



DESENVOLUPAMENT DE TÈCNIQUES ANALÍTIQUES PER A LA DETERMINACIÓ DE RADIONÚCLIDS

Montserrat Mola Arques

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TESI DOCTORAL

Dirigida per

Dr. Francesc Borrull i Dra. Carme Aguilar

Departament de Química Analítica i Química Orgànica



UNIVERSITAT ROVIRA I VIRGILI

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2013

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UNIVERSITAT ROVIRA I VIRGILI
Departament de Química Analítica
i Química Orgànica

El Dr. FRANCESC BORRULL BALLARÍN, Catedràtic del Departament de Química Analítica i Química Orgànica de la Facultat de Química de la Universitat Rovira i Virgili, i

La Dra. CARME AGUILAR ANGUERA, Professora Agregada del Departament de Química Analítica i Química Orgànica de la Facultat de Química de la Universitat Rovira i Virgili,

FEM CONSTAR:

Que la present Tesi Doctoral, que porta per títol: “DESENVOLUPAMENT DE TÈCNiques ANALÍTiques PER A LA DETERMINACIÓ DE RADIONÚCLIDS”, presentada per MONTSERRAT MOLA ARQUES per optar al grau de Doctor per la Universitat Rovira i Virgili, ha estat realitzada sota la nostra direcció, a l’Àrea de Química Analítica del Departament de Química Analítica i Química Orgànica d’aquesta universitat, i que tots els resultats presentats són fruit d’experiències realitzades per l’esmentada doctoranda.

Tarragona, 20 de juny de 2013.

Dr. Francesc Borrull Ballarín

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A Rosalia

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A totes aquelles persones que m'han ajudat d'una forma o d'una altra a realitzar aquesta tesi o com a mi m'agrada pensar "gran aventura evolutiva". Tothom qui em coneix sap que sóc molt sincera, així que en aquestes línies seré més sentimental i menys professional per tal d'explicar el que sento.

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1. INTRODUCCIÓ

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Durant els últims anys, molts científics han mostrat a través dels seus estudis els riscos que hi ha associats a la presència de radionúclids en el medi ambient [1-3]. En general, aquests científics s'han centrat en el desenvolupament de nous mètodes analítics per a quantificar els diferents radionúclids individuals que contenen les diferents mostres i estudiar la procedència i comportament d'aquests dins del medi ambient.

Tot i que hi ha un elevat nombre de publicacions que estudien la radioactivitat en mostres ambientals, també cal remarcar que es continua investigant la determinació de radionúclids individuals ja que comporta compostos que interfereixen en la detecció. Per assolir aquest objectiu s'han desenvolupat mètodes que involucren diferents etapes de tractament de mostra, anomenades globalment processos radioquímics. En aquests, hi ha diferents etapes com la digestió, la preconcentració, la separació i extracció dels radionúclids d'interès i la preparació de la font a mesurar.

Aquesta tesi doctoral ha estat realitzada en el laboratori de la Unitat de Radioquímica Ambiental i Sanitària (URAI), integrat dins del Servei de Recursos Científics i Tècnics de la Universitat Rovira i Virgili i la seva direcció recau en el Grup de Cromatografia i Aplicacions Mediambientals, d'aquesta mateixa universitat. Aquesta tesi és una continuació de la línia establerta amb una primera tesi doctoral realitzada per la Dra. Marta Palomo, que es va basar en l'estudi de la radioactivitat ambiental. Aprofundint en alguns aspectes, com ara el desenvolupament d'una sèrie de mètodes de cara a la determinació de diferents radionúclids i basant-nos amb les primeres trobades d'aquesta primera tesi de radioactivitat, en mostres de fangs de l'ETAP i mostres sòlides i d'aigua del riu Ebre, s'ha plantejat la present tesi. En la qual trobem un aspecte estudiat més detalladament, com la problemàtica actual de la detecció i classificació d'indústries *naturally occurring materials* (NORM) que generen a partir de matèries primeres, productes i/o residus amb alts continguts de radionúclids. Aquesta tesi ha tractat aquestes dues temàtiques principals i els estudis s'han ubicat en la conca del riu Ebre, on trobem diverses activitats industrials que aporten radionúclids al medi.

1.1. La conca del riu Ebre

La conca del riu Ebre es troba a la vessant nord-est de la Península Ibèrica. Aquesta té una longitud aproximada d'uns 910 Km amb més de 200 afluents i una conca hidrogràfica de 85000 Km² aproximadament, des del naixement situat en la comunitat autònoma de Cantàbria (a Reïnosa) fins la desembocadura del riu en el Delta de l'Ebre (Catalunya) (Figura 1.1.). D'aquesta manera l'Ebre esdevé un dels rius més cabalosos d'Espanya amb un cabal mitjà de 729 m³ s⁻¹, 933 m³ s⁻¹ i 926 m³ s⁻¹ a Saragossa, Ascó i Tortosa, respectivament, durant el mes d'abril del 2013 (vist en el SAIHEbro).

Dintre de la conca trobem diversos embassaments situats estratègicament per a controlar les reserves d'aigua segons les necessitats de la població, generar explotació hidroelèctrica i protegir les zones geogràfiques properes, de les crescudes del riu. Hi trobem un total de 20 embassaments i/o assuts, on els principals a destacar de nord a sud en són quatre, l'embassament de l'Ebre (541 hm³), el de Mequinensa (1530 hm³), el de Riba-Roja (209.5 hm³) i el de Flix (4.2 hm³).

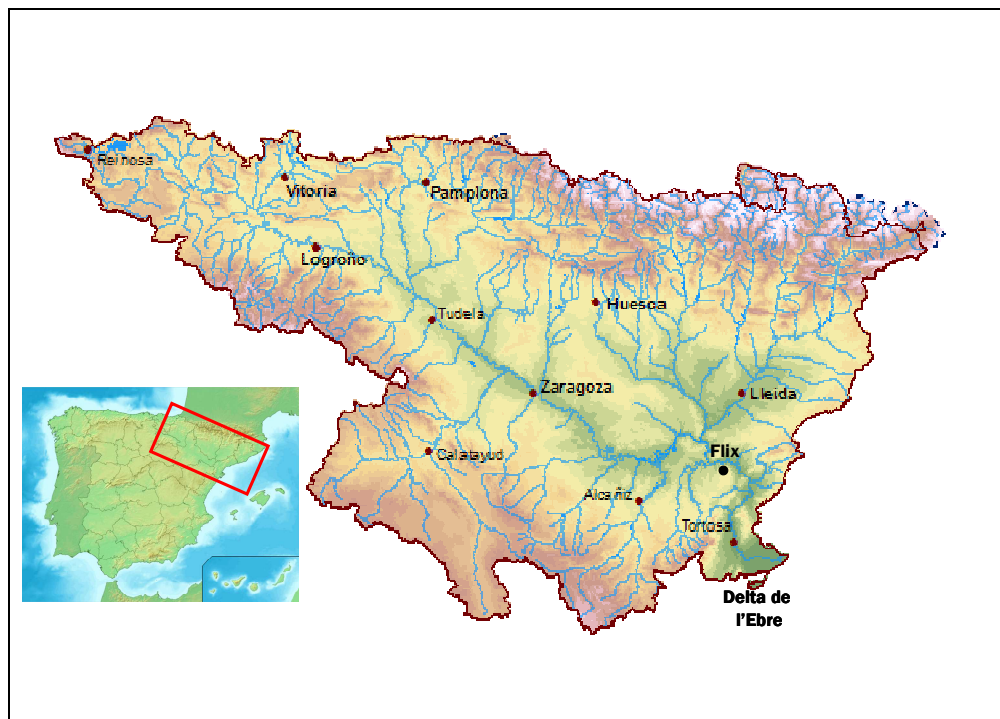


Figura 1.1. Representació de la conca de l'Ebre i les seves subconques hidrogràfiques. Font: *Confederación Hidrográfica del Ebro* (<http://www.chebro.es>)

1.1.1. Industrialització en la conca del riu Ebre

Tal i com es mostra en la Figura 1.2. en el riu Ebre hi ha un gran consum antropogènic de l'aigua per part de diversos sectors. Com podem veure, l'ús industrial que engloba els 470 Hm³ any⁻¹ d'indústria no nuclear i els 3354 Hm³ any⁻¹ de la refrigeració de les centrals nuclears és un dels sectors més importants en quant a consum. Cal destacar que les activitats industrials localitzades en la conca de l'Ebre estan basades principalment amb la producció energètica mitjançant 340 centrals hidroelèctriques, 3 centrals tèrmiques de carbó, 3 centrals tèrmiques de gas, 200 parcs eòlics i 2 centrals nuclears amb un total de tres reactors, el de la Central Nuclear Santa Maria de Garoña i els dos de la Central Nuclear d'Ascó [4].

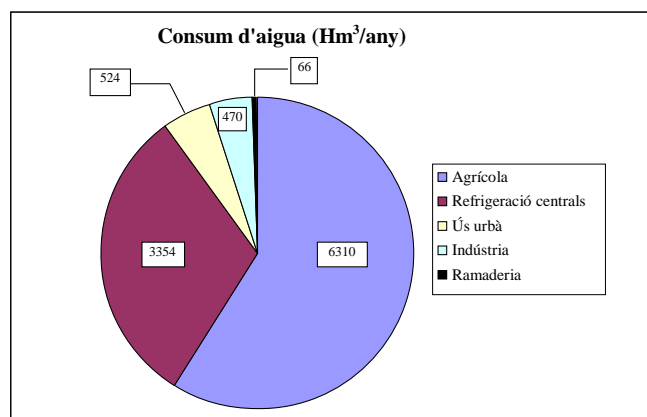


Figura 1.2. Consum d'aigua del riu Ebre en els principals sectors

A banda d'aquest tipus d'indústria hi trobem indústries del sector químic, el metal·lúrgic, l'alimentari, d'aqüicultura, automobilístic, etc. Per exemple, podem destacar Miranda d'Ebre o Flix com a punts de la conca de l'Ebre on l'aigua del riu s'utilitza en nombrosos usos industrials. El municipi de Flix (Ribera d'Ebre) té uns 4.000 habitants (any 2009) i una extensió de 117 Km² i 6.070 ha [5], i el principal motor econòmic de la zona és i sobretot ha estat la indústria Electroquímica de Flix S. A. instal·lada a la riba dreta de l'embassament [6].

Donat que l'activitat industrial de la zona pot tenir un impacte sobre el medi és necessari avaluar i tenir un control sobre la qualitat de l'aigua, mitjançant diverses analítiques d'aigua, del sòl i la vegetació de les ribes, l'estudi d'organismes vius, etc. En el següent apartat destacarem diferents estudis realitzats en mostres biològiques on es podrà veure l'efecte bioindicador.

1.1.2. Bioindicadors de l'aigua

Respecte a les analítiques de l'aigua d'un riu una altra forma de garantir la qualitat de l'aigua és observant i analitzant els éssers vius que habiten en el medi estudiat. És a dir, fer ús dels indicadors biològics de l'estat de l'aigua, controlant la seva composició i abundància aquàtica. Per aquest motiu, a Europa es van començar a utilitzar mostres biològiques com ara les algues, els peixos, els bivalves, entre altres, per a la vigilància de la qualitat de les aigües en l'àmbit d'aplicació de diferents directives com ara la directiva marc de l'aigua (DMA) 2000/60/CE [7] i la directiva de tractament d'aigües urbanes residuals (91/271/EEC) [8]. Tenint en compte que nosaltres ens ubicarem en aquesta zona concreta de la conca del riu Ebre, hem de veure les diferents espècies autòctones i invasores que habiten al llarg de la seva xarxa hidrogràfica.

La proliferació d'algues hidròfites, és a dir plantes aquàtiques, en algunes zones és molt abundant i es poden trobar diversos tipus formant bancs. La *Potamogeton*

pectinatus, la *Cladophora glomerata*, la *Lemma minor*, el *Myriophyllum spicatum* i la *Ceratophyllum demersum* en són un clar exemple, i les trobem a la superfície de l'aigua del riu, bé estiguin arrelades al substrat o flotant.

