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Additional Information

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15 **Sequential determination of uranium and plutonium in**
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26

27 **Abstract**

28 This study describes a rapid method for sequential determination of uranium and plutonium
29 isotopes in soil and sediment samples [and its application to the study of Anthropocene](#)
30 [sedimentary records](#). Different pretreatment methods have been tested (open-vessel
31 digestion, borate salts fusion and NaOH salt fusion) achieving the complete dissolution of
32 the sample in case of fusion methods. LiBO₂ and Li₂B₄O₇ (80/20) flux was finally selected
33 because a higher amount of sample can be analyzed (up to 5 grams). Moreover, separation
34 steps with extraction chromatographic resin UTEVA were optimized. Average recoveries
35 obtained for uranium and plutonium were acceptable, 59 % and 72 % respectively, and
36 relative bias were below ± 15 %. The time to complete the separation is approximately 11
37 hours [without ashing the samples](#) and, consequently, it can be used in emergencies.

38 **Keywords**

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

40 **Introduction**

41 Uranium and plutonium isotopes are mainly alpha emitters that can be present in the
42 environment and are important to be controlled. Uranium isotopes are naturally found in
43 the earth's crust in a mass proportion of 99.28 % for ^{238}U ($T_{1/2} = 4468 \cdot 10^6$ years), 0.72 %
44 for ^{235}U ($T_{1/2} = 704 \cdot 10^6$ years) and 0.0057 % for ^{234}U ($T_{1/2} = 0.25 \cdot 10^6$ years) [1]. ^{238}U and
45 ^{234}U are usually present in secular equilibrium in soils and sediments, with an average
46 activity of 30 Bq kg⁻¹ [2]. ^{235}U activity in nature is much smaller, but natural uranium can
47 be enriched to 2 – 5 % of ^{235}U to be used as nuclear fuel.

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

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

65 Different methods for uranium and plutonium determination in environmental samples
66 have been proposed in the literature [10]. Moreover, rapid and sequential methods for
67 actinides determination in emergency response must be developed [11]. In particular, soils

68 and sediments are complex matrices to be analyzed by radiochemical separation, being the
69 complete dissolution of the sample the critical step of the procedure. Conventional leaching
70 methods with a mixture of acids ($\text{HNO}_3/\text{HCl}/\text{H}_2\text{O}_2$) in an open-vessel or microwave
71 digester have been used for soil and sediment dissolution [12]. However, these techniques
72 may not be suitable for dissolution of refractory materials such as tetravalent oxides,
73 silicates or hot particles [11]. In this case, total dissolution with a mixture of acids including
74 HF produced good results for a small amount of sample (< 0.5 g) [13], but HF must be
75 removed by evaporation or HBO_3 complexation and its use is restricted in some countries.
76 Moreover, the sample could not completely dissolve, and the residue contains most of
77 uranium and thorium radionuclides into the structure of insoluble minerals such as zircon,
78 apatite, titanite, allanite, etc. [14].

79 According to the literature, fusion methods with an inorganic flux at high temperatures get
80 to destroy the mineral structure of soils and sediments and dissolve completely the sample.
81 The most commonly used fluxes are lithium borates [15–19], sodium hydroxides [20–22]
82 combined with peroxides [23], sodium and potassium carbonates [14, 24] or sulfates [25]
83 and mixtures of them [26]. The flux is mixed with 0.2 to 20 g of sample in proportions
84 from 1:1 to 1:15. In addition, the material of the crucible and the melting temperature
85 depend on the flux employed. Graphite, platinum or platinum with gold (95/5 %) crucibles
86 are used for lithium borate and sodium or potassium carbonate fluxes with high
87 temperatures (900 – 1200 °C). A less aggressive fusion is performed with NaOH in
88 zirconium crucibles at approximately 600 °C. Recently, a low-temperature fusion method
89 (250 °C) using NH_4HSO_4 and NH_4HF_2 was also proposed [27]. The fusion is used to carry
90 out for 10 to 30 minutes in a muffle furnace or a fusion machine, which is usually used for
91 X-ray fluorescence analysis [11].

92 After sample dissolution, polyethylene glycol (PEG) is added to remove silica and boric
93 acid present in the matrix and the flux after borates fusion [15, 16, 19]. Then, actinides are
94 pre-concentrated from the rest of the **interfering elements** of the matrix. Iron hydroxide or
95 calcium and lanthanum fluorides are usually used for coprecipitation, and sodium nitrite
96 adjusts Pu^{+3} to Pu^{+4} to be retained in the extraction chromatographic column [15, 18, 20,
97 22]. Then, actinides are usually separated with extraction chromatographic resins to

98 determine individually their activity. In emergency situations some of them are sequentially
99 determined to reduce time [15, 18, 20, 22].

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

108 **Experimental**

109 *Reagents and materials*

110 All the chemicals used were of analytical or reagent grade. Standard solutions of ^{242}Pu (9.9
111 $(0.2) \text{ Bq g}^{-1}$) and ^{232}U ($17.9(0.5) \text{ Bq ml}^{-1}$) supplied by AEA Technology (Harwell, UK) and
112 CIEMAT (Madrid, Spain) respectively were used as tracers. Standard solution of ^{243}Am
113 ($286(1) \text{ Bq g}^{-1}$) supplied by CIEMAT was used as an [interference](#) in the separation. They
114 were diluted to the appropriate activity.

