



# Determination of trace element concentrations and stable lead, uranium and thorium isotope ratios by quadrupole-ICP-MS in NORM and NORM-polluted sample leachates

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## ABSTRACT

This work focuses on the monitoring of the potential pollution in scenarios that involve NORM-related industrial activities (environmental or in-door scenarios). The objective was to develop a method to determine extent and origin of the contamination, suitable for monitoring (i.e. simple, fast and economical) and avoiding the use of too many different instruments. It is presented a radiochemical method that allows the determination of trace element concentrations and  $^{206}\text{Pb}/^{207}\text{Pb}/^{208}\text{Pb}$ ,  $^{238}\text{U}/^{234}\text{U}$  and  $^{232}\text{Th}/^{230}\text{Th}$  isotope ratios using a single sample aliquot and a single instrument (ICP-QMS). Eichrom UTEVA<sup>®</sup> extraction chromatography minicolumns were used to separate uranium and thorium in sample leachates. Independent ICP-MS determinations of uranium and thorium isotope ratios were carried out afterwards. Previously a small aliquot of the leachate was used for the determination of trace element concentrations and lead isotope ratios. Several radiochemical arrangements were tested to get maximum performances and simplicity of the method. The performances of the method were studied in terms of chemical yields of uranium and thorium and removal of the potentially interfering elements. The established method was applied to samples from a chemical industry and sediments collected in a NORM-polluted scenario. The results obtained from our method allowed us to infer not only the extent, but also the sources of the contamination in the area.

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## 1. Introduction

Monitoring of industrial-derived inorganic pollution of environmental scenarios has been a constant concern during the last decades, involving the control of toxic element concentration levels. In some specific non-nuclear industries, radioactivity levels must also be controlled, because enhanced levels of naturally occurring radioactive materials (NORM) are handled through various industrial operations [1]. Spread-out problems regarding the NORM industries are the massive use of raw ores containing high concentrations of those radionuclides, forcing thus to monitor not only potentially toxic elements, but also natural radionuclides from  $^{238}\text{U}$  and  $^{232}\text{Th}$ -Series. The monitoring of those industries is a key matter in the European laboratories due to Chapter 7 from the European Council Directive EURATOM96/29 (1996) [2] and derived subsequent national regulations.

The monitoring and control of the potential contamination in an area must cover two interrelated aspects: an evaluation of the severity of the potential pollution (by analysing element concentrations) and the origin of the source of pollution, for example using isotope ratios (IRs) such as  $^{206}\text{Pb}/^{207}\text{Pb}/^{208}\text{Pb}$  [3,4],  $^{238}\text{U}/^{234}\text{U}$  [5,6] and  $^{232}\text{Th}/^{230}\text{Th}$  [7–9].

Two independent instrumentations are commonly required to fulfil both requirements (determination of inorganic pollutant concentrations and isotope ratios). For U and Th isotope ratio analysis a radiometric approach is usually followed (e.g., semiconductor alpha spectrometry). That is combined with the use of AAS, ICP-OES or ICP-MS for the trace element concentration analyses and MS techniques for lead isotope ratio analysis. The use of a single instrument and a unified method allowing the sequential determination of the inorganic pollutant concentrations and isotope ratios, would simplify laboratory requirements and management.

Sector focusing ICP-MS instruments offers excellent performance for isotope ratios, although their cost is very high. ICP-QMS measurements can provide all the necessary parameters for a fast monitoring of stable elements and lead, thorium and uranium isotope ratios, minimising the cost of the determinations and saving

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time. Moreover, the extraction of the required information from the same aliquot minimises sample consumption and also avoids that sample heterogeneities would decouple the results between different kinds of analyses [10] (trace element concentrations and IRs).

The low concentration of minor abundance isotopes such as  $^{234}\text{U}$  and  $^{230}\text{Th}$ , the limited performances of quadrupole instruments for isotope ratio determinations [11,12] and the presence of spectrometric interferences (see below for details) have sometimes precluded the use of ICP-QMS as a routine method for the simultaneous determination of these elements. The application of radiochemical methods previous to the ICP-QMS analysis can resolve some drawbacks of the technique in terms of interferences and limit of detection. There are a large variety of radiochemical methods allowing the separation of U and Th isotopes, many of them designed for measurements by alpha-spectrometry, TIMS or SF-ICP-MS [13,14]. The feasibility of their application to ICP-QMS measurements is not straightforward, since the instrumental limitations, precision, limits of detection and potential interferences vary from those techniques to ICP-QMS. SF-ICP-MS and ICP-QMS instruments use the same technique for analytes' ionisation. However, sector field instruments provide signal/background ratios several orders of magnitude larger than quadrupole instruments. Hence, a method designed specifically for SF instruments could use this advantage in order to minimise sample mass amount, i.e. even if the analyte concentration is small in the aspirated solution, the instrumental performances of a SF instrument could overcome this limitation providing enough precision to perform the analysis but it won't be achievable when using ICP-QMS. The methods specifically designed for the analysis by ICP-QMS of isotope ratios of U or (to a minor extension) Th couple subsequent steps of liquid–liquid extraction, ion exchange or chromatographic resin columns or a combination of some of them, hence resulting in time-consuming methods [7,10,15].

Our aim is to find a suitable radiochemical method that (i) concentrates uranium and thorium isotopes with high and reproducible recoveries, (ii) removes interfering elements to minimise both sample matrix effects and the presence of interferences for ICP-MS measurement and (iii) allows ICP-MS measurement of uranium and thorium isotopes, together with element concentrations, eventually lead isotope ratios. The implemented method has to fulfil the following criteria: (a) multi-element analysis and lead, thorium and uranium IR analyses must be performed from a single sample aliquot, (b) analyses must be performed exclusively on an ICP-QMS and (c) the method must be as simple (quick) as possible.

We have tested several methods based on the separation of U and Th using Eichrom UTEVA<sup>®</sup> resin. Its functional group (diamyl amylphosphonate, DAAP) has a high affinity for actinides in their tetravalent or hexavalent oxidation state. We focused our work on testing the performances of the selected approaches in terms of feasibility for ICP-QMS measurements. The fractionation of the target analytes (Pb, Th, U and trace elements) and the potential interferences throughout the general scheme has been studied.

## 2. Experimental

### 2.1. Sampling scenario

Samples were collected in 2001 in the Huelva Estuary (SW of Spain). Contamination in this Estuary (which is formed in the confluence of Odiel and Tinto rivers) has been monitored through the years since it is one of the most contaminated estuaries in the world. It is strongly affected by acid mine drainage (AMD) and phosphoric acid production plants, resulting in high concentrations of heavy metals, such as Fe, Cu, Zn and Mn [15,16].

**Table 1**

Operating conditions of the Agilent 7500c ICP-QMS used in this work.