En relació a la ictiofauna (peixos) de la conca de l'Ebre, aquesta compta amb 15 espècies autòctones com ara la truita comú, el llop de riu o la tenca i 15 espècies exòtiques introduïdes per l'home com ara el silur, la carpa, la perca americana [9]. D'aquestes últimes espècies es pot destacar el silur com a espècie invasora i cal remarcar que en aquests últims anys ha augmentat considerablement la seva població en la conca del riu Ebre. Aquest va ser introduït en el pantà de Mequinensa l'any 1977 per pescadors esportius i està provocant problemes ecològics per la seva voracitat.

Els bivalves constitueixen un grup important dels ecosistemes aquàtics pel seu paper com a organismes filtrants i per representar un recurs tròfic important per a altres animals. En la conca s'han trobat tres famílies autòctones de bivalves (*Sphaeriidae*, *Unionidae* i *Margaritiferidae*) i dos que són invasores (*Corbiculidae* i *Dreissenidae*). Les famílies invasores tenen un gran poder de colonització, les dues creixen en enormes colònies que poden tapar conductes de reg, etc. [10]. D'aquestes últimes, destaquem el musclo zebra (*Dreissena polymorpha*, Figura 1.3.), ja que està considerat com una de les 100 espècies invasores més perjudicials del planeta pel seu impacte ambiental i econòmic [11]. A Catalunya, se'n van detectar poblacions importants l'any 2001 als embassaments de Riba-Roja i Flix i des d'allà aquesta espècie s'ha anat dispersant al llarg de l'Ebre.



Figura 1.3. Exemples de musclo zebra (*Dreissena polymorpha*)

Aquestes espècies de biota que es troben en el medi aquàtic, estan directament en contacte amb radionúclids d'origens diversos que estan dissolts en l'aigua. Hi ha estudis actuals que mostren el contingut de radionúclids en mostres de biota, principalment els radionúclids naturals descendents de la cadena de ^{238}U i d'antropogènics com per exemple el ^{137}Cs [12-15], i els resultats d'aquests estudis fan palesa la capacitat d'absorbir i acumular radionúclids per part d'aquests organismes. Per això, també hi ha diversos treballs on s'han utilitzat les mostres de biota com a bioindicadors de possibles contaminacions radiològiques en zones afectades per

indústries. Destacant en aquesta tesi les indústries que contribueixen a augmentar els nivells de radionúclids naturals en l'entorn com la indústria metal·lúrgica, la del fosfat, la petroquímica i l'explotació minera [2,16-20].

En la conca del riu Ebre, en concret en l'últim tram abans de la seva desembocadura al mar Mediterrani, trobem a mode d'exemple el treball realitzat per Nadal i col. [2] centrat en determinar el ^{210}Pb i el ^{210}Po en diferents tipus d'aliments com ara arròs, peix, marisc, vegetals i fruites. Les concentracions mitjanes trobades de ^{210}Pb i ^{210}Po van estar entre 6 i 237 Bq kg⁻¹ en el cas del peix i el marisc i de 0.1 a 2.3 Bq kg⁻¹ en el cas de l'arròs, fruites i vegetals. Per tant, la major absorció de radionúclids es va veure en les diverses espècies aquàtiques de peix i marisc (mol·lusc, anxova, sardina, etc.), capturats en els voltants del Delta de l'Ebre en el mar Mediterrani. Un altre exemple centrat en la mateixa zona és l'estudi realitzat per Palomo i col. [20] que mostra les activitats de diversos radionúclids artificials i naturals determinats en dos tipus d'algues aquàtiques (*Cladophora glomerata* i *Cynodon dactylon*) localitzades en la conca del riu Ebre. Les majors activitats van ser trobades en l'espècie de la *Cladophora* en l'embassament de Flix (105 ± 43 Bq kg⁻¹ de ^{214}Bi i 100 ± 58 Bq kg⁻¹ de ^{214}Pb), una zona influenciada per la indústria de fosfat dicàlcic. En global aquests treballs ens mostren que els radionúclids dissolts a l'aigua estan en contacte i poden ser incorporats a les espècies aquàtiques i llavors depenent de l'espècie i classe de biota apareixen diferents capacitats d'assimilació i retenció dels diferents radionúclids.

Són pocs els estudis de biota realitzats en la zona de la conca del riu Ebre, per això a continuació es mostraran altres exemples d'estudis similars que s'han realitzat en altres indrets del món. Per exemple, Carvalho i col. [12] varen comparar les concentracions de radionúclids naturals (^{40}K , ^{226}Ra , ^{210}Po , ^{210}Pb) i altres d'origen antropogènic com el ^{137}Cs i radionúclids de plutoni (^{238}Pu i $^{239+240}\text{Pu}$), trobades en diferents espècies de peixos comercials del nord de l'Atlàntic (peix-vermell, tauró, bacallà i mero). Els radionúclids màxims contribuents a la radiació van ser el ^{210}Po (entre 0.03 i 5.5 Bq kg⁻¹) i el ^{40}K (entre 0.10 i 0.15 Bq kg⁻¹), amb una contribució molt petita dels antropogènics. A més també varen analitzar espècies de peixos abissals i mol·luscs, mesurant concentracions molt similars a les de les espècies costaneres respecte del ^{210}Po . Si comparem les concentracions de ^{210}Po obtingudes en aquest treball amb les obtingudes en el treball de Nadal i col., observem activitats molt superiors en el cas de l'anàlisi de peixos en les mostres recollides en l'últim tram del riu Ebre. Aquesta zona situada al final de la conca del riu Ebre, tal com hem explicat anteriorment, rep influència de diverses activitats industrials.

També es pot destacar un treball publicat aquest any 2013 per Khandaker i col. [16] en què, en una zona costanera rica en activitats industrials petroquímiques i de metalls es van mesurar diversos radionúclids naturals en crustacis (cranc) i mol·luscs ("Kerang") que formen part de la dieta de Malàsia. Les activitats obtingudes per al mol·lusc van ser de 5.34±0.52 Bq kg⁻¹, 2.44±0.21 Bq kg⁻¹, 281±0.52 Bq kg⁻¹, per al ^{238}U (^{226}Ra), ^{232}Th (^{228}Ra) i ^{40}K , respectivament. També es van obtenir resultats molt

similars en el cas dels crustacis. En un altre estudi amb el mostreig localitzat en una zona sense influència industrial a Golden Horn (Turquia), les activitats màximes trobades en l'espècie de mol·lusc anomenada *Mytillus* van ser molt semblants a l'estudi anterior en el cas del ^{232}Th (3.6 Bq kg^{-1}), ara bé en el cas del ^{238}U van ser inferiors al límit de detecció ($<1.4 \text{ Bq kg}^{-1}$) [13]. Aquest fet mostra la capacitat bioindicadora que tenen aquestes espècies de mol·luscs front les activitats antropogèniques existents en el medi ambient.

En general podem dir que és evident l'absorció i acumulació de radionúclids en espècies de biota. Aquest fet, ens mostra diferents concentracions de radionúclids trobades entre zones industrialitzades o no. Per tant, és recomanable realitzar un control i avaluació d'algunes espècies dintre del medi, tant en zones influenciades per activitats antropogèniques com les que no, per tal de localitzar possibles accidents o augments d'activitats que poden ser nocives per als éssers vius.

1.2. Indústria NORM

UNIVERSITAT ROVIRA I VIRGILI
DESENVOLUPAMENT DE TÈCNiques ANALÍTIQUES PER A LA DETERMINACIÓ DE RADIONÚCLIDS
Montserrat Mola Arques
Dipòsit Legal: T.1294-2013

Tal i com hem presentat en el capítol anterior, hi ha la presència d'indústries que contribueixen a augmentar els nivells de radionúclids naturals en el medi i de forma inadequada entre la població. Aquest tipus d'indústria preconcentra en forma de subproductes residuals en el medi, radionúclids naturals procedents de les cadenes de desintegració del ^{238}U (Figura 1.4.), ^{232}Th i el ^{235}U , també anomenades sèries d'actínids d'urani i tori i finalment, el ^{40}K . Totes aquestes cadenes de decaïment generen nombrosos radionúclids fins arribar a un radionúclid estable de plom. Apareix una necessitat de realitzar controls i estudis amb diverses mostres ambientals, per tal de comprovar les concentracions dels diferents radionúclids naturals.

Com a conseqüència de l'emmagatzematge o reutilització dels residus formats per aquest tipus d'indústria, per exemple com a material de construcció o en la recuperació de terrenys afectats per l'explotació minera, l'agricultura, etc., augmenten els nivells de radiació en alguns llocs de treball i vivendes. Aquest fet pot resultar difícil de controlar, ja que pot succeir en zones properes i/o llunyanes a aquestes activitats industrials.

A continuació en aquest apartat es presenta aquest tipus de indústria, anomenada NORM (*Naturally Occurring Radioactive Material*). En primer lloc, comentarem alguns exemples d'aquesta, centrant la nostra atenció en una zona situada en la conca del riu Ebre. En segon lloc, mitjançant un capítol de llibre publicat recentment per aquest grup de recerca, es presentarà l'estat de la qüestió referent a aquesta temàtica d'una forma general.

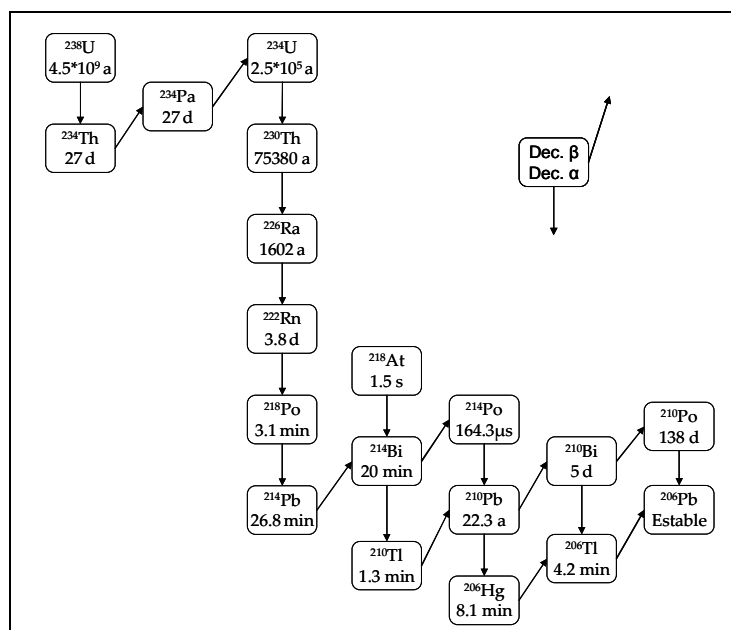


Figura 1.4. Sèrie de decaïment de l' ^{238}U en que s'inclou el període de desintegració de cada radionúclid.

1.2.1. Indústria NORM en l'últim tram del riu Ebre

Ja s'ha comentat anteriorment que en el medi hi trobem diverses fonts antropogèniques que generen subproductes residuals amb concentracions de radionúclids que poden augmentar les activitats de radiació naturals, ja existents, en el medi i els éssers vius que l'habiten. Concretament en aquest estudi ens centrem en l'últim tram del riu Ebre, amb una llargària d'aproximadament 110 Km des de Flix fins la desembocadura en el Delta de l'Ebre, per la presència d'una planta de producció de fosfat dicàlcic (DCP) situada en l'embassament de Flix i una estació de tractament d'aigua potable (ETAP) situada uns 53 Km riu avall, concretament a l'Ampolla.

