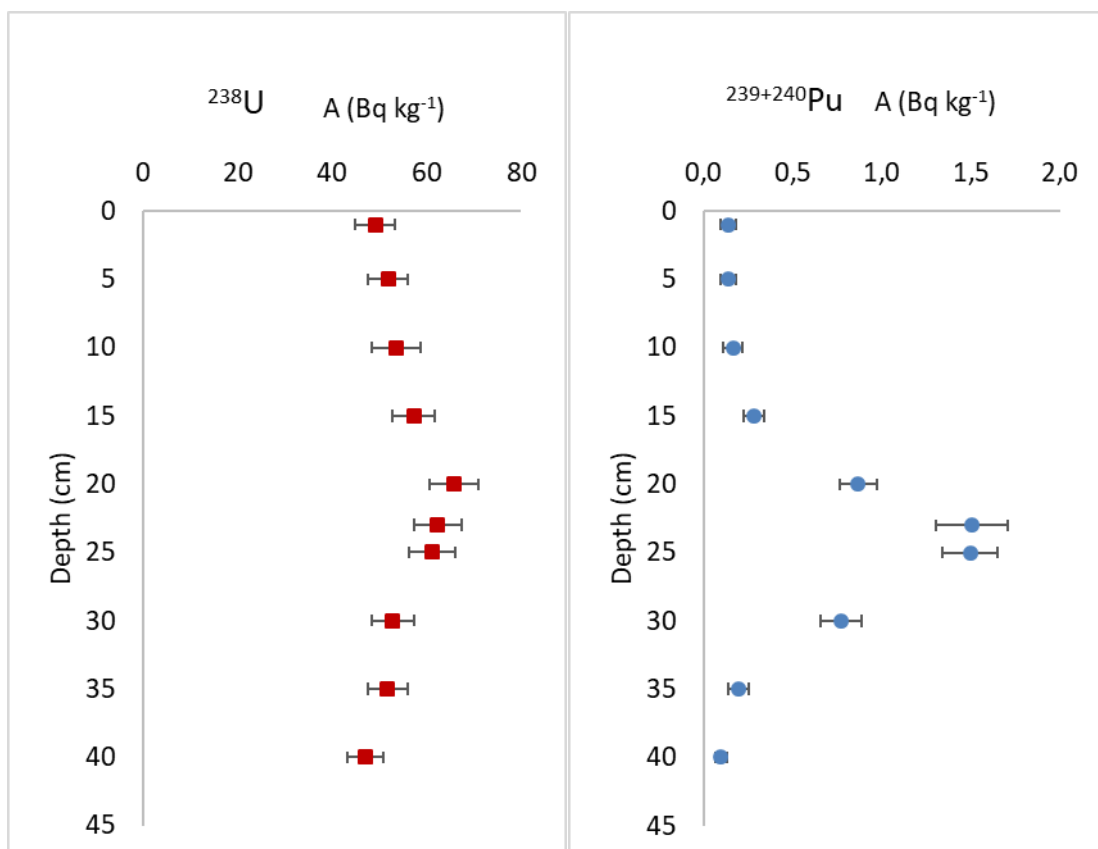


340

341 **Fig. 4** Uranium and plutonium activities with depth in Core 1 (Mape) from the Urdaibai  
342 estuary, Cantabrian coast of Spain (uncertainties calculated for  $k=2$ ).

343





344

345 **Fig. 5** Uranium and plutonium activities with depth for Core 2 (Miengo-2) from the  
 346 Suances estuary, Cantabrian coast of Spain (uncertainties calculated for  $k=2$ ).

### 347 **Conclusions**

348 A fast and sequential procedure for uranium and plutonium determination in soil and  
 349 sediment samples has been developed. Different pretreatment methods have been tested  
 350 (open-vessel digestion, borate salts fusion and NaOH salt fusion). Unlike open-vessel  
 351 method, both fusion methods achieved the complete dissolution of the samples. However,  
 352 borate salts fusion was selected due to its simplicity and because it allows the analysis of  
 353 higher amounts of sample, from 1 to 5 grams. In addition, the separation method with  
 354 extraction chromatographic resin UTEVA was optimized for the sequential separation of  
 355 uranium and plutonium isotopes. Then, each fraction was electrodeposited and measured  
 356 by alpha spectrometry to determine their activity.

357 The final method selected based on borate fusion was tested with sediment samples  
 358 obtaining acceptable recoveries for uranium and plutonium, an average of 58.9 % (RSD:

359 18 %) and 72.0 % (RSD: 19 %), respectively. The method was validated with a reference  
360 material and an intercomparison sample, obtaining relative bias below  $\pm 15$  % in all cases  
361 and good reproducibility. In addition, the analysis of samples from two profiles of recent  
362 estuarine sediments from the Cantabrian coast of Spain permitted identify Anthropocene  
363 records due to the presence of  $^{239+240}\text{Pu}$  activity.