RF Power (W)	1550, torch shield
Sampling depth (mm)	5.9
Quantitative analysis mode	
Carrier gas (L min <sup>-1</sup> , Babington nebuliser)	1.1
ORS	H <sub>2</sub> (4.5 L min <sup>-1</sup> ), He (2.5 L min <sup>-1</sup> )
Internal standard	<sup>6</sup> Li, <sup>103</sup> Rh, <sup>209</sup> Bi
Sample flow rate (L min <sup>-1</sup> )	0.4
Replicates	3
Isotope ratio mode	
Carrier gas (L min <sup>-1</sup> , PFA nebuliser)	0.5
Auxiliary gas (L min <sup>-1</sup> )	0.4
ORS	Off
Sample flow rate (L min <sup>-1</sup> )	0.05
Dwell time (ms)	230: 30, 232: 1; 234: 25; 238: 0.9
Replicates	7–10
Ce <sup>16</sup> O <sup>+</sup> /Ce <sup>+</sup> (%)	0.7–1.2
Th <sup>1</sup> H <sup>+</sup> /Th <sup>+</sup> (%)	(1.0–1.4) × 10 <sup>-3</sup>
(M – 1) <sup>+</sup> /M <sup>+</sup> (%)	<4 × 10 <sup>-2</sup>
(SnSn) <sup>+</sup> /Sn <sup>+</sup> (%)	<4 × 10 <sup>-4</sup>
Mass bias correction	External, linear

Furthermore, several phosphoric acid production plants discharged wastes to the Odiel river through years. The main used ore was phosphate rock (PR) from Morocco containing high activity concentrations of U-Series radionuclides under nearly secular equilibrium [5,17]. The discharged waste, phosphogypsum (PG), contains large fractions of radium, thorium and lead isotopes.

### 2.2. Samples and reagents

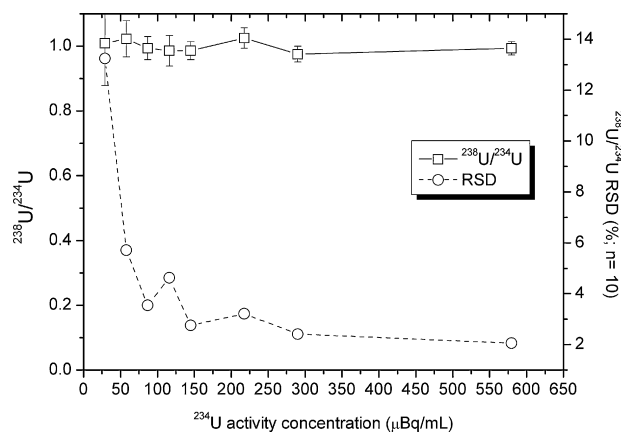
The analysed samples comprise NORM matrices (PR and PG) and NORM-polluted riverbed sediment samples. The samples were stored in polyethylene sealed bottles. Before analysis, the samples were dried at 65 °C to a constant weight and sieved by 10 μm mesh.

Suprapure grade HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and HCl (Merck) and 18.0 MΩ cm<sup>-1</sup> deionised water (Millipore) were used for samples leaching, chromatographic separations and solution matrix adaptation, when required. Al(NO<sub>3</sub>)<sub>3</sub> and oxalic acid (Panreac) were analytical grade. 2 mL pre-packed minicolumns of Eichrom's UTEVA resin (TRISKEM, France) were used for the chromatographic separation and purification of Th and U.

### 2.3. ICP-MS setup

Quantitative elemental analysis and isotope ratio determinations were carried out using an Agilent 7500c ICP-QMS provided with an Octopole Reaction System (ORS). Operating conditions are provided in Table 1. Element concentrations (Pb, Th, U and interfering elements), quality checks, recoveries/interfering elements decontamination monitoring and the calculation of dead time for count rates correction were carried out using a mix of single element standard solutions diluted to the required concentrations. The U.S. EPA 2008 methodology was used in order to check for calibration accurateness and precision and to test the presence of memory effects, sample matrix effects, etc.

Isotope ratio analyses were done using a PFA-100 micronebuliser working under self-aspiration regime being the ORS off. Mass bias correction was performed by bracketing the samples between certified IR standard solutions and a blank solution using the linear approach. NIST-981, NIST, U.S.A. was used for lead. IRMM-035 and IRMM-056 were used for thorium and uranium, respectively (Institute for Reference Materials and Measurements, Geel, Belgium). Every four samples, a certified reference material solution or a replicated sample was analysed as an unknown sample in order to test



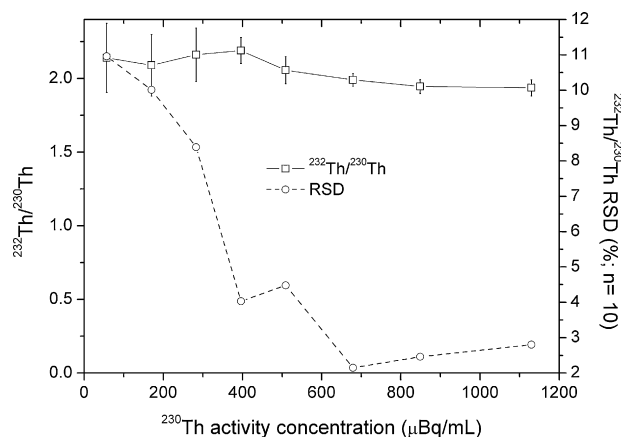
**Fig. 1.1.** Dependence of  $^{238}\text{U}/^{234}\text{U}$  isotope ratio value (expressed in terms of activity ratio) and RSD with  $^{234}\text{U}$  concentration.

the accuracy, short-term analysis reproducibility and precision of the results.

Standard solutions of lead, thorium and uranium at the  $10\text{ ng mL}^{-1}$  concentration level were self-aspirated using different dwell times in order to minimise the internal uncertainty. Dwell time was fixed for every isotope to be considered in the isotope ratio calculations, and the relative standard deviation (RSD) dependence with element concentration was studied as suggested in previous works [18,19]. Therefore, it is possible to establish a concentration discrimination level providing enough counting statistics to produce the required RSD level. In our case, it has been established at the 3% level, which is a typical value of relative counting uncertainty in alpha spectrometry. Data from Figs. 1.1 and 1.2 show that these values are obtained when activity concentrations in the aspirated solutions range  $0.25\text{ mBq mL}^{-1}$  for  $^{234}\text{U}$  and  $0.7\text{ mBq mL}^{-1}$  for  $^{230}\text{Th}$ .