1.2.1.1. Indústria del fosfat dicàlcic

En l'embassament de Flix trobem a una de les bandes del riu, un complex industrial anomenat Societat Electroquímica de Flix (SEQF), fundat el 1897. En els seus orígens el seu funcionament es va centrar en la producció de sosa emprant mercuri, mitjançant el mètode electrolític. L'any 1973 es va iniciar la producció de fosfat dicàlcic, el qual té un ús com a suplement alimentari inorgànic que conté un 18% de fòsfor i entre un 25 i 30% de calci. Es tracta d'un suplement idoni per complementar la dieta orgànica dels animals domèstics i s'utilitza en les dietes de pollastres, porcs, vaques destinades a la producció de carn i de llet, ovelles i gall d'indi. Concretament, aquest producte s'obté a partir del mineral fosforita ($\text{Ca}_3(\text{PO}_4)_2$) d'origen principalment marroquí, el qual té un alt contingut de radionúclids descendents de la cadena de ^{238}U . En aquest sentit, segons uns estudis realitzats en aquesta mateixa factoria de DCP per Casacuberta i col. [3,21] es van mesurar en aquesta matèria primera, activitats de l'ordre de $1706 \pm 5 \text{ Bq kg}^{-1}$, $1690 \pm 5 \text{ Bq kg}^{-1}$, $1730 \pm 3 \text{ Bq kg}^{-1}$, $1669 \pm 199 \text{ Bq kg}^{-1}$ per a ^{238}U , ^{234}U , ^{230}Th i ^{226}Ra , respectivament.

El sistema de producció del fosfat dicàlcic es realitza a partir de la digestió de la fosforita mitjançant un atac amb àcid clorhídric diluït sota condicions controlades. Llavors s'obté una solució àcida anomenada "suc monocàlcic" (pas 1) que després passa per un tractament amb CaCO_3 i $\text{Ca}(\text{OH})_2$ per tal d'aconseguir la precipitació del fosfat dicàlcic (pas 2). Finalment es filtra i seca el fosfat dicàlcic. A continuació presentem més detalladament les fórmules d'aquest procés:

Pas 1:

- Reacció que es produeix amb l'obtenció del fosfat monocàlcic:
 $\text{Ca}_3(\text{PO}_4)_2 \rightarrow 4\text{HCl} \leftrightarrow \text{Ca}(\text{H}_2\text{PO}_4)_2 + 2\text{CaCl}_2$

Pas 2:

- Reaccions que es produeixen amb l'obtenció del fosfat dicàlcic:
 $\text{Ca}(\text{H}_2\text{PO}_4)_2 + \text{CaCO}_3 + 3\text{H}_2\text{O} \leftrightarrow 2(\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}) + \text{CO}_2$
 $\text{Ca}(\text{H}_2\text{PO}_4)_2 + \text{Ca}(\text{OH})_2 + 2\text{H}_2\text{O} \leftrightarrow 2(\text{CaHPO}_4 \cdot 2\text{H}_2\text{O})$

En el procés també s'obtenen com a subproductes, el fosfat tricàlcic no dissolt més les impureses no solubles de la matèria primera, formant un residu sòlid (fangs) que s'incorpora als efluent de la planta. En la història de la planta, aquest residu sòlid va ser abocat al riu de manera incontrolada durant gairebé dues dècades, dintre d'aquest temps, podem dir que l'any 1992 aquesta planta va ser la principal productora de l'estat espanyol. Degut a l'aparició d'una normativa mediambiental l'any 1995 respecte al tractament de les aigües residuals urbanes [22], en 1996 s'inicià el procés d'una planta de tractaments residuals (EDAR) construïda dins del complex industrial. A partir del funcionament de l'EDAR es va eliminar l'aportació al riu de residus provinents de les plantes de clor alcalí i de fosfat dicàlcic sense un tractament previ i també s'emmagatzemaren residus en un abocador anomenat el Racó de la Pubilla. Per tenir-ne una idea de la quantitat de residu sòlid generat que s'estima en 200 Kg per tona de fosfat dicàlcic produït, s'obté una proporció dividida entre el 35% d'insolubles, el 31 % de fluorur de calci i el 34% de fosfat tricàlcic. Aquests són els principals causants de la contaminació ambiental generada en aquest indret, els quals un cop abocats al riu es van acumular i concentrar en forma de fangs sedimentats a la riba enfront del complex industrial (Figura 1.5.).

Respecte als fangs, hi ha un estudi recent de Casacuberta i col. [3] que mostra les activitats mitjanes de dues mostres residuals generades per aquesta DCP, les quals contenen $5036 \pm 7 \text{ Bq kg}^{-1}$ d' ^{238}U , $6287 \pm 6 \text{ Bq kg}^{-1}$ d' ^{234}U i $10090 \pm 8 \text{ Bq kg}^{-1}$ de ^{230}Th . Aquesta activitat més elevada en el cas del ^{230}Th ens mostra que no hi ha equilibri entre els diferents radionúclids de la cadena de l' ^{238}U , degut al procés industrial i a l'aport de material NORM. A través d'un altre estudi realitzat per Costa [23] es va realitzar un tipus de caracterització radiològica dels fangs sedimentats en l'embassament de Flix, amb un mostreig a diferents profunditats. Finalment, activitats màximes de $11723 \pm 198 \text{ Bq kg}^{-1}$ d' ^{238}U , $9361 \pm 181 \text{ Bq kg}^{-1}$ de ^{226}Ra , i $3500 \pm 157 \text{ Bq kg}^{-1}$ de ^{210}Pb es van trobar, les quals són cent vegades superiors a les activitats mitjanes dels sediments superficials del riu Ebre ($20.7 \pm 0.9 \text{ Bq kg}^{-1}$ d' ^{238}U , $23 \pm 7 \text{ Bq kg}^{-1}$ de ^{226}Ra i $18 \pm 1 \text{ Bq kg}^{-1}$ de ^{210}Pb).

Si comparem algunes de les dades presentades anteriorment, per exemple el contingut d' ^{238}U del mineral fosforita determinat per Casacuberta i col. (amb una mitjana de 1706 Bq kg^{-1}) i la mitjana calculada en els fangs (5036 Bq kg^{-1}) hi trobem un factor d'enriquiment de 3. A més, si comparem l'activitat de la fosforita amb l'activitat màxima trobada per Costa d'una mostra extreta dels fangs (11723 Bq kg^{-1}) hi trobem un factor d'enriquiment de ~ 7 . Aquests factors d'enriquiment fàcilment calculables a partir d'una fracció de les dues activitats implicades, ens mostren que hi ha una preconcentració de radionúclids per part del procés químic industrial.

Una altra dada d'interès donada per l'Agència Catalana de l'Aigua (ACA) [24], és la suma de fangs que té aquesta formació sedimentària residual procedent principalment del complex industrial i material al·luvial, obtenint entre unes 200.000 i 360.000 tones mètriques. Es va calcular també una estimació amb màxims de $240 \cdot 10^9$

Bq, $420 \cdot 10^9$ Bq i $730 \cdot 10^9$ Bq per al ^{238}U , ^{226}Ra i ^{210}Pb , respectivament, que contindria la totalitat dels residus acumulats. Aquests fangs tenen una composició d'origens diversos, a part dels radionúclids esmentats, com ara diversos metalls pesants (mercuri, ferro, níquel, etc.) i compostos organoclorats (DDT, hexaclorobenzè, policloroestirè, etc.). Per aquest motiu diverses zones dels fangs acumulats es podrien catalogar com a sòl contaminat, segons els criteris establerts en el Reial Decret 9/2005 [25].

Arran de tots els valors obtinguts en diversos estudis i de l'impacte que podrien causar aquests fangs remoguts per efectes de la naturalesa, es va aprovar un projecte d'extracció dels fangs sedimentats, el qual ja s'està duent a terme aquest any 2013. En la Figura 1.5. es mostra el confinament realitzat mitjançant dics (formant un mur de contenció impermeable) ancorats al llit del riu, per tal de tenir aïllats del curs natural del riu la gran majoria de tones de fangs acumulats en l'embassament front la DCP. L'extracció posterior d'aquests es realitza de manera segura i aïllada mitjançant el seu dragatge, fent ús de les dragues de succió. L'aigua confinada amb els fangs es tracta en una EDAR i els fangs, una vegada extrets, són classificats segons els nivells de contaminants. Per una banda es poden enviar directament a l'abocador o bé per l'altra a tractaments tèrmics i/o d'oxidació per a l'eliminació de compostos orgànics, metalls pesants i radionúclids [24].



Figura 1.5. Complex industrial ERCROS amb el mur de contenció envoltant les tones de fangs acumulats enfront, en l'embassament de Flix. Font: www.tafyr.es, UTE Ebre Flix 29/01/2013.

Aquest tipus d'indústria també és present en altres llocs geogràfics i per tal de realitzar una comparativa es presenten en la Taula 1.1. les activitats mitjanes dels principals radionúclids trobats en diferents matrius (matèria primera, residu, producte final i sòl amb els residus abocats) en quatre zones geogràfiques diferents.

Taula 1.1. Comparativa d'activitats trobades en diferents matrius relacionades amb la indústria de fosfats en diferents estudis.

	Reacció Química	²³⁸ U*	²²⁶ Ra*	²³⁰ Th*	²³² Th*	Estudi/localització
Roca fosfòrica (Síria)	H ₂ SO ₄	517±50	353±28	-	2,4±0,9	[26] Síria
Residus (sòlids)		1039±75	308±63	-	2,5±0,6	
Producte final (DCP)		785±51	709±34	-	3,4±0,9	
Sòl amb residus		33±1	26±1	-	30±1	
Roca fosfòrica (Síria)	HCl	838±8	855±7	-	4,9±0,2	[27] Suècia
Residus 1 (sòlids)		178±14	142±4	-	-	
Residus 2 (sòlids)		8,0±0,5	78±8	-	-	
Producte final (DCP)		954±38	15±1	-	-	
Sòl amb residus 1 (Odiel)	H ₂ SO ₄	714±23	896±54	-	-	[28,29] Huelva
Sòl amb residus 2 (Tinto)		252±7	646±39	-	-	
Roca fosfòrica (Marroc)	HCl	1706 ± 5	1669±199	1730±3	22±8	[3,30] Flix
Residus (sòlids)		1952±19	376±35	3885±103	138±5	
Producte final (DCP)		1363±576	55±2	901±21	22±34	
Sòl amb residus 1		5036±7	-	10090±8	138±5	
Sòl amb residus 2		3993±1	-	8618±4	119±14	
Roca fosfòrica (Marroc)	HCl	836±11	1343±13	-	-	[23] Flix
Sòl amb residus		1900±80	1100±30	-	-	

* Bq Kg⁻¹ ± u

Concretament en la taula es mostren els resultats de set estudis, dos d'ells centrats en DCP ubicades a l'estranger (Síria i Suècia) i la resta en les DCP de Flix i Huelva (Espanya). S'han escollit estudis on es treballa a partir del mineral fosforita amb procedència majoritàriament del Marroc i Síria [23,26-28,31], ja que segons la UNSCEAR [32,33] aquestes dues procedències de matèria primera tenen unes activitats mitjanes molt semblants, entre els 1300 i 1850 Bq kg⁻¹ d'²³⁸U i entre els 1400 i 1570 Bq kg⁻¹ de ²²⁶Ra. Tal i com podem veure en la taula, en general la roca fosfòrica de Síria presenta concentracions més baixes dels radionúclids avaluats que la del Marroc. En el cas dels residus finals que s'obtenen en aquest tipus d'indústria gairebé totes les concentracions són majors que en la matèria primera. Amb l'excepció de l'estudi de Gäfvert i col. [27], que tot i que mostren unes concentracions de radionúclids en la roca fosfòrica utilitzada d'uns 850 Bq kg⁻¹ (²³⁸U i ²²⁶Ra), en els

fangs residuals (1 i 2) trobem concentracions baixes, per exemple, 178 ± 14 i 8.0 ± 0.5 Bq kg⁻¹ d'²³⁸U. En el cas del ²²⁶Ra també veiem en general que les activitats dels residus són inferiors a les de la matèria primera degut a que és un radionúclid que segueix el flux del CaCl₂ durant la reacció química i es manté de forma soluble, per tant, també es troba en concentracions destacades en l'aigua residual, no incloses en aquesta taula. Si ens fixem en el producte final en tots els casos, veiem que d'augment de les activitats gairebé no n'hi ha ja que es troben activitats comparables amb la matèria primera. Finalment, si comparem els resultats de les activitats residuals trobades, acumulades al sòl dels voltants de la indústria, veiem que en el cas de Flix les concentracions de tots els radionúclids estudiats són molt més elevades que en els altres estudis presentats. Per exemple el grup de Villa i col. [28,29] que estudia les activitats trobades en l'estuari dels rius Tinto i Odiel (Huelva) on es troben les basses residuals de fosfoguix (resultat de l'atac amb H₂SO₄ sobre la roca fosfòrica amb procedència del Marroc), van mesurar en el riu Odiel, entre el 1989 i 1990, activitats mitjanes de 714 ± 23 Bq kg⁻¹ i 896 ± 54 Bq kg⁻¹ per al ²³⁸U i ²²⁶Ra, respectivament. Però cal remarcar que les concentracions mitjanes en l'estudi de Flix realitzat per Costa [23] presenten concentracions d'²³⁸U de més del doble d'activitat.