364 The time needed to complete separation is approximately 11 hours without ashing the  
365 samples (at 525 °C, at least 2 h), so it can be also used in emergency situations.

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## 377 **Compliance with ethical standards**

378 **Conflict of interest:** All authors declare that there is no conflict of interest.

## 379 **References**

- 380 1. Soppera N., Bossant M., Dupont E (2014) JANIS 4: An Improved Version of the NEA  
381 Java-based Nuclear Data Information System, Nuclear Data Sheets 120:294-296
- 382 2. UNSCEAR (2010) Sources and Effects of Ionizing Radiation. Volume I: Sources:  
383 Report to the General Assembly, Scientific Annexes A and B. UNSCEAR 2008 Report.

- 384 United Nations, New York: United Nations Scientific Committee on the Effects of  
385 Atomic Radiation. United Nations sales publication E.10.XI.3
- 386 3. Waters CN, Syvitski JPM, Gałuszka A, Hancock GJ, Zalasiewicz J, Cearreta A,  
387 Grinevald J, Jeandel C, McNeill JR, Summerhayes C, Barnosky A. (2015) Can nuclear  
388 weapons fallout mark the beginning of the Anthropocene Epoch?, *B Atom Sci* 71:46–  
389 57
- 390 4. IAEA (2015) The Fukushima Daiichi Accident, Technical radiological consequences,  
391 Vol 4. Viena: International Atomic Energy Agency
- 392 5. EPA (2012) EPA 402-R-12-006, Radiological Laboratory Sample Analysis Guide for  
393 Incident Response - Radionuclides in Soil. Montgomery: U.S. Environmental Protection  
394 Agency
- 395 6. Mietelski JW, Wojtycza J, Zalewski M, Kapała J, Tomankiewicz E, Gaca P (2018)  
396 Plutonium and thorium isotopes in the bottom sediments of some Mazurian Lakes  
397 (Poland), *J Radioanal Nucl Chem* 318:2389–2399
- 398 7. Corcho-Alvarado JA, Diaz-Asencio M, Froidevaux P, Bochud F, Alonso-Hernández  
399 CM, Sanchez-Cabeza JA (2014) Dating young Holocene coastal sediments in tropical  
400 regions: Use of fallout  $^{239,240}\text{Pu}$  as alternative chronostratigraphic marker, *Quat*  
401 *Geochronol* 22:1-10
- 402 8. Waters CN, Zalasiewicz J, Summerhayes C, Barnosky AD, Poirier C, Gałuszka A,  
403 Cearreta A, Edgeworth M, Ellis EC, Ellis M, Jeandel C, Leinfelder R, McNeill JR,  
404 Richter DDeB, Steffen W, Syvitski J, Vidas D, Wagnreich M, Williams M, Zhisheng A,  
405 Grinevald J, Odada E, Oreskes N, Wolfe AP (2016) The Anthropocene is functionally  
406 and stratigraphically distinct from the Holocene, *Science* 351 (6269), aad2622
- 407 9. Zalasiewicz J, Waters CN, Summerhayes C, Wolfe AP, Barnosky AD, Cearreta A,  
408 Crutzen P, Ellis E, Fairchild IJ, Gałuszka A, Haff P, Hajdas I, Head MJ, Ivar do Sul JA,  
409 Jeandel C, Leinfelder R, McNeill JR, Neal C, Odada E, Oreskes N, Steffen W, Syvitski  
410 J, Vidas D, Wagnreich M, Williams M (2017) The Working Group on the Anthropocene:  
411 Summary of evidence and interim recommendations, *Anthropocene* 19:55–60
- 412 10. Qiao J, Hou X, Miró M, Roos P (2009) Determination of plutonium isotopes in waters  
413 and environmental solids: A review, *Anal Chim Acta* 652:66–84
- 414 11. Croudace I, Warwick P, Reading D, Russell B (2016) Recent contributions to the rapid  
415 screening of radionuclides in emergency responses and nuclear forensics, *Trends Anal.*  
416 *Chem.* 85:120–129