115 Pt-Au crucibles (95/5 %) of 100 ml were supplied by 8853 S.p.A. (Milan, Italy) and Zr
116 crucibles of 100 ml with lid were supplied by J.P. Selecta (Barcelona, Spain). The
117 extraction chromatography resins employed in this work were UTEVA resin in columns
118 ($100\text{-}150 \mu\text{m}$ particle size) and the separation was performed in a 12 position vacuum box,
119 both available by Triskem International (Bruz, France). Stainless steel disks of 25 mm
120 diameter available from Tecnasa S.L. (Madrid, Spain) were used for electrodeposition.

121 *Soil and sediment samples*

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

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

130 *Equipment*

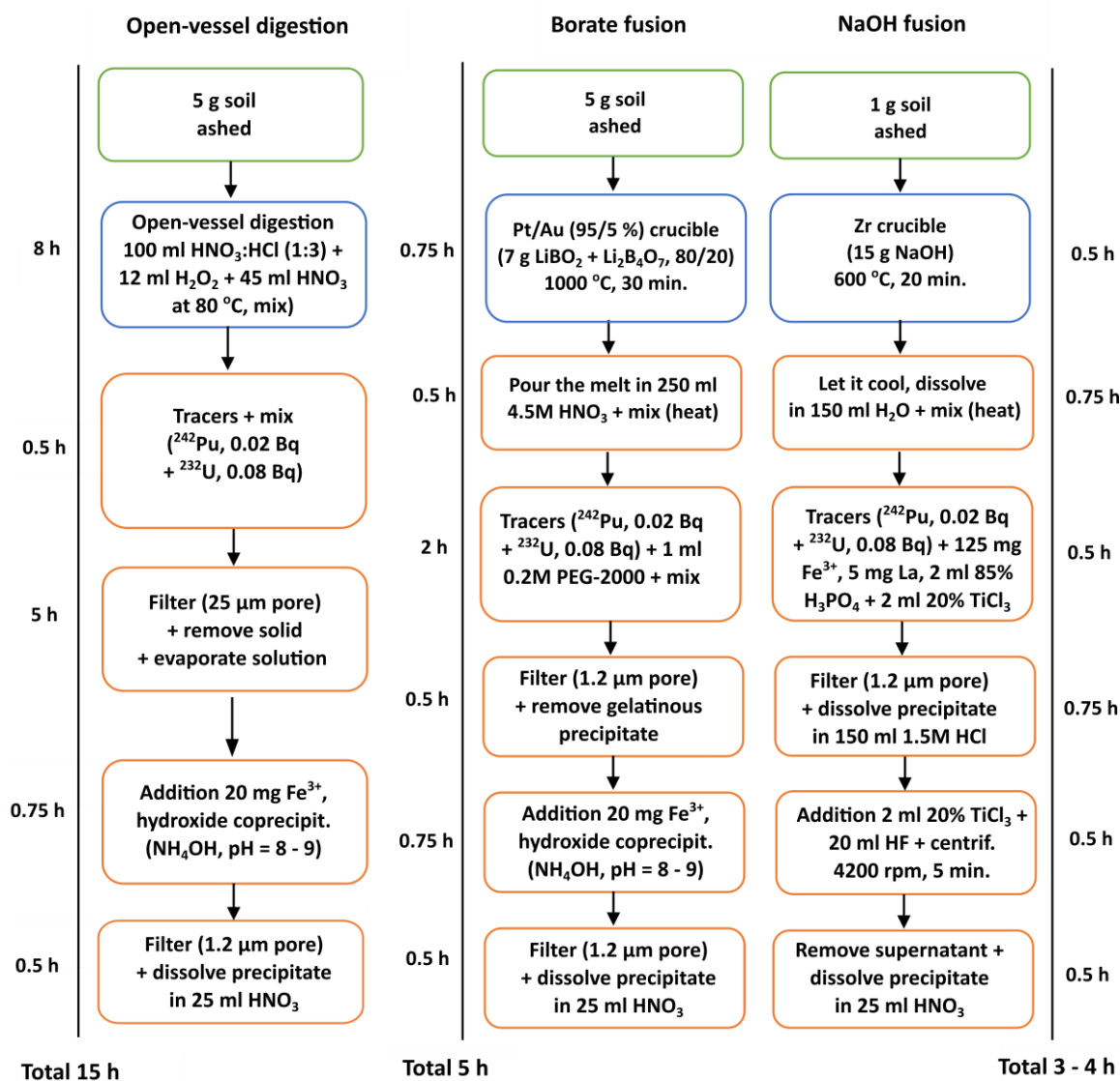
131 A muffle furnace LKN 85 (Nannetti) was used for the calcination of the soil and sediment
132 samples and a muffle furnace R-3L (J.P. Selecta) was used for the fusion of the calcined
133 samples. A centrifuge Mixtasel BLT (J.P. Selecta) was used to centrifuge 50 mL
134 polyethylene falcon tubes. The samples were measured in EG&G ORTEC 576A Dual
135 Alpha spectrometers, using surface barrier detectors of 450 mm² active area (BR-SNA-
136 450-100).