1.2.1.2. Estació de tractament d'aigua potable (ETAP)

Com ja hem comentat anteriorment, abans de la desembocadura de l'Ebre es troba el Consorci d'Aigües de Tarragona (CAT) (veure Figura 1.6.), una planta potabilitzadora d'aigua (ETAP) procedent del riu Ebre i que abasteix a un total de 61 municipis i 29 indústries de la província de Tarragona [34]. El procés de potabilització i subministrament, començats l'any 1989, consisteixen en una sèrie de passos realitzats dintre de les instal·lacions de la planta. Aquests són principalment: l'oxidació de l'aigua, la correcció del pH, la decantació de partícules en suspensió després de realitzar una coprecipitació d'aquestes mitjançant l'addició del clorur fèrric (FeCl₃), la filtració de l'aigua a través de filtres de sorra i filtres de carbó actiu granulat i finalment, la postcloració garantint una desinfecció i qualitat de l'aigua lliure de bacteris i fongs, apte per al consum humà.

El pas de la formació del precipitat és el que destacarem de la resta, ja que mitjançant l'addició de l'agent precipitant FeCl₃ es formen uns agregats o partícules coagulades (coagulació-floculació), les quals contenen de forma preconcentrada tot tipus de compostos (metalls pesants, radionúclids, compostos orgànics, etc.) que transportava l'aigua en suspensió. Llavors aquests sedimenten en forma de fangs en els decantadors i són retirats en eres on es deixen secar a l'aire lliure (Figura 1.6. Zona I) i després són acumulats per anys (Zona II). Segons diversos estudis aquests residus generats durant el funcionament d'aquestes indústries es poden considerar com a NORM [35-37].

En un primer treball realitzat pel nostre grup de recerca i que es va centrar en aquesta ETAP es destaca l'acció preconcentradora mitjançant l'ús de l'agent

coagulant, ja que es va observar que l'ETAP tenia la capacitat d'eliminar entre un 12 i un 16% de l'activitat alfa total present en l'aigua, degut principalment al procés de coagulació amb FeCl_3 [38]. Aquests resultats obtinguts són concordants amb els publicats per autors com Gåfvert i col. [37] i Wisser [39] que posaven de manifest la capacitat dels diferents processos de tractament per eliminar els radionúclids dissolts a l'aigua amb processos de coagulació, d'intercanvi iònic i d'osmosi, etc. En un altre treball de Palomo i col. [35] podem veure les concentracions de diferents radionúclids individuals en els fangs produïts per diverses plantes de tractament d'aigües d'Espanya, mostrant la seva capacitat de preconcentrar a aquests. En concret, els fangs procedents de les ETAP mostren activitats de radionúclids més elevades que els fangs produïts a les EDAR i també és destacable que hi ha diferències entre les concentracions dels diferents radionúclids mesurats en els fangs originaris de diferents ETAP, degut a l'origen de l'aigua i al procés de tractament, sobretot amb l'agent coagulant utilitzat. Aquest efecte del coagulant queda especialment remarcat en estudis previs realitzats per Gåfvert i col. [37] i Baeza i col. [40] on avaluen la capacitat de diversos coagulants (FeCl_3 i $\text{Al}(\text{SO}_2)_3$) en l'eliminació de radionúclids naturals i artificials. Tots aquests estudis anteriors corroboren que l'ús del coagulant de ferro té més capacitat que el coagulant d'alumini en radionúclids naturals com ara l'urani i el radi, entre altres.

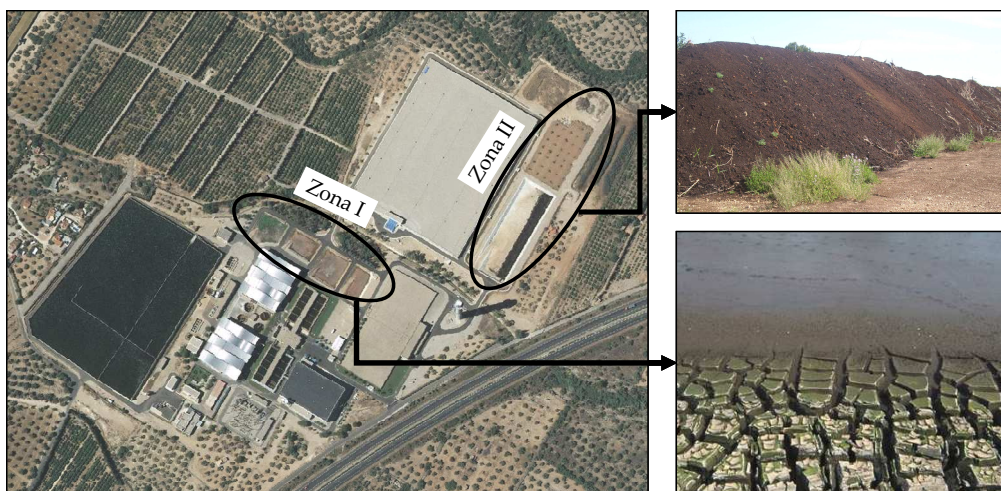


Figura 1.6. Vista aèria de la ETAP i localització de les Zones I i II amb fangs produïts durant el procés de la planta. Font: Consorci d'Aigües de Tarragona (CAT).

Arrel dels resultats obtinguts en aquests treballs i considerant que existeix la normativa del Reial Decret 1310/1990 [41] que regula la reutilització dels fangs de les plantes de tractament d'aigües per a l'ús agrícola la qual té en compte la concentració dels metalls pesants, però no especifica res sobre els emissors radioactius, és interessant que en futurs estudis es continuï realitzant un control de la concentració

d'emissors radioactius. A més tenint en compte que els fangs de les plantes de tractament d'aigua es reutilitzen en diversos casos, com per exemple en el cas de la fabricació de materials destinats per a la construcció com ara el ciment [42,43].

1.2.2. Capítol publicat indústria NORM

Per detallar més informació sobre la indústria NORM, s'inclou a continuació el capítol realitzat pel nostre grup d'investigació, publicat en Nova Science Publishers i anomenat "*Introduction and impact of radioisotopes in the environment due to NORM industries*" [44]. En aquest capítol es dóna una visió més global d'aquest tipus d'indústries i la seva problemàtica, on s'explica l'estat de la temàtica actual tenint en compte punts molt importants com ara la legislació, l'exposició de la població i/o treballadors i la seva presència en el medi ambient.

INTRODUCTION AND IMPACT OF RADIOISOTOPES IN THE ENVIRONMENT DUE TO NORM INDUSTRIES

*Montserrat Mola, Antonio Nieto, Alejandra Peñalver,
Carme Aguilar and Francesc Borrull*

Unitat de Radioquímica Ambiental i Sanitària (URAIIS).
Department of Analytical Chemistry and Organic Chemistry,
Rovira i Virgili University, Marcel·lí Domingo, s/n,
43007 Tarragona (Spain)

Abstract

In the last few years, increasing attention has been paid to the consequences of industrial operations that tend to concentrate natural occurring radioactive materials (NORM) in by-product waste streams, achieving relatively high activity concentration of these isotopes that can contribute negatively to the environment. In this group of contaminants, different elements such as several or all of the radioactive isotopes of the three natural decay series (^{235}U , ^{238}U and ^{232}Th) as well as ^{40}K are included.

These kinds of contaminants are unregulated in most countries, even though different regulatory agencies have become increasingly concerned about both their presence in the environment as a result of different industrial activities as well as any issues raised by the possible exposure of workers or the public.

The main aim of this chapter is to show the relationship of several industries that deal with or process NORM with the increase in the activity concentration of various isotopes in the environment due to the industrial activities carried out. It is also important to evaluate the radiological impact of these radionuclides on the environment and the determination of them in it.

Introduction

Radionuclides of natural origin are ubiquitous in both working and public environments, although their activity concentrations vary considerably. Exposures to natural sources are, in most cases, not a matter for regulatory concern. However, in some cases, exposures to natural sources may warrant consideration as to whether controls should be applied. One such situation is where the conditions are conducive

to the build-up of elevated concentrations of radon in air. Another situation is the mining and/or processing of material where the activity concentrations of radionuclides of natural origin in the material itself, or in any material rising from the process, are significantly elevated. Such materials have come to be referred to as Naturally Occurring Radioactive Materials (NORM).

Human exposure to NORM may be increased as a result of human manipulation of raw materials from the earth's crust. This technologically enhanced NORM may be a by-product of a range of industrial processes and other activities including mining, extracting, concentrating, processing or combusting raw materials containing radioactive isotopes [1]. Table 1 shows a summary of the most important industries that use NORM, and the radionuclides present in each industry as well the main routes from which any worker can be exposed to these radionuclides.

As can be observed in table 1, there are different types of industries that contribute to the increase of the presence of the different radionuclides that belong to the decay series of ^{238}U and ^{232}Th . Both series include numerous radionuclides in their decay chains before reaching a stable end nuclide, as shown in Figure 1. Uncontrolled activities associated with enhanced levels of NORM can contaminate the environment and pose a risk to human health [3]. These risks can be alleviated by the adoption of controls to identify where NORM is present and by the control of NORM-contaminated equipment and waste while protecting workers. The general principles of radiation protection are primarily implemented by means of good protective measures at the workplaces. Hence, exposure control and adequate dosimetry are the most critical components of a health and safety programme.

Table 1. Classification of NORM industries [2]

Industry	Isotopes	Factor of concern
Production of uranium, thorium, gold, silver, copper, nickel, iron, aluminium, molybdenum, zinc, titanium, tungsten, vanadium, potassium, coal and phosphates.	^{238}U , ^{226}Ra , ^{232}Th , ^{210}Po , ^{210}Pb , ^{228}Ra	Radon, aerosol inhalation, residues and dumping
Production of zirconium and monazite	^{238}U , ^{226}Ra , ^{232}Th	Aerosol inhalation, external radiation
Oil and gas extraction	^{226}Ra , ^{228}Ra	Aerosol inhalation during the maintains, residues
Geothermal energy	^{222}Rn , ^{238}U	Radon, dumping
Water treatment, paper industry, ceramics industry, pigments and cement production	^{226}Ra , ^{222}Rn , ^{210}Pb , ^{228}Ra , ^{234}U , ^{235}U , ^{238}U	Radon, aerosol inhalation, residues, dumping and sludge.