- 417 12. Casacuberta N, Lehritani M, Mantero J, Masqué P, Garcia-Orellana J, Garcia-Tenorio  
418 R (2012) Determination of U and Th  $\alpha$ -emitters in NORM samples through extraction  
419 chromatography by using new and recycled UTEVA resins, *Appl Radiat Isot* 70:568–  
420 573
- 421 13. Lozano JC, Herranz M, Mosqueda F, Manjón G, Idoeta R, Quintana B, García-Tenorio  
422 R, Bolívar JP (2017) Low-level determination of Th-isotopes by alpha spectrometry.  
423 Part 2: evaluation of methods for dissolution of samples and for test sample preparation,  
424 *J Radioanal Nucl Chem* 314:2519–2529
- 425 14. Jurečič S, Benedik L, Planinšek P, Nečemer M, Kump P, Pihlar B (2014) Analysis of  
426 uranium in the insoluble residues after decomposition of soil samples by various  
427 techniques, *Appl Radiat Isot* 87:61–65
- 428 15. Luo M, Xing S, Yang Y, Song L, Ma Y, Wang Y, Dai X, Happel S (2018) Sequential  
429 analyses of actinides in large-size soil and sediment samples with total sample  
430 dissolution. *J Environ Radioact* 187:73-80
- 431 16. Sahli H, Röllin S, Putyrskaya V, Klemt E, Balsiger B, Burger M, Corcho Alvarado JA  
432 (2017) A procedure for the sequential determination of radionuclides in soil and  
433 sediment samples, *J Radioanal Nucl Chem* 314:2209–2218
- 434 17. Reading D, Croudace I, Warwick P, Britton R (2015) A rapid dissolution procedure to  
435 aid initial nuclear forensics investigations of chemically refractory compounds and  
436 particles prior to gamma spectrometry, *Anal Chim Acta* 900:1-9
- 437 18. IAEA (2009) IAEA/AQ/11A, Procedure for the Rapid Determination of Pu Isotopes  
438 and Am-241 in Soil and Sediment Samples by Alpha Spectrometry, IAEA Analytical  
439 Quality in Nuclear Applications Series No. 11. Viena: International Atomic Energy  
440 Agency
- 441 19. Croudace I, Warwick P, Taylor R, Dee S (1998) Rapid procedure for plutonium and  
442 uranium determination in soils using a borate fusion followed by ion-exchange and  
443 extraction chromatography, *Anal Chim Acta* 371:217-225
- 444 20. Maxwell S, Culligan B, Hutchison J, McAlister D (2015) Rapid fusion method for the  
445 determination of Pu, Np, and Am in large soil samples, *J Radioanal Nucl Chem*  
446 305:599–608
- 447 21. EPA (2014) EPA 402-R-14-004, Rapid Method for Sodium Hydroxide Fusion of  
448 Concrete and Brick Matrices Prior to Americium, Plutonium, Strontium, Radium, and

- 449 Uranium Analyses for Environmental Remediation Following Radiological Incidents.,  
450 Montgomery: U.S. Environmental Protection Agency
- 451 22. Maxwell S, Culligan B, Noyes G (2010) Rapid separation method for actinides in  
452 emergency soil samples, *Radiochim Acta* 98:793–800
- 453 23. Galindo C, Mougin L, Nourreddine A (2007) An improved radiochemical separation  
454 of uranium and thorium in environmental samples involving peroxide fusion, *Appl*  
455 *Radiat Isot* 65:9-16
- 456 24. EPA (2012) Rapid Method for Fusion of Soil and Soil-Related Matrices Prior to  
457 Americium, Plutonium, and Uranium Analyses for Environmental Remediation  
458 Following Radiological Incidents. Montgomery: U.S. Environmental Protection  
459 Agency
- 460 25. Mantero J, Lehritane M, Hurtado S, García-Tenorio R (2010) Radioanalytical  
461 determination of actinoids in refractory matrices by alkali fusion, *J Radioanal Nucl*  
462 *Chem* 286:557–563
- 463 26. Braysher E, Russell B, Woods S, García-Miranda M, Ivanov P, Bouchard B, Read D  
464 (2019) Complete dissolution of solid matrices using automated borate fusion in support  
465 of nuclear decommissioning and production of reference materials, *J Radioanal Nucl*  
466 *Chem* 321:183–196
- 467 27. Wang H, Ni Y, Zheng J, Huang Z, Xiao D, Aono T (2019) Low-temperature fusion  
468 using  $\text{NH}_4\text{HSO}_4$  and  $\text{NH}_4\text{HF}_2$  for rapid determination of Pu in soil and sediment  
469 samples, *Anal Chim Acta* 1050:71-79
- 470 28. Leorri E, Cearreta A, García-Artola A, Irabien MJ, Blake WH (2013) Relative sea-level  
471 rise in the Basque coast (N Spain): Different environmental consequences on the coastal  
472 area, *Ocean Coast Manage* 77:3–13
- 473 29. Absi A (2005) Evolución del impacto radiactivo ambiental en la ría de Huelva tras el  
474 cambio en la gestión de los residuos de las industrias de producción de ácido fosfórico,  
475 Seville University: Doctoral Thesis
- 476 30. MARLAP (2004) Part II: Chapter 13. Sample Dissolution, (Volume II), EPA 402-B-  
477 04-001B. In *Multi-Agency Radiological Laboratory Analytical Protocols Manual*.
- 478 31. Hallstadius L (1984) A method for the electrodeposition of actinides, *Nucl Instrum*  
479 *Methods* 223:266-267
- 480 32. Currie LA (1968) Limits for qualitative detection and quantitative determination.  
481 Application to radiochemistry, *Anal Chem* 40 (3):586–593