#### 2.4. Radiochemical procedure

Element concentrations and lead isotope ratios were determined after applying the U.S. EPA 3050B method, filtering and subsequently diluting a small aliquot of the filtrate. This method does not provide total sample dissolution but it offers a reasonable assessment of the worst-case environmental scenarios where components of the sample become soluble and mobile [20]. Total digestion of the sample requires either alkaline fusion (which introduces extremely high sample matrix effects requiring dilution



**Fig. 1.2.** Dependence of  $^{232}\text{Th}/^{230}\text{Th}$  isotope ratio value (expressed in terms of activity ratio) and RSD with  $^{230}\text{Th}$  concentration.

factors that could make difficult analytes quantification, [21]) or the use of hydrofluoric acid (see, e.g., [22]), which is highly toxic, cannot be introduced into our ICP-QMS instrument and must be previously removed by evaporating or by reaction with boric acid. However, boric acid produces intense matrix effects unless very large dilution factors are applied [23], and evaporation can lead to uncontrolled analyte losses in volatile compounds. Since the aim of this work is to develop a fast method for NORM contamination monitoring, the digestion of the refractory matrix is not indispensable. Previous works support this approach. They establish that to infer the source of the pollution in NORM samples the information required (elements and isotope ratios) can be achieved without performing total sample dissolution [24–28]. On the other hand, it will improve the robustness of the chemical separation, since the incorporation of methods to dissolve the refractory matrix can seriously affect the performances of the chromatography columns [22]. After leaching and filtration, a small aliquot is diluted for element concentration and lead isotope ratios analyses, while the remaining solution is used to concentrate and purify uranium and thorium.

The extraction efficiency of the leaching method was tested through analysis of certified reference samples IAEA SL-1 and NIST SRM-1646 (lake and estuarine sediment samples respectively). It was better than 75% for Mg, V, Cr, Mn, Fe, Co, Zn, As, Cu, Pb and U; it was comprised between 50 and 75% for Th, and it was less than 50% for Al, Ca and Ti. Short-term repeatability ( $\sim 3$  days) of the leaching efficiency was better than 10% through 4 sample replicates, excepting for Al, Ca and Ti [29]. Regarding stable lead isotope ratios, the analyses of the IAEA SL-1 sediment reference samples provided results for  $^{206}\text{Pb}/^{207}\text{Pb}$  isotope ratio ( $1.219 \pm 0.003$ ) in good agreement with those provided by Lindeberg et al. ( $1.217 \pm 0.003$ ) [30].

The radiochemical setup was based on the one by Horwitz et al. [31], designed to be coupled with alpha-spectrometry. Several modifications were made to the original method, in order to improve its performances; the six different options tested, which are based in Refs. [31–35] are displayed in Fig. 2, and they were applied in order to avoid stripping together U and Th [36] due to the potential overlapping of thorium hydrides on uranium isotopes. Every radiochemical procedure was tested using 2–4 sample replicates. All the tests were performed using true sediment samples instead spiked artificial solutions. The fractionation of potential spectrometric interferences throughout the applied procedures was also analysed. All the solutions generated during each radiochemical scheme (leaching solution, loading elute, wash elute, conditioning elute, thorium stripping solution and uranium stripping solution) were submitted to multielemental analysis after convenient dilution.

The main interferences potentially overlapping the masses of our interest (Pb: 206, 207, 208; Th: 230, 232; U: 234, 238) are Tl hydrides (lead isotopes), Cd and In dimers and Os and Pt argides (at mass 230), Sn dimers and Os argides (232), Sn dimers, Pt and Hg argides and Th hydrides (234) and Sn dimers and Pt argides (238). A feasible method fitting to the criteria previously established must allow separation of U and Th isotopes, and a convenient removal of Cd, In, Os, Pt, Hg and Sn.

A comparison among the concentrations found in the leachate and those other concentrations found in those solutions allow us to calculate the chemical yield of each element (both analyte and interferences) in each solution, avoiding in this way the use of chemical yield tracers for U and Th and allowing the evaluation of the impact of interferences in U and Th less abundant isotopes. All the uncertainties have been given account by expansion according to GUM guide, excepting type-B uncertainties, which could be important when considering the samples' dilution factors.

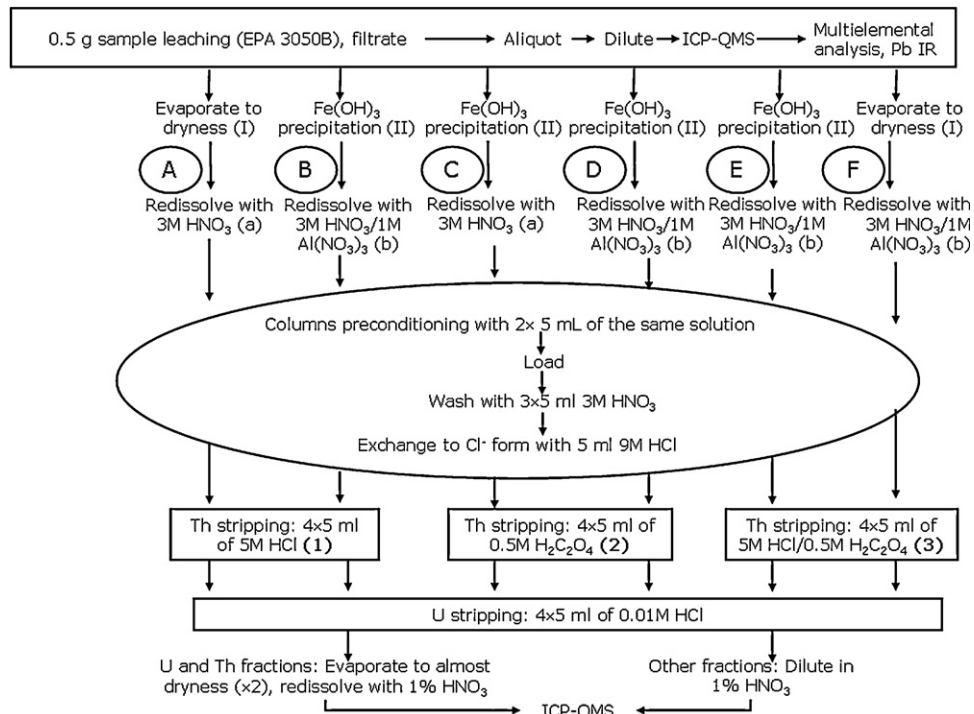


Fig. 2. Radiochemical combinations used in this work.

3. Results

The recoveries of U and Th were tested for different setups using the options described above (Table 2). According to their chemical yields and crossover, the most suitable setups (E and F) were selected. The differences of fractionation behaviour for U and Th depending on the nature of the sample were tested using sediment and PG samples (Figs. 3.1 and 3.2). Their performances were also analysed in terms of trace element fractionation (Table 3) and capacity of decontamination of interfering elements (Table 4). For the reasons explained below, the procedure E was chosen. It was validated for U, Th and IRs using sediment, phosphogypsum and phosphate rock samples previously submitted to intercomparison exercises or previously analysed by using conventional, well-established, radiometric methods in our research group (Table 5). The potential of the method to detect not only the levels of contamination, but also to deduce the source of the contamination, was

tested measuring environmental samples from the Huelva estuary. Results are provided in Table 6 (trace element concentrations) and Table 7 (U and Th activity concentrations and IRs) and Fig. 4 (Pb IRs).