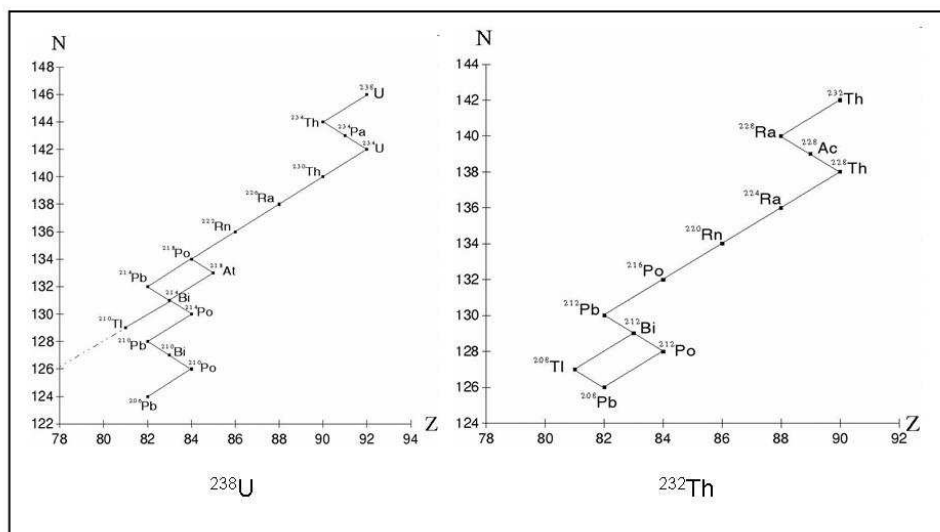


Figure 1. Decay series of ^{238}U and ^{232}Th .

NORM Industries

NORM industries are of major interest since the enhancement of some naturally occurring radioisotopes as a result of the industrial processes carried out may be of radiological concern to both workers and members of the public. The term “NORM industries”, according to the International Atomic Energy Agency (IAEA) definition, refers to any mining operation, or other industrial activity involving a mineral or raw material, that has the potential to increase the effective dose received by industrials due to exposure to naturally occurring radionuclides contained in or release from such material [4]. In the following section, we describe the main processes and the waste generated by the most important group of industries involved with the presence and enhancement of natural radionuclides in the environment.

a) Fossil Fuel Power Stations

A fossil-fuel power station is a power station that burns fossil fuels such as coal, among others, to produce electricity. Central station fossil-fuel power plants are designed on a large scale for continuous operation. In many countries, such plants provide most of the electrical energy used. Fossil fuels, such as coal, contain naturally occurring radioisotopes from the ^{238}U and ^{232}Th series, as well as ^{40}K , among these radioisotopes one of the most characteristic is the ^{210}Po and ^{210}Pb which are presents in the fly ash. Coals are known to concentrate elements as a result of interactions of organic matter with numerous processes. The geochemistry of coal is

strongly influenced by a number of geological parameters, including the nature of rocks near the coal basin and the rate of subsidence and uplift of the drainage area. Other dominant factors that control the geochemical properties of coal are the following: the environment of coal deposition, the weathering of coal, the presence of intrusive rocks, and the self-burning of coal seams. The depositional environment, the climatic and hydrological conditions and the nature of country rocks are more important in the early stages of coalification. Rank, tectonic setting and groundwater chemistry have greater influence on coal geochemistry in the later stages of coalification. It should also be noted that the original plant species that formed the coal could have taken up some elements by biological and physico-chemical processes. Factors such as bacterial activity and pH of waters influence the deposition of elements in coal [45]. The concentration of radionuclides in coal depends on the geological setting but ranges from a few Bq to 500 Bq·kg⁻¹ for ²³⁸U and up to 100 Bq·kg⁻¹ for ²³²Th. In a review by Gentzis *et al.* [45] published in 2000, there is a summary of the average concentration of different radionuclides found in different coals from Australia, Canada, UK and USA. These results are showed in Table 2.

Table 2. Mean concentrations of selected radionuclides (Bq·kg⁻¹) in coals from Canada, Australia, the US, the UK and the world. Data for the Canadian, Australian, US and UK coals [45].

	Canadian coals	US coals	UK coals	Australian coals	World coals
²³⁸ U	13- 47	6 - 73	8 – 31	8 – 47	15 – 20
²³⁰ Th	20- 93	NA	9 - 25	21 – 68	NA
²³² Th	9 - 23	4 – 21	7 – 19	11 – 69	7 – 110
²¹⁰ Pb	12 – 64	12 – 78	NA	20 – 33	10 – 50
²²⁶ Ra	9 - 36	9 - 59	8 - 22	19 - 24	1 - 250

NA= not available.

As we can see in Table 2, a rule about the activity concentrations of the different radionuclides cannot be determined. These results are in line with previous reports in which it has been established that coal properties are different in each country and are influenced by several parameters.

In the study of Tsikritzis *et al.* [6], a mine of lignite, a fuel used to produce electricity, was investigated. In the ash samples analysed, different radionuclides were determined using gamma spectrometry. The radionuclide that showed the highest activity was ²³⁸U, in a range between 159 and 1006 Bq·kg⁻¹.

Another radionuclide that showed significant activity was the ²²⁶Ra (138-896 Bq·kg⁻¹). Radionuclides found at lower levels in the ash samples were ⁴⁰K, ²³⁵U, ²²⁸Ra and ²³²Th. In another study [7] where the same radionuclides were quantified in a lignite factory in Ptolemais (Greece), the average activity concentrations of ²³⁸U, ²²⁶Ra, ²³²Th and ⁴⁰K in lignite were of 84, 93, 19 and 79 Bq·kg⁻¹, respectively, while the

corresponding values in fly ash samples were 294, 276, 51 and 270 Bq·kg⁻¹, respectively.

As expected, all measured radionuclides were found to be enriched (2.7 to 3.5 times) in fly ash samples compared with those in lignite samples. The results obtained from surface soil samples collected near to this factory indicated that there was not any significant deposition of ²³⁸U or ²²⁶Ra escaping from the stacks of the lignite power plants onto the land around the city of Ptolemais. The measured specific activities of these radionuclides could be attributed to natural sources in soils.

b) Metal Production and Processing

In this group of industries, we include the industries that produce uranium, thorium, gold, silver, aluminium, and iron among other metals. The basic process in which metals and alloys are produced from metal rich ores is that of smelting. The waste production in this process is elevated and depends on the type of raw materials used. Slags, dross, fly ash, furnace coal ash and scales may be produced as a result of the smelting process. There are also likely to be stack emissions of fly ash and gases. Each metal processing involves high temperatures, and those temperatures are a potential source of emissions of ²¹⁰Po and ²¹⁰Pb into the air.

In the literature, a study from Baxter *et al.* [45] explains the presence of radionuclides in a metal refinery in England. They studied the raw material and, between 1984 and 1988, 270 samples were analysed, corresponding to approximately one analysis per 1400 tonnes of raw material. It was found that ²¹⁰Po specific activities were significantly below 1.5 × 10⁴ Bq·kg⁻¹ in most cases. For example, in 1987 only 1% by weight of the solid raw materials had ²¹⁰Po specific activities in excess of 1.5 × 10⁴ Bq·kg⁻¹ and 80.8% had values less than 2 × 10³ Bq·kg⁻¹. During the period 1977-1987, average ²¹⁰Po specific activities ranged from 1.2 × 10³ to 2.5 × 10³ Bq·kg⁻¹. In the solid raw materials, other radionuclides were also found, such as ²³⁸U, ²²⁶Ra, ²³²Th and ²¹²Pb. As well as in the raw material, all of radionuclides mentioned above were also found in the gaseous and solid wastes between 0.13 (²¹⁰Pb) to 7 Bq·kg⁻¹ (²²²Rn) and between 1.3 (²¹²Bi) and 2×10³ Bq·kg⁻¹ (²³²Th), respectively.

In the study of Evseeva *et al.* [9], different samples collected in the village of Vodnyi (Ukhtinskii region, Komi Republic), where it is located a facility for mining and processing radium bearing ore that operated from 1931 to 1956. That area was radioactively contaminated at the sites of spillage of highly radioactive formation waters and waste storage. They studied different places including the waste storage facility. The study shows that in the waste storage facility, the activity of different radioisotopes was higher than in other places in the village. For instance, one of the sampling points was inside the waste storage facility and it revealed ²³⁸U, ²²⁶Ra, ²¹⁰Pb, ²¹⁰Po and ²³²Th, while it was the ²²⁶Ra radionuclide which showed the most activity (49×10⁻² Bq·L⁻¹). Meanwhile, the point that showed the lowest concentration was the sample collected from the river. At this sample point, the radionuclide that showed

the maximum activities was also the ^{226}Ra ($3.4 \times 10^{-2} \text{ Bq}\cdot\text{L}^{-1}$). Other radionuclides were found in the river sample, such as ^{238}U , ^{210}Pb , ^{210}Po and ^{232}Th between 0.05 and 1.06 $\text{Bq}\cdot\text{L}^{-1}$. The main conclusion of this study was that the water samples from the sources of creeks flowing from the radioactive waste storage facility to the Ukhta River had a significant toxic effect. A significant genotoxic effect was characteristic of all samples studied.

c) Oil and Gas Extraction

Radioactive materials such as uranium and thorium were incorporated in the Earth's crust when it was formed. These normally exist at trace concentrations (parts per million – ppm) in rock formations. Decay of these unstable radioactive elements produces other radionuclides that, under certain conditions (dependent upon pressure, temperature, acidity *etc*) in the subsurface environment, are mobile and can be transported from the reservoir to the surface with the oil and gas products being recovered. As has been explained in Gerchikov *et al.* [10], there are no such thing as 'typical' discharges for an oil or gas production plant. Discharges of natural radionuclides depend strongly on the type of reservoir, specific production conditions and the years of exploitation of the reservoir. Production of oil and gas is accompanied by water which is co-produced from the well and so is known as 'produced water'. A reference ratio of 0.33 between the volumes of produced oil and water is used as a reference average value for all oil producing platforms in the sea area of interest over their lifetime. This means that for each cubic metre of oil, 3m^3 of water is assumed to be co-produced [11]. Produced water contains radionuclides which have been mobilised from the reservoir rocks and, in addition to being present in the produced water, they are also deposited as scales on the pipes, valves and vessels. These pipes may be descaled offshore or at onshore descaling facilities. The main releases of NORM in offshore oil and gas production originate from three different sources:

- Produced water released offshore (^{228}Ra , ^{226}Ra and ^{210}Pb).
- Scale from offshore mechanical descaling released offshore (^{228}Th , ^{228}Ra , ^{226}Ra and ^{210}Pb).
- Scale from coastal descaling site discharged into the sea or disposed on land (^{228}Th , ^{228}Ra , ^{226}Ra and ^{210}Pb).

In the case of sludge samples and scales from different wells, there is a very large variability in radionuclide concentrations because of the differences in the nature of the reservoirs and other conditions [12, 13]. Activity concentrations in sludges and scales vary from virtually zero to up to several hundred $\text{Bq}\cdot\text{g}^{-1}$. The most common radionuclides found in the sludge affected by these industries are ^{228}Th , ^{228}Ra , ^{226}Ra and ^{210}Pb .

There are several works in the literature about the assessment of the radiological impact of the oil refining industry [14, 15]. A comprehensive radiological study by Bakr [14] on the oil refining industry in Egypt was carried out. Scales, sludge, water and crude oil samples were collected at each stage of the refining process. The results showed that ^{226}Ra was the main predominant radionuclide, and it was determined in the collected samples and its activity ranged from $2700 \text{ Bq}\cdot\text{kg}^{-1}$ in crude oil samples to $6 \text{ Bq}\cdot\text{kg}^{-1}$ in sludge samples. The activity concentrations of ^{232}Th ranged from $14 \text{ Bq}\cdot\text{kg}^{-1}$ to $900 \text{ Bq}\cdot\text{kg}^{-1}$ in crude oil samples and from $17 \text{ Bq}\cdot\text{kg}^{-1}$ to $885 \text{ Bq}\cdot\text{kg}^{-1}$ in sludge samples.

d) The Phosphate Industry

One of the most important sectors that is classified as a NORM industry is phosphate production and processing [16]. In this industry, phosphate rocks are used as raw materials for the production of phosphoric acid, fertilizers and other phosphorous-containing materials. There are four main processes involved in the industrial activity in this sector:

- The wet acid process using sulphuric acid (H_2SO_4)
- Hydrochloric acid (HCl) treatment
- Nitric acid (HNO_3) treatment
- Thermal processing

In the sulphuric acid, hydrochloric acid and nitric acid processes, the chemical reaction is similar, i.e. acidification of the ore. However, the waste products and by-products are markedly different with differing implications for NORM waste production. The method most commonly used in Europe to produce fertilizers is treatment with phosphoric acid [17].