137 *Procedure*

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

144 **Sample pretreatment**

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



149

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

153 In the open-vessel digestion, 5 g of ashed soil or sediment sample (at 525 °C, at least 2
154 hours) are mixed with concentrated HNO₃, HCl and H₂O₂ for 8 hours. The tracers are added
155 to calculate the recovery of the separation when all the elements of the sample should be
156 already in solution and the isotopic equilibrium with tracers can be reached. Then, the
157 sample is filtered to remove the residue with the refractory compounds that are difficult to
158 dissolve. After evaporation, the actinides are coprecipitated with iron hydroxides and
159 dissolved in 8 M HNO₃ to perform the column separation. The time needed to complete
160 the open-vessel pretreatment is 15 hours, which is not suitable in case of emergency.

161 In the borate fusion method, 5 g of ashed soil or sediment sample are fused in a Pt/Au (95/5
162 %) crucible mixed with 7 g of a mixture of LiBO₂ and Li₂B₄O₇ (80/20) at 1000 °C. This
163 flux permits the dissolution of alkaline or metallic oxides (CaO, MgO, Al₂O₃, etc.) and
164 acidic or non-metallic oxides such as silica (SiO₂) and rutile (TiO₂) [30]. Samples with a
165 high carbonate content must be pretreated with concentrated HNO₃ and H₂O₂ to avoid an
166 aggressive reaction during fusion. The fused samples are dissolved in 4.5 M HNO₃ after
167 pouring the hot melt. After dissolution and addition of tracers, polyethyleneglycol (PEG-
168 2000) is added to the solution to remove silica and boric acid in form of a gelatinous
169 precipitate. After filtration, actinides are coprecipitated with iron hydroxides and dissolved
170 in 8 M HNO₃. The time to complete this fusion method is 5 hours, which is suitable for
171 rapid methods and emergencies.

172 Finally, in the sodium hydroxide fusion the melting temperature is lower (600 °C), and
173 zirconium crucibles are less expensive than platinum crucibles. This is a widely used fusion
174 for soil and sediment dissolution [20-22], but sometimes high refractory compounds can
175 not be dissolved [11]. In this case, the ashed soil or sediment samples are mixed with 15 g
176 of NaOH and the crucible is covered with a lid to avoid losses. After fusion, the melt cools
177 and is dissolved in distilled water. Tracers and several carriers are added to coprecipitate
178 actinides as proposed by Maxwell et al. [20]: Fe³⁺ to produce actinides coprecipitation,
179 La³⁺ and PO₄³⁻ to increase Am and U coprecipitation respectively, and TiCl₃ to reduce
180 soluble U(VI) to more insoluble U(IV). After filtering, the precipitate is dissolved in diluted
181 HCl and a following actinides coprecipitation is performed in form of LaF₃ and CaF₃ to
182 remove interfering elements such as Si, Ti, Ca, Fe, etc. The precipitate is dissolved in 25
183 ml of 8 M HNO₃ to pass through the column. However, samples with high calcium content

184 are difficult to dissolve in this small volume and we restricted the method to 1 g of sample.
185 This fusion method is completed in 3 – 4 hours.

186 ***Sample separation and measurement***

187 Sequential separation of uranium and plutonium after sample pretreatment was performed
188 with the extraction chromatographic resin UTEVA. According to the technical
189 specifications of the resin, different solutions were tested to optimize the separation.
190 Eighteen tests were carried out with samples of 20 ml 8 M HNO₃-NaNO₂ spiked with ²³²U
191 (0.06 Bq), ²⁴²Pu (0.02 Bq) and ²⁴³Am (0.02 Bq) to calculate the chemical yield in the
192 separation and to detect the presence of **interferences** in each fraction. Fe³⁺ (20 mg) were
193 also added to simulate the sample obtained after pretreatment. Sample solution and thorium
194 elution were the same in all tests, but uranium and plutonium elutions were optimized.

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

197 **Results and Discussion**

198 In the following section, the study of the separation steps with UTEVA for sequential
199 separation of uranium and plutonium isotopes is presented. After the selection of the
200 separation method, the different pretreatment options of soil and sediment samples were
201 tested and the recoveries and activities obtained are shown. The final method was tested
202 with sediment samples and validated with intercomparison soil samples. Moreover,
203 plutonium and uranium in two cores of estuarine sediments from the Cantabrian coast of
204 Spain were analyzed.

205 ***UTEVA separation optimization***

206 Uranium and plutonium separation was performed with UTEVA column. After loading the
207 sample (20 ml 8 M HNO₃-NaNO₂) through the column, plutonium (IV), uranium and
208 thorium are retained in the resin, and it is washed with 10 ml 8 M HNO₃ to remove iron
209 and americium isotopes. Thorium is removed with 4 ml 9 M HCl and 20 mL 5 M HCl.