4. Discussion

4.1. Chemical fractionation of Th and U

Setup A produced high recoveries for uranium but very low recoveries for thorium (Table 2), unlike other authors [32,35] that obtained good recoveries for thorium using setup A in coral (mainly calcium carbonate), uranite and MOX sample analyses. It was found that Th remained unstripped within the resin. The success of this method for Th measurement depends on the sample matrix. In this case the main components of our matrices, silicates and phosphates, might prevent the solubilisation of Th [37]. No significant

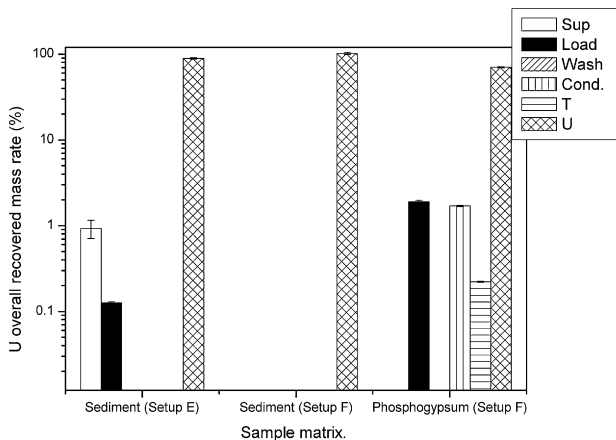


Fig. 3.1. U fractionation through the procedures described in the text as setups E and F. Sup: Supernatant. T: Th fraction. U: U fraction. Wash and Cond are the column eluates after washing the resin and conditioning it to the chloride form, respectively.

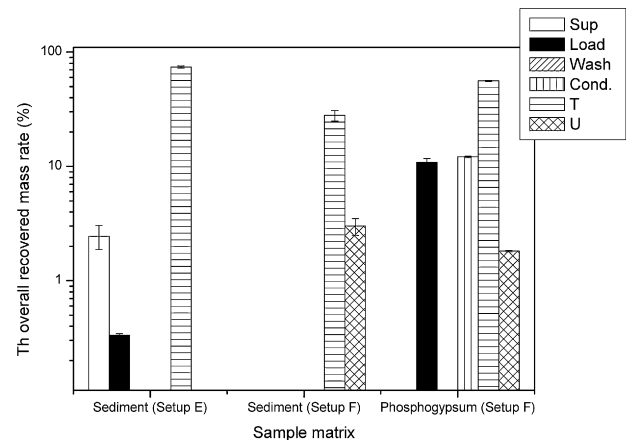


Fig. 3.2. Th fractionation through the procedures described in the text as setups E and F. Sup: Supernatant. T: Th fraction. U: U fraction. Wash and Cond are the column eluates after washing the resin and conditioning it to the chloride form, respectively.

**Table 2**  
Results (mass rates) obtained for U and Th in the fractions corresponding to uranium and thorium after application of setups A–F. Mass rates were calculated as described in the text. All the tests were applied to sediment samples except F\*, which is the setup F applied to PG samples. Setup A combines the options I + a + 1 shown in Fig. 2, setup B: II + b + 1, setup C: II + b + 2, setup D: II + b + 2; setup E: II + b + 3, setup F: I + b + 3. Phases U and T are stripping solutions for uranium and thorium, respectively. N.D.: not detected.

Phase/Setup	A (n=3)	B (n=3)	C (n=2)	D (n=2)	E (n=4)	F (n=4)	F* (n=4)
U in phase U (%)	98.2 ± 0.4	94.6 ± 0.9	74.2 ± 0.8	76 ± 2	89 ± 2	102 ± 3	70.1 ± 1.0
U in phase T (%)	3.7 ± 0.3	2.7 ± 0.4	2.77 ± 0.03	1.45 ± 0.03	N.D.	N.D.	N.D.
Th in phase U (%)	N.D.	N.D.	26.2 ± 0.3	42.0 ± 0.5	N.D.	3.0 ± 0.5	1.82 ± 0.03
Th in phase T (%)	6.59 ± 0.15	2.3 ± 0.6	44.4 ± 0.9	23.7 ± 0.4	74 ± 2	41 ± 3	56.1 ± 0.7

differences among setups A and B were detected: hydroxides precipitation did not introduce any difference in the performances of the resin. The results suggest that both setups are to be discarded. No higher HCl concentrations were tested as according to Kd published values [31], that could increase U recovery, but not Th recovery.

The application of setups C and D produced higher recoveries in Th than setups A and B but U recoveries decrease slightly. Thorium and uranium were not fully extracted from the column; furthermore, the application of this Th stripping procedure leads to a high crosstalk. U is extracted using low HCl concentration, where Kd-values of Th for UTEVA resins are low. Therefore, a certain amount of Th might remain unstripped within the resin bed, being eluted

during the uranium stripping. The higher the Th fraction retained in the resin, the higher the fraction leaking into the U fraction. The retained fraction is higher when Th linkage to the resin during the sample load is weaker (i.e., using 3 M HNO<sub>3</sub>, setup C, instead 1 M Al(NO<sub>3</sub>)<sub>3</sub>/3 M HNO<sub>3</sub>, setup D). No higher HCl molarities were tested as that could increase the uranium recoveries, but not thorium recoveries.

The method that best performs is setup E. Cross contamination is negligible and recoveries of both U and Th are high enough as to provide adequate concentrations for the determination of isotope ratios. However, this setup includes an actinide precipitation step, which increases sample preparation time in approximately 5–10%. In order to check if this step can be skipped, setup F was

**Table 3**  
Summary of elements fractionation (%) for sediment and phosphogypsum samples. 3 replicates were performed per test. The results are shown as weighted averages ± weighted uncertainty. Sup: Supernatant (after hydroxide precipitation, if any). Load: Elute obtained after loading U and Th in the resin. Wash and Cond. are the solutions collected after washing the resin and conditioning it to chloride form. N.D.: Not detected.