Across the European Union, there have been significant changes in the industry, with a move away from the production of phosphoric acid from phosphate ore and its associated production of large amounts of phosphogypsum. Discharges of phosphogypsum by EU countries are, in fact, a thing of the past.

The thermal process uses high temperatures to reduce the phosphate to produce phosphorus, calcium silicate slag and calcinate [45]. There are several works based on the study of the production of phosphate-based products in the NORM activity field. The raw material (phosphate rock) in industrial processes leads to the input of several different radionuclides, resulting in increased natural radioactivity in the immediate environment. Various studies have verified natural radionuclide accumulations resulting from phosphoric acid production [19-22]. For instance, Villa *et al.* [22] studied an area of the Estuary of the Tinto and Odiel rivers (Huelva) and evaluated the ^{226}Ra and ^{210}Pb activities in bottom sediment samples collected from 1990 to 2005, the influence of the waste dumped by the phosphate industry and its

temporal evolution. The maximum activity concentration of ^{226}Ra was found in the year 1990. The concentration in this year varied between 0.037 and $0.087 \text{ Bq}\cdot\text{L}^{-1}$ and for ^{210}Pb was between 0.004 and $0.047 \text{ Bq}\cdot\text{L}^{-1}$. In conclusion, the authors observed that the activities decreased considerably due to the self-cleaning and dilution of this contamination after direct releases into maritime areas ceased in 1998 [23, 24]. Bolívar *et al.* [25] also studied the zone of Huelva affected by the phosphate industry. In this case, six different soil samples were studied. The maximum activity concentration of ^{226}Ra , in the analysed sediments, was $31.7 \text{ Bq}\cdot\text{kg}^{-1}$ in superficial samples while in deep samples the activity decreased to $25.9 \text{ Bq}\cdot\text{kg}^{-1}$. The other isotope of Ra studied, the ^{228}Ra , had different behaviour. The activities were slightly higher in deep samples than in superficial samples. The maximum activity was $39.3 \text{ Bq}\cdot\text{kg}^{-1}$ in superficial samples and $40.8 \text{ Bq}\cdot\text{kg}^{-1}$ in deep samples. Other radionuclides studied were ^{228}Th and ^{40}K . In these cases, the concentrations in deep samples were higher than in superficial samples. The maximum activity for thorium was $37.2 \text{ Bq}\cdot\text{kg}^{-1}$ and for potassium was $668 \text{ Bq}\cdot\text{kg}^{-1}$.

In Spain, there is an important dicalcium phosphate (DCP) factory (Flix) and various studies have been published about its effect on the environment [26-28]. In one study of Casacuberta *et al.* [26], the concentrations of the naturally occurring ^{238}U , ^{235}U and ^{232}Th decay series in DCP samples indicated that the radioactive equilibrium in the phosphate rock was disrupted during industrial chemical processing. Samples of DCP used for animal consumption contained high activities and were classified into two subgroups. Group A samples were characterised by low ^{230}Th activities ($<150 \text{ Bq}\cdot\text{kg}^{-1}$), but high activities of ^{210}Pb ($\sim 2 \times 10^3 \text{ Bq}\cdot\text{kg}^{-1}$), ^{210}Po ($\sim 800 \text{ Bq}\cdot\text{kg}^{-1}$) and slightly elevated values of ^{226}Ra ($102 \text{ Bq}\cdot\text{kg}^{-1}$). In contrast, samples from group B had high activities of ^{230}Th ($103 \text{ Bq}\cdot\text{kg}^{-1}$) but low activities of ^{226}Ra , ^{210}Pb and ^{210}Po ($<30 \text{ Bq}\cdot\text{kg}^{-1}$). These differences were due to the chemical behaviour of the various elements during the production process. Group A samples were produced by wet-acid digestion of the phosphate rock via hydrochloric acid, whereas group B samples were obtained through phosphate rock digestion with sulphuric acid.

e) Titanium Oxide Pigment Production

Another industry that generates NORM waste is the pigment industry. Titanium oxide pigment is produced from the ores rutile (TiO_2) and ilmenite ($\text{TiO}_2\cdot\text{FeO}$). In addition, tin slag can be used as the raw material in either process. In the original sulphuric acid process, ilmenite is dried and ground, mixed with concentrated sulphuric acid and heated until an exothermic reaction starts between the titanium raw material and sulphuric acid. A solid reaction cake is formed that is composed mainly of titanium and iron sulphates. The reaction cake is dissolved in a mixture of water and recovered process acid. Ferric iron in the solution is reduced to the ferrous form in separate reduction tanks with scrap iron as the reducing agent. The reduced solution is settled and filtered to remove unreacted solids and much of the iron is

removed by cooling and crystallisation into hydrated ferrous sulphate (copperas, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). After removal of the copperas by centrifugation, the solution is concentrated. The pure white precipitate is calcinated in a kiln at about 1000°C to form the TiO_2 crystals of the required size and shape.

In the chloride process, rutile, cokes and chlorine react at about 1000°C to form a mixture of chlorides including the highly volatile TiCl_4 . The other chlorides are separated from TiCl_4 in a series of condensation steps. After purification by distillation, the TiCl_4 is oxidised to TiO_2 and finished into pigment.

The highly purified TiO_2 pigment, virtually 100% of the rutile input, is practically completely free of the natural radionuclides contained in the ore. Emissions to the air, apart from the radon in the ore, are negligible. Consequently, all radioactivity from the ore appears in the liquid effluent and solid wastes. The partitioning of the radionuclides between solid waste and discharged wastewater depends on the treatment of the acidic liquid waste stream. Radium and radioactive isotopes of lead tend to remain in solution if the pH endpoint is not high enough [4].

The largest plants produce bricks and roofing tiles. The firing temperature of the ovens is between 1000°C and 1200°C . The clays usually have concentrations of the radionuclides from the decay chains ^{238}U and ^{232}Th in the order of few $\text{Bq}\cdot\text{kg}^{-1}$. Between 40% and 100% of the ^{210}Po is volatilised in the firing process. The fraction of the throughput of ^{210}Po emitted depends on the extent of the off-gas cooling and cleaning to abate dust and HF emissions. Copper [29], showed that in the produced pigment, the activity concentration of uranium and thorium was negligible. However, in the neutralised residue slurry, the average activity was $1200 \text{ Bq}\cdot\text{kg}^{-1}$ for ^{232}Th and $350 \text{ Bq}\cdot\text{kg}^{-1}$ for ^{232}U . In the solid waste, the maximum activity was $1400 \text{ Bq}\cdot\text{kg}^{-1}$ for ^{232}Th and $500 \text{ Bq}\cdot\text{kg}^{-1}$ for ^{232}U .

f) Cement Production

Another sector considered as a NORM industry is cement production. Production of cement involves the heating, calcining and sintering of blended and ground raw materials, typically limestone and clay or shale and other materials, to form clinker. This clinker burning takes place at a material temperature of 1450°C in kilns. The clinker is ground and mixed with small amounts of gypsum to give Portland cement. In addition, blended cements are produced from cement clinker with blast furnace slag and fly-ash. Large cement plants produce in the order of 9000t of cement per day (3.3 billion tonnes [30]). Because of the very high temperature of the raw materials in the kilns, volatilisation of ^{210}Po and ^{210}Pb is the main potential risk of aerial discharge.

The naturally occurring radionuclides present in building materials, including soil, are ^{226}Ra , ^{232}Th and ^{40}K [31, 32], which are the main sources of radiation of building materials. In the study of Xinwei [33], eight kinds of building materials from Xi'an (China) were collected. The concentrations of ^{226}Ra , ^{232}Th and ^{40}K in the selected

building materials ranges from 19 to 68 Bq·kg⁻¹, 13 to 51 Bq·kg⁻¹ and 63 to 713 Bq·kg⁻¹, respectively.

Another study, where different building materials were analysed [34], found different radionuclides, such as ²²⁶Ra, ²³²Th and ⁴⁰K. The activity concentrations of these radionuclides measured in the Portland cements, as well as in the raw materials used for the preparation of the cement, were higher than the minimum detectable activity. The activity of ²²⁶Ra was between 17 and 91 Bq·kg⁻¹, for ²³²Th was between 15 and 18 Bq·kg⁻¹ and for ⁴⁰K was between 154 and 212 Bq·kg⁻¹. The results obtained in this study were comparable to the results reported by other authors such as Papastefanou *et al.* [35] in samples from Greece. It is also important to monitor atmospheric samples, where there is a high risk of the presence of radon. As an example, in the study of Baykara *et al.* [36], building materials produced in the city of Elazig (Turkey) and its direct radiation exposure to the public was studied. The average indoor radon concentration was 364 Bq·m⁻³ in newly constructed buildings.

g) Waterworks

Water treatment plants can be also considered as NORM industries. In most cases, the water used by these plants is surface water, although in some cases the procedence can be different, and water from other different origins can be used for this purpose as well water. From a radiation protection point of view for the workers, the radionuclide of greatest interest today in waterworks is ²²²Rn from the uranium decay series. In most cases, the activity concentration of radionuclides in waterworks samples were at levels of few Bq.

In fact, the incoming water treated in these plants can contain such radionuclides as radium or uranium due to the geological media in which the waters flow. When this water is treated, it passes through various filters to remove the contaminants. This treatment may lead to the generation of radioactive wastes such as sludge samples or also to the radiological contamination of the filters used [37-39]. For example, Palomo *et.al.* [39] studied sludge samples from eleven potable water treatment plants (PWTP), three waste water treatment plants (WWTP) and one industrial water treatment plant (IWTP), located in different areas of Spain, mainly in Catalonia. In Figure 2, we can see the places where these samples were taken. These samples were analysed for their radiological content in order to determine whether they could be considered as industries affected by NORM.

In general, samples from the PWTPs showed higher activity values for the alpha and gamma emitting isotopes than the WWTPs and the IWTP. For example, sludge samples from the area located in the north of Catalonia showed values of ²³⁴U, ²³⁵U and ²³⁸U in the range of 84-792 Bq·kg⁻¹, 3-26 Bq·kg⁻¹ and 63-585 Bq·kg⁻¹, respectively. In general, for PWTP, the values obtained for the gamma emitter and alpha emitter isotopes showed that both the geology and the industrial activities correlate with the values measured. The magnitude of these results demonstrates the need to measure

the radionuclide content of these samples before reaching a decision about their final disposal. In the study of Gäfvert *et al.* [37], the efficiency of a waterworks with an average production rate of $1.3 \text{ m}^3 \cdot \text{s}^{-1}$, providing several large cities in the province of Scania with drinking water was studied regarding its capacity to remove several natural and anthropogenic radionuclides. The raw water is surface water from Lake Bolmen which is transported through an 80 km long tunnel in the bedrock before it enters the waterworks. The results showed a high removal capacity for uranium (about 85%), thorium (90%), plutonium (95%) and polonium (90% in the coagulation– flocculation process) while caesium, strontium and radium pass through the purification process with almost unchanged activity concentrations. In this part of the chapter, we have outlined the most important and most studied industries considered as NORM industries. However, there are other industries included in this group such as geothermal industry, the production of zirconium and monazite, among others.

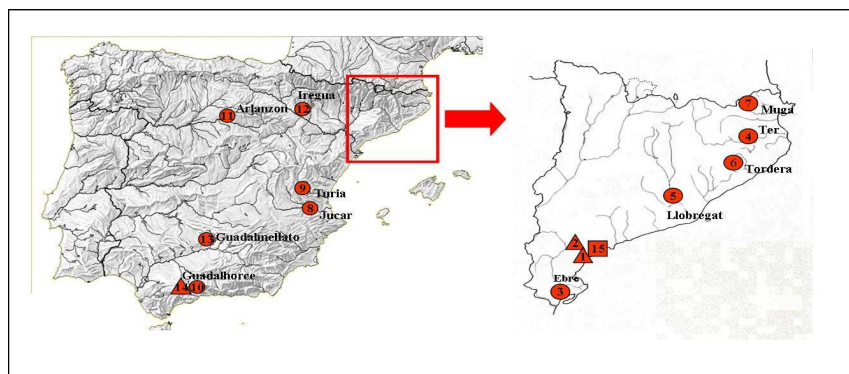


Figure 2. Map of Spain indicating the location of the different water treatment plants from which sludge samples were taken. In particular, the map shows the eleven potable water treatment plants (PWTP) (● 3-13), the three waste water treatment plants (WWTP) (▲ 1, 2 and 14) and also the industrial water treatment plant (IWTP) (■15) selected for this study.