210 Then, different options for uranium and plutonium elution were tested to improve chemical
 211 yields (R) and avoid the presence of interferences. They were selected taking into account
 212 the UTEVA specification sheet supplied by Triskem. Each of the eluted solutions with the
 213 uranium and plutonium fractions were electrodeposited according to Hallstadius [31] and
 214 measured by alpha spectrometry.

215 Among the different options, plutonium isotopes can be eluted by changing their oxidation
 216 state. Pu⁴⁺ can be reduced in the resin to Pu³⁺ with a reducing agent, such as hydroxylamine,
 217 *rongalite* (sodium hydroxymethanesulphinate), TiCl₃, etc. With this valence, plutonium
 218 behaves similarly to Am³⁺ and can be eluted from the resin. Other option is the addition of
 219 oxalic acid to form a complex with plutonium. If Pu⁴⁺ is considered to behave similarly to
 220 Np⁴⁺, oxalic acid can be used to separate uranium from plutonium. According to the
 221 UTEVA specification sheet, Np/Pu can be eluted from the resin with HCl containing 0.05
 222 M oxalic acid, while U is retained.

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

225 **Table 1** Different tests (number of replicates in brackets) for plutonium and uranium
 226 elution steps with UTEVA and their corresponding recoveries (R (%)). RSD: Relative
 227 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 ₃	-	-
	U	15 mL 0.1 M HNO ₃	84.7	Pu (15 %)
	Pu	15 mL 0.1 M HNO ₃ -0.3 M NH ₂ OH·HCl	74.5	U (1.5 %)
P3 [x4]	Cleaning	5 mL 8 M HNO ₃	-	-
	Pu	15 mL 2 M HNO ₃ -0.05 M oxalic acid	94.7 (4 %)	Th (5 %)
	U	15 mL 0.01 M HNO ₃	86.3 (4 %)	Th (2 %)
P4 [x4]	Cleaning	5 mL 8 M HNO ₃	-	-
	Pu	15 mL 2 M HNO ₃ -0.3 M NH ₂ OH·HCl	62.5 (44 %)	No

	U	15 mL 0.01 M HNO ₃	81.9 (3 %)	Pu (30 %)
P5 [x6]	Cleaning	5 mL 8 M HNO ₃	-	-
	Pu	20 mL 2 M HNO ₃ – 0.04 M rongalite	92.7 (6 %)	No
	U	20 mL 0.01 M HNO ₃	48.7 (34 %)	No

228 Plutonium elution with oxalic acid in hydrochloric media before uranium elution (P1)
 229 produced good chemical yields for both isotopes (approximately 75 %) but some ²³²U
 230 appeared in the plutonium fraction. For this reason, separation steps of P2 were proposed,
 231 where plutonium (Pu³⁺) was eluted after uranium by reduction to Pu³⁺ with hydroxylamine.
 232 Both recoveries obtained were acceptable, but plutonium activity appeared in uranium
 233 fraction (15 % approximately). In test P3, plutonium was eluted with oxalic acid in nitric
 234 media. However, ²²⁸Th from ²³²U chain was observed in both fractions and this option was
 235 discarded. Finally, hydroxylamine and *rongalite* (sodium hydroxymethanesulfinate) were
 236 selected as reductant agents in tests P4 and P5, respectively. Plutonium was not completely
 237 eluted with hydroxylamine and part of it was obtained in the uranium fraction (P4).
 238 Therefore, *Rongalite* was tested, obtaining high recoveries (> 90 %) for plutonium, and
 239 acceptable recoveries (50 % approximately) for uranium. This method (P5) was finally
 240 selected due to the acceptable uranium and plutonium recoveries and mainly because no
 241 interferences were observed in both fractions, unlike in the other tests (P1-P4).

242 *Pretreatment optimization*

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

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

Method	Sample	R (%) U	A (Bq kg ⁻¹) ²³⁸ U	A (Bq kg ⁻¹) ²³⁴ U	A (Bq kg ⁻¹) ²³⁵ 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 %)