	Sup.	Load	Washing	Cond.	Th	U
Sediment (setup E)						
Mg	9.2 ± 0.9	85 ± 3	10.7 ± 0.4	0.39 ± 0.04	N.D.	N.D.
Ca	49.8 ± 1.8	37.1 ± 1.1	11.6 ± 0.2	N.D.	N.D.	N.D.
V	0.31 ± 0.04	96 ± 3	12.3 ± 0.4	0.61 ± 0.03	N.D.	0.013 ± 0.005
Cr	0.25 ± 0.04	99 ± 3	12.5 ± 0.4	0.63 ± 0.04	N.D.	N.D.
Mn	0.87 ± 0.06	74.5 ± 1.9	9.52 ± 0.25	0.425 ± 0.014	N.D.	N.D.
Co	40.1 ± 1.3	30.7 ± 1.0	4.07 ± 0.12	0.307 ± 0.009	N.D.	N.D.
Ni	98 ± 10	7.8 ± 0.9	0.3 ± 0.3	0 ± 3	N.D.	N.D.
Cu	86 ± 3	12.3 ± 0.4	1.65 ± 0.05	0.105 ± 0.004	N.D.	N.D.
Zn	52.8 ± 2.1	8.9 ± 0.3	0.86 ± 0.04	N.D.	N.D.	N.D.
As	0.78 ± 0.19	80.1 ± 2.3	10.1 ± 0.3	0.52 ± 0.04	N.D.	N.D.
Sr	53.5 ± 1.5	26.2 ± 0.7	3.51 ± 0.09	(48 ± 21) × 10 <sup>-3</sup>	N.D.	N.D.
Mo	48 ± 4	50 ± 3	8.4 ± 0.6	2.92 ± 0.16	N.D.	N.D.
Tl	70.1 ± 2.4	4.6 ± 0.6	12.1 ± 0.7	3.6 ± 0.7	4.3 ± 0.2	3.6 ± 0.3
Pb	0.36 ± 0.05	87.4 ± 1.8	11.67 ± 0.24	0.517 ± 0.011	N.D.	N.D.
Sediment (setup F)						
Mg	–	95 ± 23	12 ± 12	N.D.	N.D.	N.D.
Ca	–	82.6 ± 2.2	20.1 ± 5.5	N.D.	N.D.	N.D.
V	–	102.2 ± 1.4	15.32 ± 0.12	N.D.	N.D.	N.D.
Cr	–	102.9 ± 1.0	15.44 ± 0.15	1.8 ± 0.05	0.417 ± 0.013	0.264 ± 0.011
Mn	–	95.3 ± 1.3	15.95 ± 0.12	N.D.	N.D.	0.05 ± 0.03
Co	–	100.2 ± 1.4	15.44 ± 0.15	N.D.	N.D.	N.D.
Ni	–	103.3 ± 1.7	13.0 ± 0.17	N.D.	0.539 ± 0.022	0.209 ± 0.014
Cu	–	81.9 ± 1.4	13.44 ± 0.11	N.D.	5.5 ± 0.3	5.7 ± 0.9
Zn	–	77.1 ± 2.1	15 ± 8	N.D.	N.D.	N.D.
As	–	102.4 ± 1.5	15.75 ± 0.04	0.39 ± 0.08	N.D.	N.D.
Sr	–	68.2 ± 1.5	32 ± 4	N.D.	N.D.	N.D.
Mo	–	N.D.	N.D.	N.D.	9.22 ± 0.15	8.92 ± 0.12
Pb	–	105.4 ± 2.1	N.D.	N.D.	0.174 ± 0.004	N.D.
Tl	–	72.3 ± 2.2	16.6 ± 2.1	3.3 ± 0.6	5.33 ± 0.2	5.1 ± 0.3
Phosphogypsum (setup F)						
Mg	–	29.7 ± 1.7	0.047 ± 0.013	N.D.	N.D.	0.48 ± 0.08
V	–	72.7 ± 1.1	7.47 ± 0.18	7.1 ± 0.7	1.78 ± 0.20	0.869 ± 0.019
Cr	–	79.5 ± 1.7	5.20 ± 0.22	2.9 ± 0.3	N.D.	1.03 ± 0.06
Mn	–	59 ± 4	N.D.	14.3 ± 4.7	N.D.	N.D.
Co	–	89 ± 4	N.D.	8.94 ± 0.13	N.D.	1.033 ± 0.013
Ni	–	41.2 ± 0.7	0.59 ± 0.22	N.D.	N.D.	N.D.
Cu	–	94 ± 4	N.D.	9.9 ± 0.7	14.0 ± 0.8	6.86 ± 0.19
Zn	–	72 ± 3	3.41 ± 0.12	N.D.	2.40 ± 0.12	1.42 ± 0.11
As	–	90 ± 5	N.D.	6 ± 4	N.D.	N.D.
Sr	–	48.2 ± 0.5	3.73 ± 0.04	0.21 ± 0.09	0.043 ± 0.011	N.D.
Mo	–	0 ± 5	21.2 ± 1.1	19 ± 4	4.2 ± 1.0	30.3 ± 1.5
Tl	–	73.6 ± 3.8	13.6 ± 2.3	8.3 ± 0.8	3.32 ± 0.23	1.1 ± 0.4
Pb	–	99.8 ± 1.2	14.01 ± 0.23	6.3 ± 0.6	N.D.	3.84 ± 0.10

**Table 4**

Summary of interfering elements fractionation (%) for sediment and phosphogypsum samples. 3 replicates were performed per test. The results are shown as weighted averages  $\pm$  weighted uncertainty. Sup: Supernatant (after hydroxide precipitation, if any). Load: Elute obtained after loading U and Th in the resin. Wash and Cond. are the solutions collected after washing the resin and conditioning it to chloride form.

Phase	Supernatant	Load	Conditioning	Wash	Thorium	Uranium
Sediment (setup E)						
Cd	66 $\pm$ 2	13.9 $\pm$ 0.7	2.44 $\pm$ 0.12	N.D.	N.D.	N.D.
In	0.22 $\pm$ 0.05	84 $\pm$ 2	11.1 $\pm$ 0.4	0.41 $\pm$ 0.10	N.D.	N.D.
Sn	3.2 $\pm$ 0.3	85 $\pm$ 4	11.3 $\pm$ 0.5	N.D.	N.D.	N.D.
Pt	0 $\pm$ 0	20 $\pm$ 48	3 $\pm$ 6	N.D.	4 $\pm$ 2	7 $\pm$ 5
Sediment (setup F)						
Cd		88 $\pm$ 1	N.D.	N.D.	N.D.	N.D.
In		73 $\pm$ 7	12 $\pm$ 3	N.D.	1.4 $\pm$ 0.3	21 $\pm$ 2.3
Sn		52.0 $\pm$ 1.5	3.82 $\pm$ 0.16	N.D.	1.27 $\pm$ 0.06	2.2 $\pm$ 0.6
Pt		N.D.	N.D.	N.D.	N.D.	N.D.
Phosphogypsum (setup F)						
Cd		50.0 $\pm$ 1.4	4.44 $\pm$ 0.1	N.D.	0.611 $\pm$ 0.014	1.71 $\pm$ 0.03
In		64 $\pm$ 7	N.D.	N.D.	1.7 $\pm$ 0.3	20 $\pm$ 3
Sn		48.9 $\pm$ 1.2	1.83 $\pm$ 0.09	15.3 $\pm$ 0.9	1.13 $\pm$ 0.11	2.2 $\pm$ 0.6
Pt		44 $\pm$ 18	0.06 $\pm$ 0.12	14 $\pm$ 4	4 $\pm$ 3	2.5 $\pm$ 0.8