Legislation

The naturally occurrence of radioactive materials has not been extensively legislated in Europe to date. The European Union prepared and adopted the Council Directive 96/29/Euratom [40]. Title VII of this Council Directive entitled “The European Basic Safety Standards Directive Concerning Significant Increase in Exposure due to Natural Radiation Sources” was included in the directive following the publication of the International Atomic Energy Agency (IAEA) of the International Basic Safety Standards for Protection against Ionising Radiation and the Safety of Radiation Sources (BSS) [41].

The primary scope of the Directive remains “all practices which involve a risk from ionising radiation from an artificial source or from a natural radiation source in cases where natural radionuclides are or have been processed in view of their radioactive, fissile or fertile properties”. Nevertheless, the directive also applies to “work activities which involve the presence of natural radiation sources and lead to a significant increase in the exposure of workers or member of the public which cannot be disregarded from the radiation protection point of view”.

Following the publication of the Directive, the European Commission asked for research to assist Member States in the area of NORM and subsequently published related guidance, in particular radiation protection 95 (RP95) [42] and radiation protection 122 Part II (RP122) [43]. Such documents are not regulations; they are simply guidance, so there is no obligation upon Member States to adopt these recommendations. For instance, RP95 provides reference levels for identifying those industries for which workers exposure should require regulatory control. Guidance RP122 relates to the exemption and clearance and is also of most relevance to the workplace. No guidance has yet been developed regarding discharges.

The IAEA Draft Safety Guide DS161 [44] is another set of guidelines which provides recommendations about radioactivity limits in solid waste, mainly derived from non-nuclear industries [45]. The emphasis of this guidance is on the realistic assessment of doses so its aim is to estimate doses as close as possible to those that would actually be received by members of the public.

The European Commission has not yet produced guidance for the assessment of doses to members of the public from NORM discharges. It has, however, produced guidance on the assessment of doses from discharges from nuclear facilities which has been used as the basis for developing guidance relation to NORM discharges.

Due to this lack of legislation, each European State has its own specific legislation for NORM industry or none at all. In the Radiation Protection 135 (RP135) guidance [46], a classification of the Member States in three different categories on the basis of the information (about the legislation of the definition of NORM industries and the control of these industries) provided for each State was carried out as follows:

- Category 1: Legislation relating to/encompassing NORM has been enacted and industries have been identified and some controls put in place. In this category are: Germany, Greece, Luxembourg, Netherlands, UK and Finland.
- Category 2: Legislation in draft form or industry identification incomplete or discharge controls at an early development stage. In this category we can include: Belgium, Denmark, Spain, Ireland, Italy, Austria, France and Sweden.
- Category 3: Legislation incomplete and identification of industries process not underway. In this category only Portugal was included.

For the determination of the required regulatory control of NORM, it is necessary to compare the activity concentrations and the doses due to exposure of workers and the public with certain criteria. According to the BSS, exposure to natural sources shall normally be considered as chronic exposure situation and, if necessary, shall be subject to the requirements for intervention, except for public exposure delivered by effluent discharges, by disposal of radioactive waste arising from NORM activities, and for occupational exposure.

The selection of appropriate criteria for defining the scope of regulatory control is a critical issue for NORM. Although in some cases, the radiological hazards can be very significant, the number of industries potentially subject to regulatory control is very large and inappropriate selection of criteria could result in many industries being regulated without any net benefit in terms of risk reduction. For this reason, the concepts of exclusion, exemption and clearance are of utmost importance in defining the scope of regulatory control of NORM.

The BSS glossary defines “excluded” as “outside the scope of standards” and expands on this by stating that “any exposure whose magnitude or likelihood is essentially unamenable to control through the requirements of the Standards is deemed to be excluded from the Standard”. So exclusion is an important concept for limiting the scope of regulatory control, specifically for natural radionuclides. The European Commission in the Council Directive 96/29/Euratom also used exclusion to limit the scope of regulatory control for natural radionuclides, and they encompass both practices and intervention situations in this directive.

The BSS uses the concept of exemption only in the context of practices. This concept determines a priori which practices, sources and radioactive materials may be freed from the requirements for practices, and hence regulatory control, based on certain criteria. Exemption should be granted if the regulatory body is satisfied that the practices or sources meet the exemption criteria or the exemption levels specified in Schedule I of the BSS, or other exemption levels specified by the regulatory body on the basis of the exemption criteria. In Table 3, we summarise the exempt activity concentration of some radionuclides that appears in Schedule I of the BSS.

In guidance RP122 part II, published by the European Commission, it expressed its opinion of the clearance and exemption of natural radioactive sources. The Commission considered the impracticability of using the trivial dose concept for the establishment of reference levels for regulatory control of natural radioactive sources and made a distinction between the derivation of levels for exemption of artificial and natural sources. As in the case of BSS, the exemption levels for artificial sources are based on the concept of triviality of risk, associated with a dose of 10 μ Sv in a year. Instead of considering the worldwide range of activity concentrations, in RP122 part II, the European Commission uses the variation in the range of natural radiation background doses as a basis for setting the reference 1 ± 0.3 mSv in a year. The European Commission considers the variation of 0.3 mSv as a suitable dose criterion

to calculate activity concentrations for exemption (and clearance) of regulatory control of natural radionuclides.

Table 3. Exempt activity concentration for some radionuclides reported in Schedule I of the BSS

Nuclide	Activity Concentration (Bq·g ⁻¹)	Nuclide	Activity Concentration (Bq·g ⁻¹)
Rn-222	1x10 ¹	U-230	1x10 ¹
Ra-223	1x10 ²	U-232	1x10 ⁰
Th-226	1x10 ³	U-234	1x10 ¹
Th-227	1x10 ¹	U-nat	1x10 ⁰
Th-228	1x10 ⁰	U-239	1x10 ²
Th-nat	1x10 ⁰	U-240	1x10 ³
Po-210	1x10 ¹	Pb-210	1x10 ¹

The concept of clearance is also used in the BSS. Clearance is intended to establish which sources under regulatory control can be removed from this control. This concept is related to clearance levels that are defined as values established by the regulatory authority and expressed in terms of activity concentrations and/or total activity at a below which sources of radiation may be released from regulatory control.

Another important value that has to be taken into account is the action level. This issue refers to the concept of intervention. If the dose rate could not be reasonably reduced to below the action level, the numerical value of the action level could be used to define when the requirements for practices should apply. One radionuclide that is legislated is radon. The action level defined in the BSS is the action level for radon and in workplaces is a yearly average concentration of 1000 Bq·m⁻³ [47]. Moreover, the content of radon was regulated in indoor environments. In old buildings, the annual average limit was 400 Bq·m⁻³ and for new buildings, 200 Bq·m⁻³. These values were summarised in the Commission Recommendation 90/143/EURATOM [48].

Exposure of Workers and Members of the Public

The industrial activities involving exposure from natural sources involve bulk amounts of materials containing high activities of naturally occurring radionuclides, and this can lead to a radiation dose in working areas which is not insignificant if we consider the radiation protection rules. Moreover, through such kind of industrial activities, members of the public may also be exposed to radiation. Over the last few years, particularly after the implementation of the IAEA Basic Safety Standards [41], special attention has been given to exposures to enhanced levels of naturally

occurring radioactive materials. Most NORM industries have not been subject to radiological protection measures and there is a lack of knowledge regarding the implementation of dosimetry programmes, to whom they should apply and how to put them into practice.

Appropriate legislation for NORM industries has not been implemented in many countries. In the previous part of the chapter, we mentioned that there are different guidelines such as guidances Radiation Protection 95 [42] and Radiation Protection 122 [43] and the most important conclusion related to this topic from these reports was that rather than an individual dose criterion, a dose increment in addition to background exposure of the order of 0.3 mSv for workers as well as members of public is appropriate.

It is important to take into account the possible routes of exposures of workers and, accordingly, exposure to gamma radiation and the inhalation of dust are the main routes. When radionuclides are released into the environment, there are a number of different ways in which they can lead to radiation doses to individuals. The different ways are referred to as exposure pathways and radiation doses need to be assessed for each important exposure pathway. There are many different possible exposure pathways and it is not necessary to consider every possibility in a realistic assessment of doses. Once these main routes are known, it is important to take appropriate control measures which may include special arrangements for the storage of bulk materials, limitation of exposure time and dust control, so normal common-sense precautions should be taken to avoid all unnecessary exposures to radiation. Beyond this, assessments should be made to estimate the doses to workers from such natural radionuclides. If actual doses are less than 1 mSv per year then no special precautions are required. If annual doses exceed 1 mSv, then the normal scheme for controlling exposures can usually be applied. If doses exceed 6 mSv per year, then it may be appropriate to define a controlled area. If actual doses exceed 1 mSv per year but are less than 6 mSv per year, it would be appropriate to consider, for example, whether doses could effectively be reduced and whether there is a possibility that doses increase either over time or as the result of an accident. If doses are low and cannot effectively be reduced and if there is no realistic potential for accidents, then few radiation protection measures are likely to be required beyond whatever is necessary to ensure that doses do not increase. Guidance on the exposure of workers is broadly consistent with the annual effective doses referred to above for terrestrial natural radiation sources.

Depending on the types of discharge, there are different pathways that should be always considered. For example, when the discharge is in the atmosphere, the possible pathways are the ingestion of radionuclides in terrestrial food (milk, meat, vegetables and fruit), the inhalation of radionuclides in the atmosphere and external irradiation from radionuclides in the atmosphere and deposited on the ground.

When the discharge is in the aquatic biota, we have to consider three different environments: marine environments, estuarine environments and rivers. The

pathways that should be considered in marine discharges are the ingestion of radionuclides in the main marine foods (i.e. fish, crustaceans and molluscs) and the external irradiation from gamma-emitting radionuclides on beaches. In estuarine discharges, the pathways are the ingestion of radionuclides in the foods taken from estuaries and the external irradiation from gamma-emitting radionuclides on estuarine sediments. In river discharges, the pathways are similar to those mentioned above for estuaries and marine discharges, i.e. the ingestion of radionuclides in fish taken from rivers and the external irradiation from gamma emitting radionuclides on river-bank sediments.

Apart from the pathways that should always be considered, there are other pathways that should be considered if local conditions indicate that they are appropriate, in the case of both atmospheric and aquatic discharges.

The dose to be compared with the applicable dose criterion will be the sum of the doses to the reference group from the relevant exposure pathways. For example, the total dose to a typical member of the reference group from atmospheric discharges will, in general, be the sum of the doses from external irradiation from radionuclides deposited on the ground, inhalation of radionuclides within the plume and resuspended following deposition, and ingestion of radionuclides in terrestrial foods. Therefore:

$$\underline{\text{Total dose from atmospheric discharges} = \text{Inhalation dose} + \text{External dose} + \text{Ingestion dose}}$$

Radiation Protection 122 Part II [43] explains how to calculate the dose coefficients. In order to calculate it, this guideline sets six different age groups but the workers are included in the last group (higher than 17 years). The coefficients to calculate the dose for workers, e.g. landfill workers, are in Table C1 of the EU Basic Safety Standards, whereas the dose coefficients from Tables A and B were used for the general public. The calculation of radiological doses according to these age groups, the corresponding set of dose coefficients and the derivation of exemption/clearance levels is as follows. The external γ dose is calculated using the following formula:

$$H_{ext} = D_{ext} \cdot t_e \cdot f_d \cdot f_{dec}$$

where:

H_{ext} [($\mu\text{Sv}\cdot\text{a}^{-1}$)/($\text{kBq}\cdot\text{kg}^{-1}$)] individual annual dose from external irradiation per $\text{kBq}\cdot\text{kg}^{-1}$,

D_{ext} [($\mu\text{Sv}\cdot\text{h}^{-1}$)/($\text{kBq}\cdot\text{kg}^{-1}$)] average dose rate during the exposure year,

t_e [$\text{h}\cdot\text{a}^{-1}$] exposure time,

f_d [-] dilution factor,

f_{dec} [a] decay time.