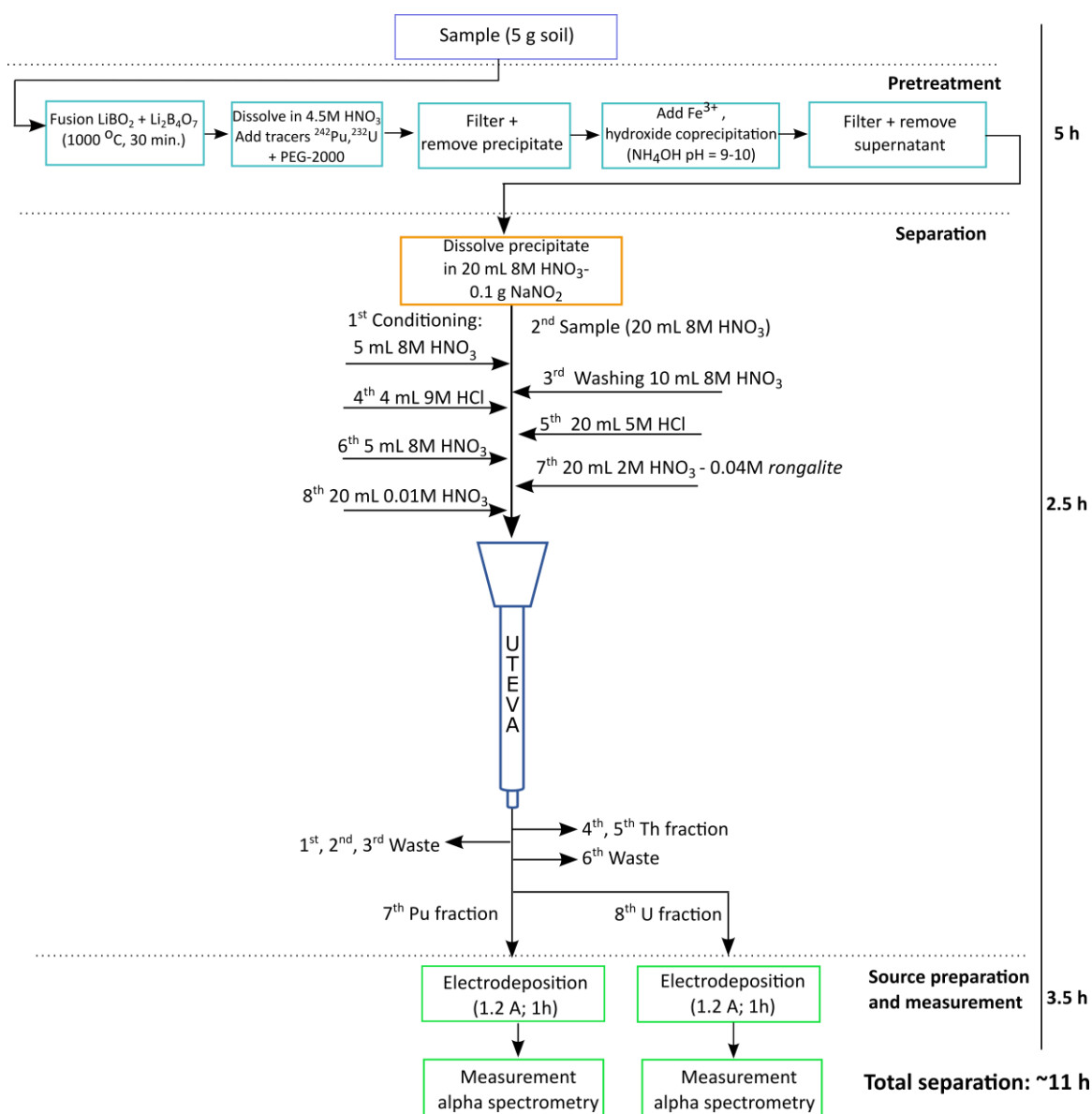
254 As can be seen in Table 2, average recoveries obtained for uranium and plutonium were
 255 higher in case of the open-vessel digestion method. However, these samples were also
 256 analyzed by gamma spectrometry through ²¹⁴Pb peak (351.92 keV) and assuming secular
 257 equilibrium in ²³⁸U chain. The average activities obtained for ²³⁸U and ²³⁴U were 20 Bq kg⁻¹
 258 ¹ approximately. Therefore, these recoveries are not correct and lower activities were
 259 obtained, because the open-vessel digestion method without HF can not extract completely
 260 uranium isotopes from the matrix.

261 Uranium activities calculated with borate fusion and NaOH fusion methods were close to
 262 the values obtained by gamma spectrometry, despite the lower recoveries obtained in some
 263 cases and the high relative standard deviation obtained for ²³⁵U due to their low activities.
 264 Secular equilibrium was confirmed with ²³⁴U/²³⁸U ratios close to 1 in all cases. For these
 265 reasons, fusion methods were faster and more suitable than open-vessel digestion method
 266 to pretreat soil and sediment samples for analyzing uranium and plutonium isotopes.
 267 Among fusion methods, borate fusion was selected despite the cost of platinum crucibles
 268 for two reasons: a higher amount of sample could be analyzed (up to 5 grams) to permit
 269 the analysis of low contaminated samples and the following steps of the separation are
 270 simpler.

271 Validation of the final method

272 The final method selected was based on borate fusion pretreatment, UTEVA separation,
 273 electrodeposition and measurement by alpha spectrometry. The time needed to complete
 274 the separation is approximately 11 hours **without ashing the samples**, as can be seen in Fig.
 275 2.

276



277

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

280 The method was validated with the analysis of the reference material (RM) IAEA-326, a
 281 natural soil sample with 29.4 Bq kg⁻¹ and 27.9 Bq kg⁻¹ of ²³⁸U and ²³⁴U respectively, and
 282 0.5 Bq kg⁻¹ and 0.02 Bq kg⁻¹ of ^{239/240}Pu and ²³⁸Pu respectively. Table 3 shows the results
 283 obtained for three replicates analyzed with the sequential method based on borate fusion.
 284 Uranium and plutonium recoveries were high for both elements and the activities of each
 285 isotope were calculated, obtaining relative bias below ± 13 % in all cases. ²³⁸Pu relative
 286 bias were not calculated because limits of detection (LD) of ²³⁸Pu for 5 grams of sample
 287 and 300,000 seconds of measurement were approximately 0.03 Bq kg⁻¹ [32]. Relative
 288 standard deviation of the activities between the replicates were 4 % and 8 % for uranium
 289 and plutonium isotopes respectively. In addition, dispersion between recoveries was low,
 290 17 % for uranium and 13 % for plutonium. Therefore, the reproducibility and accuracy of
 291 the method was validated.