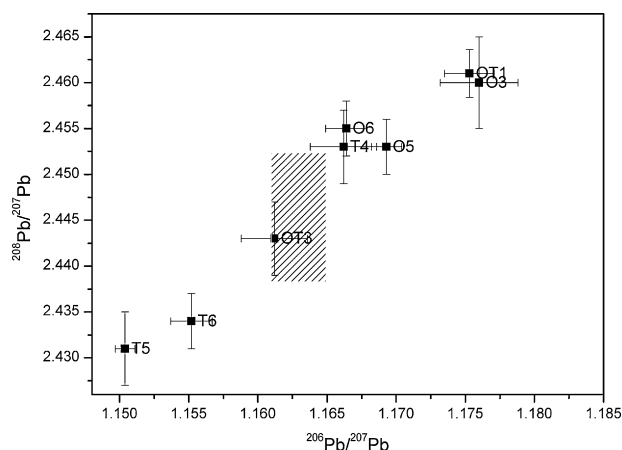
tested, avoiding the hydroxide precipitation step. In this case, the recoveries of Th were less than that for setup E.

Regarding the differences found for different sample matrices (Figs. 3.1 and 3.2), uranium recoveries were high for both matrices. Recoveries were some 10% higher when no precipitation was applied to sediment samples (no uranium was detected in the supernatant phase). The slight decrease for phosphogypsum samples is probably due to the high phosphates concentration in PG matrices. Phosphates act as complexing agents of uranium nitrate, preventing its adsorption to DP[PP] extractant matrix in the UTEVA resin despite the  $\text{Al}(\text{NO}_3)_3$  is added. This would explain the detection of uranium in both load and conditioning solutions.

The results for setups E and F show important differences for thorium. With no hydroxide precipitation in sediment samples, Th extraction recovery was greatly reduced, and crossover in the uranium fraction was observed. The results showed that during the application of setup F, thorium was weakly adsorbed to resin. That process leads to important losses of thorium during the steps of sample loading, resin washing and others when PG was processed. Therefore procedure F cannot be fully recommended.

#### 4.2. Chemical fractionation of trace elements

As shown in Table 3, most of all the elements show the same behaviour regardless their geochemistry (lithophile, siderophile, chalcophile), the applied setup (E or F) or the matrix sample. Pb



**Fig. 4.** Stable lead isotope ratios found in the sediment sample leachates analysed in this work. Shaded zone marks the signature values corresponding to galena and pyrite samples from the Iberian Pyrite Belt according to Pomiés et al. [40].

follows loading solution, hence in this case adapting the sample before isotopic analysis is very simple. The largest fraction of the other elements is lost during the solution loading into the column and the subsequent washing of the resin. However, several exceptions might appear.

A higher fraction of Ca, Sr, Co, Ni, Cu, Zn and Tl remains in the supernatant fraction when the actinide precipitation is applied. The removal of Ca is especially important for the determination of Th and U isotopes by ICP-QMS since a very high Ca concentration in the aspirated solution leads to a drastic decrease of instrumental response to actinides [36]. It might be especially important for PG samples, since Ca is approximately 20% of the total sample mass. Thus the application of a previous precipitation step is recommended as a way to better purify U and Th fractions.

If a high Tl concentration was present in a sample, Tl hydrides could interfere in  $^{206}\text{Pb}$  count rates in the first leaching filtrate. When Tl concentration (either naturally present in the sample or spiked) is similar to Pb concentration, it could be alternatively used for internal mass bias correction. Therefore, this element fractionation should be kept in mind, and it is found again that the application of the hydroxides precipitation is a good method of sample purification. In case that high Tl concentration was found in the leaching filtrate, lead isotope ratios could alternatively be measured in the precipitate, once a large proportion of Tl is removed.

Small fractions of Ti, Cr and Zn were detected in U and Th eluates. Besides, small fractions of Tl, Mn, Fe, Cu and Pb can also be sometimes detected in uranium eluates. Such fractions do not cause counting interferences in U and/or Th measurements. Furthermore, they were detected mainly in the eluates produced after application of setup F to PG samples but not if the iron hydroxide precipitation is applied (Method E).

Interfering elements Os, Au and Hg were not detected in any of the analysed phases. This is due to the combination of a small concentration in the sediment sample and the application of a high dilution factor for ICP-QMS measurement. By monitoring the U/Th fractions, it was found that their counting rates were below those achieved for  $^{234}\text{U}$  and  $^{230}\text{Th}$  isotopes by even more than one order of magnitude. As a result, the expected count rate contribution of Os, Au and Hg derived argides to total count rates on masses 230 and 234 were negligible.

Cd, In, Sn and Pt (Table 4) were detected in some of the elutions from the radiochemical setup. On the contrary to Os, Hg and Au, the complete mass balance can be established for the three first elements (not for Pt due to very low concentrations), as the analysed solutions contained 90–100% of masses introduced during the leaching. The removal of a large fraction of Cd can be achieved through the previous precipitation step with iron hydroxide (setup

**Table 5**  
Results obtained in the samples used for validation of the technique described in the text. CSN: Recommended values. N.M.: Not measured. Activity concentration is expressed in Bq kg<sup>-1</sup>. Isotope ratios are expressed as activity ratios.

Sample	<sup>238</sup> U (α)	<sup>238</sup> U (ICP)	<sup>238</sup> U/ <sup>234</sup> U (α)	<sup>238</sup> U/ <sup>234</sup> U (ICP)	<sup>232</sup> Th (α)	<sup>232</sup> Th (ICP)	<sup>232</sup> Th/ <sup>230</sup> Th (α)	<sup>232</sup> Th/ <sup>230</sup> Th (ICP)
F10, phosphate rock	694 ± 11	637 ± 9	0.999 ± 0.016	1.003 ± 0.011	11 ± 1	7.70 ± 0.24	0.0234 ± 0.0022	0.0204 ± 0.0010
CSN (phosphogypsum)	55.0 ± 1.7	57.2 ± 1.0	0.98 ± 0.03	0.949 ± 0.004	6.1 ± 0.1	3.80 ± 0.06	0.0184 ± 0.0005	0.0192 ± 0.0006
T5 (sediment)	308 ± 7	297 ± 3	0.93 ± 0.03	0.919 ± 0.006	N.M.	24.3 ± 0.4	N.M.	0.130 ± 0.003
OT1 (sediment)	N.M.	90.0 ± 0.8	N.M.	0.882 ± 0.022	30.1 ± 1.1	26.0 ± 0.3	0.304 ± 0.014	0.303 ± 0.010

**Table 6**  
Results obtained in the phosphogypsum and sediment leachates analysed in this work. The sediment samples were collected at Odiel river ("O" samples), Tinto river ("T" samples) and at the confluence of both rivers ("OT" samples). Samples F06, F17, F18 and CSN are phosphogypsum samples, while F10 is a phosphate rock sample.

Sample	Cr (μg g <sup>-1</sup> )	Ca (%)	Mn (μg g <sup>-1</sup> )	Ni (μg g <sup>-1</sup> )	Cu (μg g <sup>-1</sup> )	Zn (μg g <sup>-1</sup> )	As (μg g <sup>-1</sup> )	Sr (μg g <sup>-1</sup> )	Cd (μg g <sup>-1</sup> )	Pb (μg g <sup>-1</sup> )
O3	53.8 ± 1.1	1.21 ± 0.09	264 ± 5	27.0 ± 0.6	1328 ± 11	1163 ± 10	364 ± 3	121.0 ± 1.6	3.72 ± 0.04	399.8 ± 2.7
O5	81.8 ± 1.6	4.1 ± 0.6	275 ± 5	23.6 ± 0.9	1718 ± 25	1844 ± 32	386 ± 7	277 ± 5	7.05 ± 0.10	601 ± 6.26
O6	105 ± 9	5.9 ± 0.9	241 ± 22	23.6 ± 2.2	3056 ± 276	4547 ± 408	964 ± 87	481 ± 43	18.1 ± 1.6	1284 ± 115
T4	16.6 ± 0.4	1.03 ± 0.08	67.0 ± 1.2	9.2 ± 0.5	756 ± 17	406 ± 9	299 ± 4	51.3 ± 1.7	2.46 ± 0.08	365 ± 12
T5	52.5 ± 1.0	3.20 ± 0.19	158 ± 4	19.0 ± 0.4	1940 ± 20	1647 ± 19	1082 ± 15	406 ± 4	6.16 ± 0.13	1363 ± 10
T6	91.1 ± 1.9	6.13 ± 0.7	207 ± 4	23.7 ± 0.4	24815 ± 37	2414 ± 36	1228 ± 22	546 ± 14	12.37 ± 0.17	2105 ± 21
OT1	53.1 ± 0.8	1.98 ± 0.14	377 ± 3	27.6 ± 0.3	1643 ± 18	1558 ± 17	393 ± 4	158.8 ± 1.9	1.88 ± 0.07	568 ± 7
OT3	22.56 ± 0.20	4.37 ± 0.12	174.8 ± 2.2	9.9 ± 0.4	316 ± 6	435 ± 10	78.7 ± 1.5	395 ± 6	0.77 ± 0.06	110.2 ± 1.9
F06	30.9 ± 0.4	N.M.	0.83 ± 0.03	1.24 ± 0.06	7.0 ± 0.6	18.4 ± 0.7	18.7 ± 0.4	555 ± 6	2.66 ± 0.06	4.37 ± 0.05
F10	90.1 ± 1.4	N.M.	37.1 ± 0.8	6.94 ± 0.11	9.96 ± 0.22	87.5 ± 1.5	15.1 ± 0.3	348 ± 4	37.1 ± 0.7	3.50 ± 0.17
F17	15.72 ± 0.16	N.M.	0.80 ± 0.06	2.07 ± 0.21	6.50 ± 0.13	39.5 ± 0.7	8.3 ± 0.3	574 ± 5	2.78 ± 0.06	2.51 ± 0.12
F18	11.19 ± 0.16	N.M.	1.00 ± 0.03	0.53 ± 0.12	3.75 ± 0.05	29.7 ± 0.5	1.79 ± 0.06	573 ± 7	1.99 ± 0.12	7.7 ± 0.16
CSN	21.1 ± 0.4	N.M.	1.48 ± 0.11	41.2 ± 0.6	4.98 ± 0.07	14.78 ± 0.25	1.92 ± 0.11	549 ± 5	2.34 ± 0.04	6.51 ± 0.07

**Table 7**

Results obtained in the sediment, phosphogypsum (PG) and phosphate rock (PR) samples used in this work. Isotope ratios are expressed as activity ratios.

Sample	$^{238}\text{U}$ (Bq kg $^{-1}$ )	$^{238}\text{U}/^{234}\text{U}$	$^{232}\text{Th}$ (Bq kg $^{-1}$ )	$^{232}\text{Th}/^{230}\text{Th}$
O3	138.7 ± 0.9	0.894 ± 0.011	26.6 ± 1.1	0.184 ± 0.007
O5	320 ± 5	0.934 ± 0.006	36.0 ± 0.9	0.0829 ± 0.0011
O6	482 ± 43	0.941 ± 0.009	81 ± 7	0.1260 ± 0.0017
T3	129 ± 2	0.919 ± 0.021	15.75 ± 0.16	0.486 ± 0.016
T4	53.4 ± 1.5	0.871 ± 0.007	9.39 ± 0.19	0.397 ± 0.008
T6	476 ± 6	0.941 ± 0.005	31.2 ± 0.5	0.130 ± 0.003
OT3	36.2 ± 0.8	0.96 ± 0.03	7.77 ± 0.04	0.204 ± 0.003
F06 (PG)	611 ± 14	0.970 ± 0.006	11.8 ± 0.3	0.01152 ± 0.00020
F10 (PR)	637 ± 9	1.003 ± 0.011	7.70 ± 0.24	0.0204 ± 0.0010
F17 (PG)	250 ± 3	0.962 ± 0.009	14.6 ± 0.3	0.0212 ± 0.0004
F18 (PG)	189 ± 3	0.960 ± 0.015	13.28 ± 0.12	0.0186 ± 0.0005
CSN (PG)	57.2 ± 1.0	0.949 ± 0.004	3.80 ± 0.06	0.0192 ± 0.0006

E). On the contrary, In and Sn remain mainly in the precipitate. However, a large fraction of these elements followed the loading and the washing solution and were not retained by the resin.

Indium small mass rates remained in the Th fractions when no actinide precipitation was applied. The In initial concentration present in the sample was already small, hence the expected counting rate associated to  $^{230}\text{Th}$  is several orders of magnitude higher than those due to In and no important interferences are expected. Relatively large fractions (~20%) remain in the uranium phase, however In dimers do not overlap uranium isotopes.

Finally, the fraction of Sn lost during the loading into the column is significantly higher when the precipitation is applied. A small but measurable amount remains in the uranium fraction when no precipitation is applied.

It can be concluded that the procedure E allows Pb isotopic analysis after a convenient Tl removal (if required), being dilution factors near 2000 mL g $^{-1}$  for Pb and approximately 20 000 mL g $^{-1}$  for Tl in case lead is analysed in loading solution instead of the diluted leachate. In both cases RSD values in the range of 0.3% were achieved in the corresponding isotope ratios.