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

Sample	R (%) U	A (Bq kg ⁻¹) ²³⁸ U	LD (Bq kg ⁻¹) ²³⁸ U	A (Bq kg ⁻¹) ²³⁴ U	LD (Bq kg ⁻¹) ²³⁴ U	Rel. Bias ²³⁸ U	Rel. Bias ²³⁴ 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 ⁻¹) ^{239/240} Pu	LD (Bq kg ⁻¹) ^{239/240} Pu	A (Bq kg ⁻¹) ²³⁸ Pu	LD (Bq kg ⁻¹) ²³⁸ Pu	Rel. Bias ^{239/240} Pu	Rel. Bias ²³⁸ 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 %	-

295 In addition, our laboratory participated in the intercomparison exercise IAEA-TEL-2018
 296 with the analysis of an agricultural natural soil (Sample 04) spiked with artificial gamma
 297 emitters. Activities of ²³⁸U, ²³⁵U and ²³⁴U calculated are shown in Table 4. Relative bias
 298 for all uranium isotopes were below ± 10 % and the results were accepted for being below
 299 ± 20 % for ²³⁸U and ²³⁴U, and ± 30 % for ²³⁵U. However, it is important to highlight that
 300 the number of laboratories taking part in this international intercomparison exercise with

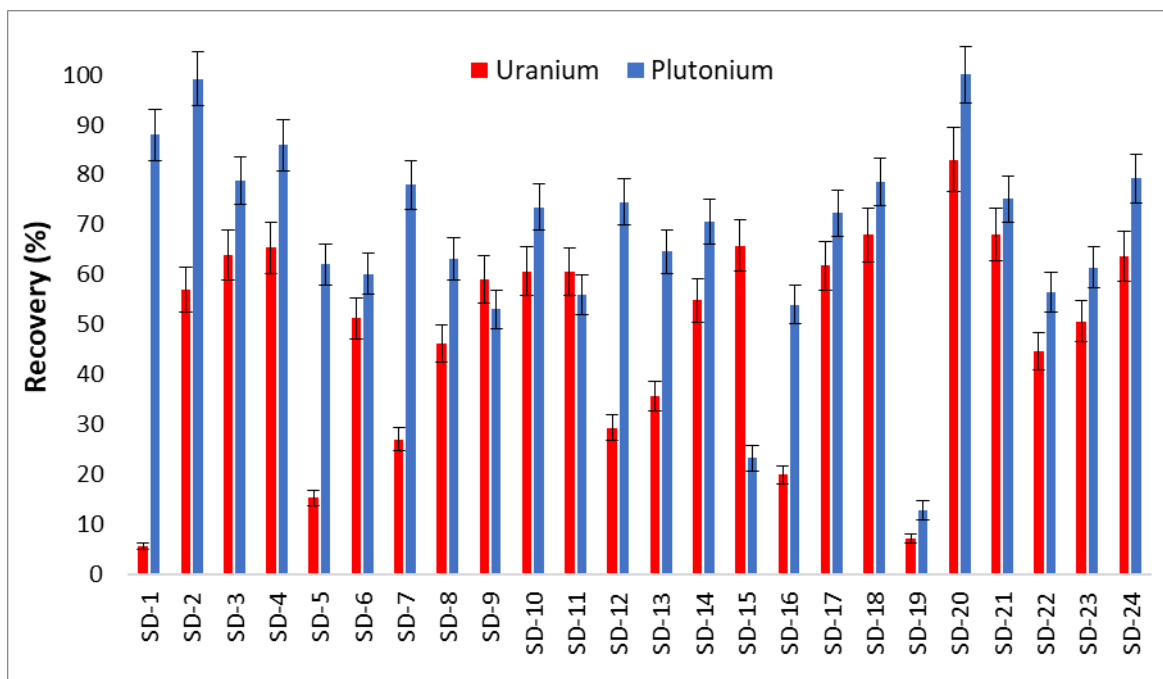
301 the analysis of uranium isotopes in the soil sample was very low. Only between 15 to 27
302 % of 267 laboratories reported results for uranium isotopes, and between 6 to 11 % obtained
303 acceptable results. This demonstrates the complexity of uranium determination in soil
304 samples and the validation of the method proposed in this work.

305 **Table 4** Results obtained for the intercomparison sample (Sample 04) of the IAEA-TEL-
306 2018: uranium recovery, and activities, limits of detection and relative bias obtained for
307 each isotope. Uncertainties calculated for $k = 2$.

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

308 *Estuarine sediments*

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



312

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

315 Uranium recoveries of 18 samples (out of 24) were higher than 30 % with an average
 316 recovery of 59 %, ranging from 36 to 83 % and a relative standard deviation (RSD) of 18
 317 %. LD for uranium isotopes ranged from 0.03 to 1 Bq kg⁻¹ depending on the recoveries.
 318 Therefore, these recoveries were suitable to determine uranium isotopes in normal soil and
 319 sediment samples with good uncertainties and limits of detection due to their range of
 320 activities.

321 In case of plutonium recovery, 22 samples (out of 24) obtained values higher than 30 %.
 322 The average value was 72 %, ranging from 53 to 100 %, and a RSD of 19 %. These high
 323 and reproducible recoveries permitted the quantification of plutonium isotopes, usually
 324 with lower activities than uranium. Their limits of detection range from 0.01 to 0.14 Bq kg⁻¹
 325 ¹ depending on the recoveries.

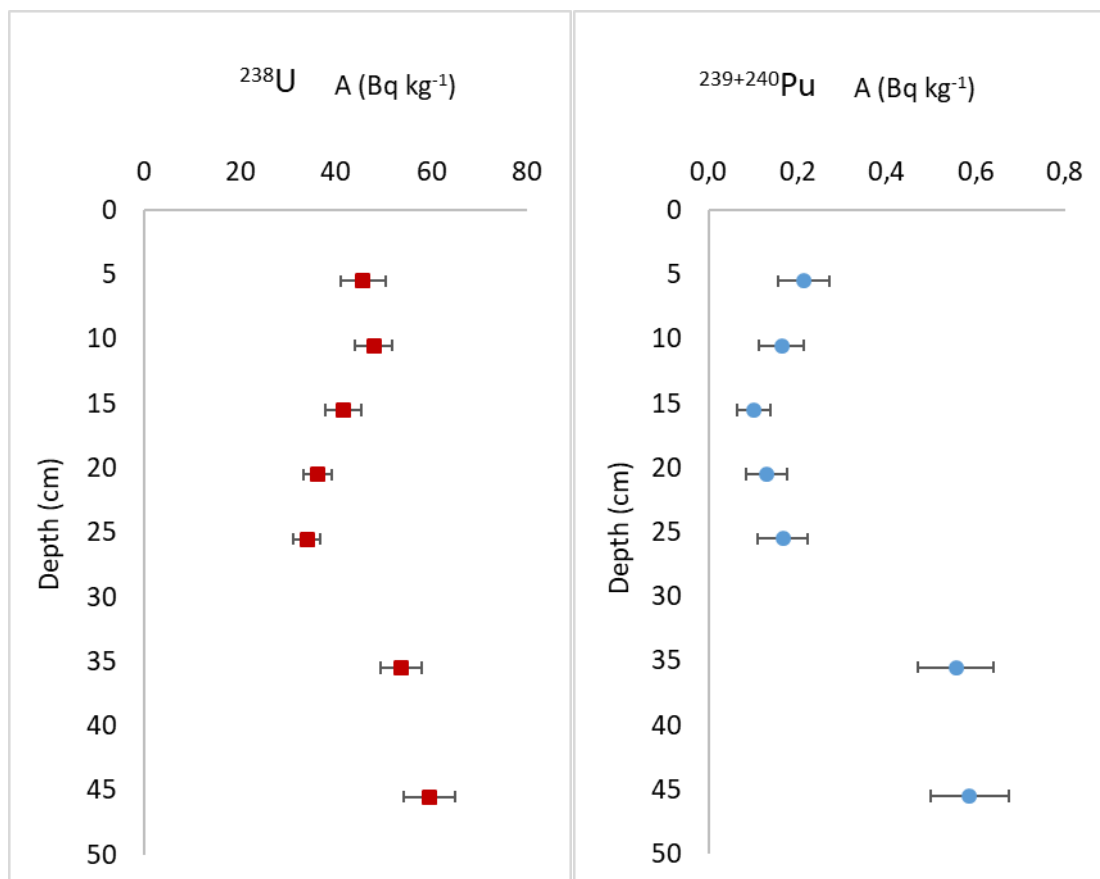
326 These estuarine sediments correspond to two cores collected for different unpublished
 327 studies of Anthropocene records in coastal areas perturbed by human activities. In order to
 328 verify the possibility of using Pu-activity concentrations (and the reference dates they
 329 provide) to validate sediment dating with ²¹⁰Pb_{excess}, Core 1 (Mape, 46-cm long) from the

330 Urdaibai estuary was retrieved in September 2007 whereas Core 2 (Miengo-2, 40-cm long)
331 from the Suances estuary was obtained in May 2016, both in the Cantabrian coast of Spain.
332 Plutonium and uranium isotopes were determined for each 1-cm layer sampled at 5-cm
333 intervals approximately, from 5 cm to 45 cm depth (except samples 30 and 40 cm depth
334 that were not analyzed) in Core 1 and from top core to 40 cm depth in Core 2.

335 All samples presented ^{238}U and ^{234}U activities between 35 and 65 Bq kg^{-1} , with average
336 $^{234}\text{U}/^{238}\text{U}$ ratios of 0.98 (RSD: 2 %), and between 1 to 3 Bq kg^{-1} for ^{235}U . Plutonium
337 activities in the samples ranged from 0.1 to 1.5 Bq kg^{-1} for $^{239+240}\text{Pu}$, and up to 0.08 Bq kg^{-1}
338 for ^{238}Pu although most of them were below the limits of detection for ^{238}Pu (0.007 to
339 0.05 Bq kg^{-1} , depending on the recovery).