Setup E was therefore chosen as the most suitable method and was used for the rest of this work. For a set of 5–10 samples, the application of this method consumes in the range of 2–2.5 working days at the laboratory, and additionally some 20 min per sample are required for isotope ratio analysis, which is thus convenient when compared to the approximately 2–3 days of counting time required for alpha particle spectrometry.

#### 4.3. Validation of the technique

Table 5 shows the results obtained for several PR, PG and sediment samples used for validation as described in Section 3. Concentrations obtained using setup E + ICP-MS were in agreement within the uncertainties to the results obtained by alpha spectrometry. Isotope ratios were in good agreement within a  $1 - \sigma$  confidence interval after calculation of A-type expanded uncertainties according to GUM approach.

Uncertainties for uranium and thorium isotope ratios are within the ranges 0.6–2.5% and 2.3–5% respectively. They are comparable to or slightly better than those obtained by alpha spectrometry, which are within a range 1.6–3% for uranium isotope ratios and within a range 4–8% for thorium isotope ratios. These results show the potential for the application of this methodology to NORM samples.

Regarding major isotope activity concentrations, those obtained by ICP-MS are less than or equal to those obtained by alpha spectrometry, as expected, bearing in mind that no chemical yield tracer was applied during the radiochemical separation.

#### 4.4. Application to environmental samples

The results for Cr, Mn, Ni, Cu, Zn, As, Cd and Pb (Table 6) are in good agreement with previously published values for this area [16,38]. These results reflect the effect of the mining activity on the estuarine sediments, being the concentration levels of some elements (Cu, Zn, As, Pb) systematically higher than “Effects Range-Median” (ERM) levels of sediment quality guidelines provided in [39]. Cd and Ni levels are also above ERM values in several samples, and systematically higher than “Effect-Range-Low” (ERL) values.

PG and PR samples are not affected by acid mine drainage (AMD). Almost all the concentrations of elements in PR were below the concentrations found in unpolluted sediments, excepting for the radioisotopes from  $^{238}\text{U}$ -Series and Cd. Trace element concentrations in PG are below natural background values in the area, being the only exceptions Ca (matrix element in the PG) and Sr due to its geochemical similarity to Ca. Mn concentrations in PG, which are several orders of magnitude below the values in PR, suggest that Mn is probably associated to the P $_2$ O $_5$  fraction during the industrial process.

The results of Table 7 for uranium isotope ratios are in good agreement with those found in [6,26]. These values are for sediment samples statistically significantly less than 1.0. The values here found for  $^{232}\text{Th}/^{230}\text{Th}$  isotope ratios are below those found by Bolivar et al. [6] by a factor ~2. Isotope ratios in the range of  $\sim 0.7 \pm 0.2$  could be considered as almost representative values of unpolluted sediments in this area [8]. The other samples showed thorium isotope ratios that range 0.06–0.13, whereas the values in PG range 0.012–0.018. Those samples having low Th IR values are reflecting the mixing of the isotopic signals due to natural processes and that other associated to industrial activities (see below for details).

The low concentration and the large dilution factor used did not allow the determination of the Pb isotope ratios in phosphogypsum samples. For sediment samples, a good correlation among  $^{208}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{207}\text{Pb}$  was found ( $r = 0.9762$ , significance better than 0.01%). It is worth to mention a few important facts: the values are scattered around the characteristic fingerprint values published for the Iberian Pyrite Belt IPB [40], which pyrite and galena ore deposits are expected to be the main contributors to the lead accumulated in the sediments. The significant deviations from the IPB characteristic values indicate the mixing with additional sources such as emissions from road traffic and coal burning in the surrounding industry [3].

The final aim of the methodology proposed is to evaluate the degree and origin of contamination in samples. The possibility of using our multiple IR data for categorisation of data has been explored by a cluster analysis using the sediment sample results.  $^{208}\text{Pb}/^{207}\text{Pb}$  IR has been not included due to its linear dependence with  $^{206}\text{Pb}/^{207}\text{Pb}$  IR. Fig. 5 shows the dendrogram allowing



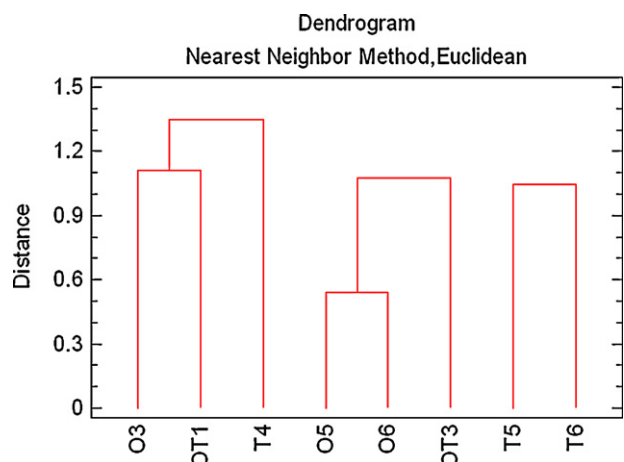


Fig. 5. Dendrogram obtained after cluster analysis of the isotope ratios collected for the sediment samples described in the text.

the identification of three large groups of samples according to their respective IRs: (1) high Th IRs (0.184–0.397), high  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios (1.1662–1.1760) and low U IRs (0.871–0.894), (2) intermediate Th IRs (0.0829–0.204),  $^{206}\text{Pb}/^{207}\text{Pb}$  close to IPB signature and high U IRs (0.934–0.959), (3) low to intermediate Th IRs (0.06–0.13), low  $^{206}\text{Pb}/^{207}\text{Pb}$  IRs (1.1504–1.1552) and intermediate U IRs (0.919–0.941). The third group associates to mixing of sediments suffering a large entrance from road pollution and liquid discharges from fertiliser plants. The second group corresponds to samples showing a large AMD signal mixed with settling sediment from Odiel river previously affected by fertiliser factories. The first group of samples comprises samples having less intense pollution from fertiliser factories and great impact of additional sources of lead: the effect of runoffs from soil cannot be discarded. The distinctive signals that we are able to detect and identify, combining IR measurements and a cluster analysis, highlight the good performances of our technique to evaluate contamination patterns.

## 5. Summary and conclusions

Different methods have been tested and tuned for the characterisation of trace element concentrations and lead, uranium and thorium isotope ratios from a same sample aliquot using ICP-QMS. According to the results found for U and Th recoveries, cross contamination and the presence of potential spectrometric interferences, setup E was chosen. This procedure allows recoveries for U and Th nearly 90% and 75%, respectively being their respective fractions of purity enough as to provide accurate and precise results. The application of this methodology to environmental samples from a quite polluted scenario shows the potential to collect information on the extension and the origin of pollution on a routine basis and using an only conventional instrument (ICP-QMS). This fact leads to simplify laboratory requirements and management.

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