340 Results of ^{238}U and $^{239+240}\text{Pu}$ for Core 1 and Core 2 are shown in Fig. 4 and Fig. 5
341 respectively. As it can be seen, ^{238}U activity in both cores is always above 30 Bq kg^{-1} and
342 it does not show a high variation with depth due to its natural origin. However, its
343 maximum values appear at the same depths as plutonium. $^{239+240}\text{Pu}$ activity in the top
344 sample is practically negligible and increases to a maximum value depending on the depth.
345 For Core 1 it appears between 35 – 36 cm and 45 – 46 cm layers, although it could still be
346 increasing below 46 cm depth. For Core 2 a peak between 22 – 23 and 24 – 25 cm layers
347 is observed. The contrasting behavior between Core 1 and Core 2 may be due to their
348 different geographical location (Urdaibai estuary and Suances estuary, respectively) and
349 sampling dates (2007 and 2016, respectively). Moreover, the sedimentary materials and
350 processes in each estuary are not the same. However, due to the artificial origin of $^{239+240}\text{Pu}$,
351 its presence and abundance in these particular layers will be a very useful marker to identify
352 Anthropocene sediments in the future.

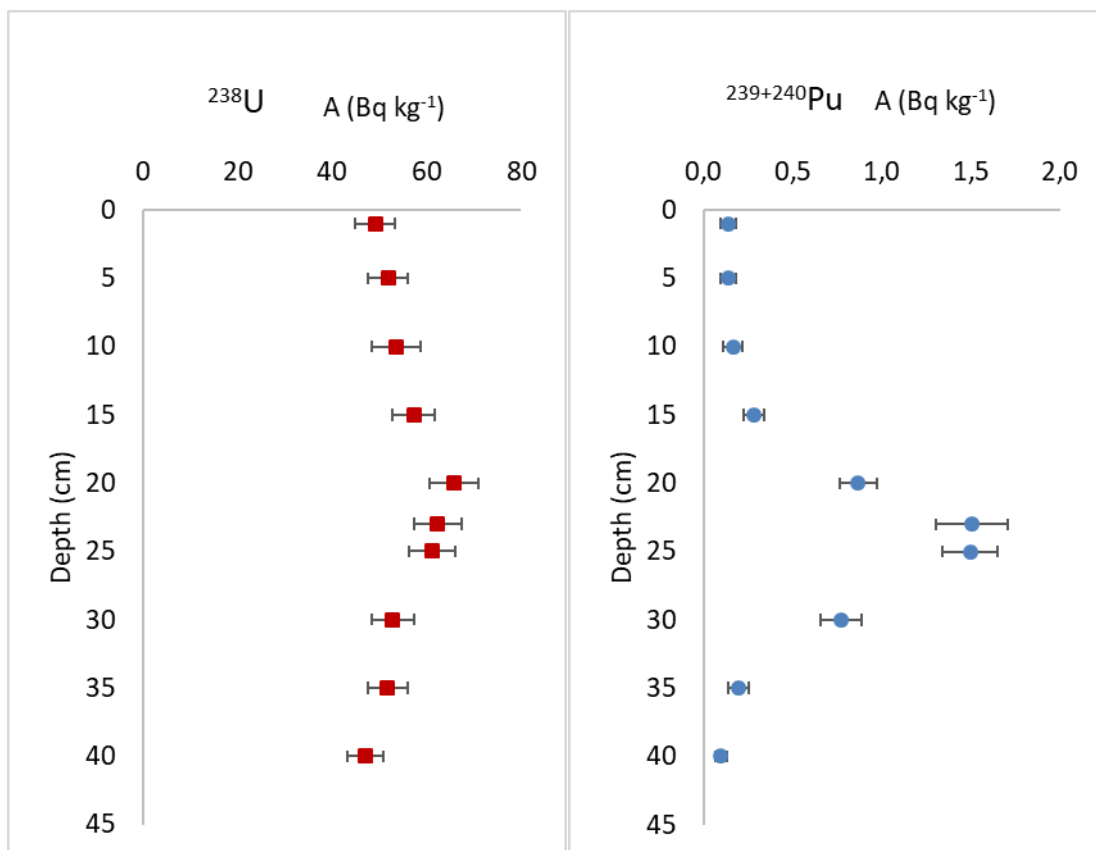
353



354

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

357



358

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

361 Conclusions

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

371 The final method selected based on borate fusion was tested with sediment samples
372 obtaining acceptable recoveries for uranium and plutonium, an average of 58.9 % (RSD:
373 18 %) and 72.0 % (RSD: 19 %), respectively. The method was validated with a reference
374 material and an intercomparison sample, obtaining relative bias below ± 15 % in all cases
375 and good reproducibility. In addition, the analysis of samples from two profiles of recent
376 estuarine sediments from the Cantabrian coast of Spain permitted identify Anthropocene
377 records due to the presence of $^{239+240}\text{Pu}$ activity.

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

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391 **Compliance with ethical standards**

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

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