Radon is one of the radionuclides for which legislation exists regarding worker exposure. Recently, the International Commission on Radiological Protection (ICPR) [47], established a radon concentration of $1000 \text{ Bq}\cdot\text{m}^{-3}$ as the reference level in workplaces, corresponding to an effective dose of $6 \text{ mSv}\cdot\text{y}^{-1}$ for fulltime work in an environment with normal ventilation conditions. Above this concentration level, action should be taken in order to minimise exposure to radon.

The legislation about the exposure of workers is not very extensive. For this reason, we consider that all governments should be focused on the establishment of laws in order to assure the security and the health of workers and, consequently, the health of the population.

Presence in Environmental Samples

The industrial activity carried out in NORM industries can also bring about an increase of the radioactivity levels in the vicinity of those industries. With this in mind, there are different studies in the bibliography focused on the evaluation of the environmental impact of NORM industries or in the measurement of different radioisotopes associated with the activity of these industries in different environmental samples.

A large proportion of the studies reported in the bibliography that focus on the environmental impact of NORM industries are related to the phosphate industry. Some studies published to date [22, 26, 28, 49, 50] have focused on the effect of the dicalcium phosphate (DCP) industry on the ecosystem. In one such study, radioactivity levels in two different species of algae (*Cladophora glomerata* (green algae) and *Cynodon dactylon* (bank grass)) were evaluated [28]. The samples were from different points along the course of the Ebro River. The results presented in this study showed that the presence of the DCP factory has had a significant influence on levels of radioactivity, as the highest activity values were observed in algae samples taken from the area surrounding that factory (Flix), where isotopes such as ^{214}Bi and ^{214}Pb presented activity values of $105 \pm 43 \text{ Bq}\cdot\text{kg}^{-1}$ and $100 \pm 58 \text{ Bq}\cdot\text{kg}^{-1}$, respectively. Insignificant differences were observed between the two biological samples analysed for uranium. However, ^{230}Th activity was found to be higher in green algae samples than in bank grass samples. This radionuclide is generated in solution by the radioactive decay of the soluble ^{234}U , which is an isotope also originated in the ^{238}U decay chain.

The same DCP plant was studied in the study of Casacuberta *et al.* [26]. In this study, a radiological risk assessment was conducted to estimate the dose that humans would receive due to the ingestion of chicken meat previously fed with certain quantities of DCP in their diets. The results suggested that the maximum radiological doses are $11 \pm 2 \mu\text{Sv}\cdot\text{y}^{-1}$. The authors conclude that the results suggest that human risk is small, although additional testing should be considered.

Al Attar *et al.* [51] studied the radiological impact of Syrian phosphogypsum (PG) piles in the compartments of the surrounding ecosystem. The study investigates the activity concentration of radionuclides (^{238}U , ^{232}Th , ^{210}Po , ^{210}Pb and ^{226}Ra) in the raw material, products and by-products of the phosphoric acid industry in Syria. The activity concentration of the radionuclides was also determined in the surrounding ecosystem to draw an overall assessment of the radiological impact of PG piles. The data revealed that the ^{226}Ra average concentration was $318 \text{ Bq}\cdot\text{kg}^{-1}$, lower than the EPA recommended for PG use in agriculture. The other radionuclides studied were found at a maximum concentration of $1014 \text{ Bq}\cdot\text{kg}^{-1}$ (^{232}Th). The annual effective dose of the radionuclides studied via inhalation and external exposure of gamma rays was only $0.082 \text{ mSv}\cdot\text{y}^{-1}$. When samples of soils were analysed, the soils situated in western and north-western wind direction were contrasted with the higher concentration of the radionuclides in soils sampled from the eastern sites. The authors recommended establishing a 50m wide protection zone around the PG piles. The metal refinery and the extraction of metals also have been evaluated for their environmental impact. For instance, Kelly *et al.* [52] analysed different environmental samples such as soil, street dust, water, grass and leaf vegetables at different distances from a tin factory located in the northeast of England. They failed to find any correlation between ^{210}Po concentrations and distance from the refinery. The overall conclusion of this work was that there was no clear evidence of radionuclide contamination above normal background levels from atmospheric discharges dust emissions from the factory or vehicles transporting materials to or from it.

Another study in the literature showed the effect of the industry of thorium extraction. Soil samples from the district of Kanyakumari (India) were studied to evaluate the assessment of radiological indices [53]. The mean activity concentrations for ^{232}Th and ^{40}K were greater than the world average values reported by United Nations Scientific Committee on Effects of Atomic Radiation for areas of normal background radiation. Radiological indices were estimated for the radiation of the natural radioactivity of all soil samples. These results indicate that the mean activities of the studied radionuclides are 31 ± 9 , 206 ± 27 and $1590 \pm 490 \text{ Bq}\cdot\text{kg}^{-1}$, respectively, for ^{226}Ra , ^{232}Th and ^{40}K for high background radiation areas. For the low background radiation areas samples, the activity concentrations are 8 ± 5 , 22 ± 20 and $295 \pm 84 \text{ Bq}\cdot\text{kg}^{-1}$, respectively, for ^{226}Ra , ^{232}Th and ^{40}K . The estimated mean total absorbed dose in air from activity concentration of ^{226}Ra , ^{232}Th and ^{40}K in high background radiation areas (that are very rich in monazite a prime ore of thorium) is $200 \pm 30 \text{ nGy}\cdot\text{h}^{-1}$ and in low background radiation areas is $29 \pm 14 \text{ nGy}\cdot\text{h}^{-1}$.

Different areas of India (Bagjata and Banduhurang) were studied to find different natural radionuclides in fish samples around uranium mining areas [54]. The mean activity of U(nat), ^{226}Ra , ^{230}Th and ^{210}Po in the fish samples was found to be 0.05, 0.19, 0.29 and $0.95 \text{ Bq}\cdot\text{kg}^{-1}$ fresh, respectively, in the Bagjata mining area, while for Banduhurang mining area it was estimated to be 0.08, 0.41, 0.22 and $2.48 \text{ Bq}\cdot\text{kg}^{-1}$ fresh, respectively. The ingestion dose was computed to be 1.88 and $4.16 \mu\text{Sv}\cdot\text{y}^{-1}$,

respectively, for both the areas which is much below the 1 mSv limit set in the new International Commission on Radiological Protection (ICRP) recommendations.

The effect of Turkish coal power plants was also evaluated in the study of Ugur *et al.* [55]. The study focused on the coast of Aegean Sea, which is affected by different coal power plants and fertilizer plants. In this study, the activity concentrations of ^{210}Po and ^{210}Pb were determined in mussel samples (*Mytilus galloprovincialis*) collected from the Turkish coast. The results showed that ^{210}Po concentrations in mussels varied between 53 ± 4 and $1960 \pm 60 \text{ Bq}\cdot\text{kg}^{-1}$. The highest activity ^{210}Po concentrations were determined in winter samples of mussels with a shell length of 4–6 cm. In general, it was observed that the ^{210}Pb concentration levels in mussels were lower than ^{210}Po concentrations. The $^{210}\text{Po}/^{210}\text{Pb}$ activity ratio in mussel samples varied between 3.64 and 137, with a mean value of 26.0. The mean value is comparable with the data given by Carvalho *et al.* [56] in the same species in Portugal.

The study of Papastefanou *et al.* [35] focused on the determination of radioactivity in the raw material of coal power plants located in Greece. The combustion of coal results in the release into the environment of some natural radioactivity, the major part of which (99%) escapes as very fine particles, while the rest in fly ash. The activity concentration of natural radionuclides measured in coals originating from coal mines in Greece varied from 117 to 435 $\text{Bq}\cdot\text{kg}^{-1}$ for ^{238}U , from 44 to 255 $\text{Bq}\cdot\text{kg}^{-1}$ for ^{226}Ra , from 59 to 205 $\text{Bq}\cdot\text{kg}^{-1}$ for ^{210}Pb , from 9 to 41 $\text{Bq}\cdot\text{kg}^{-1}$ for ^{228}Ra (^{232}Th) and from 59 to 227 $\text{Bq}\cdot\text{kg}^{-1}$ for ^{40}K . In this study, the authors suggested that the type of coal to be burned in a coal-fired power plant must be chosen carefully and must be monitored for radioactivity before the combustion. If for reasons of economy, a coal containing radioactivity must be burned, then the ^{226}Ra concentration should not exceed the rate of 370 $\text{Bq}\cdot\text{kg}^{-1}$.

Conclusion

The results of the studies mentioned in this chapter highlight the idea that exhaustive monitoring studies of different industries classified as NORM industries are essential. Moreover, the current legislation should be revised in order to include reference values of radionuclides in different raw materials, products and by-products of this kind of industries. This legislation is important to protect the workers and the member of population in general as well as to control the possible impact to the environment.

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1.3. Mostres ambientals

UNIVERSITAT ROVIRA I VIRGILI
DESENVOLUPAMENT DE TÈCNiques ANALÍTIQUES PER A LA DETERMINACIÓ DE RADIONÚCLIDS
Montserrat Mola Arques
Dipòsit Legal: T.1294-2013

Tot i que la radioactivitat natural engloba aquelles fonts radioactives que no han estat originades a causa de cap activitat humana, com ara la radiació derivada de la desintegració dels radionúclids originats en l'escorça terrestre i la radiació còsmica, també s'ha vist en el capítol anterior la problemàtica ambiental generada a partir de la presència incontrolada de radionúclids naturals produïts per la indústria NORM. Aquestes activitats industrials contribueixen a augmentar els nivells de radionúclids per sobre dels nivells naturals [32] i per tant, és important tenir un control dels nivells de radioactivitat natural mitjançant l'estudi de diverses mostres ambientals del seu entorn. Segons el tipus d'indústria NORM a estudiar i els radionúclids generats en aquestes, s'estudien uns radionúclids o d'altres. En la majoria de casos aquestes activitats industrials contribueixen a l'augment dels descendents de les cadenes de l' ^{238}U i del ^{232}Th , concretament els radionúclids més generats pels principals sectors d'aquestes indústries són l' ^{238}U , el ^{232}Th , el ^{226}Ra i el ^{228}Ra [45].

Per a detectar i quantificar aquests elements individuals és necessari desenvolupar i validar mètodes sensibles i ràpids per a l'anàlisi. Aquests mètodes inclouen diferents passos que ens ajuden a aconseguir una separació òptima del radionúclid d'interès de la resta d'interferents. Generalment, aquests passos inclouen diferents formes de preparar la mostra com ara la preconcentració de radionúclids mitjançant l'addició d'un agent coprecipitant o l'extracció i separació dels radionúclids mitjançant una resina específica. Els mètodes principalment seran escollits tenint en compte el detector a utilitzar en la mesura i el radionúclid individual a quantificar (abundància ambiental, pic energètic, equilibris seculars amb els seus descendents, característiques físico-químiques, etc.).

Existeixen molts tipus de productes utilitzats amb les finalitats anomenades anteriorment i utilitzats per al pretractament de la mostra. Ara bé, el fet de comentar diferents metodiques utilitzades en diversos estudis actuals ens ajudarà a obtenir una visió global de la investigació dintre aquest camp i cap a on evoluciona. Aquesta informació l'hem recopilat d'una forma visual mitjançant les Taules 1.2. i 1.3. on s'observen diverses metodiques classificades segons el radionúclid a extraure de mostres ambientals de diferents orígens. Ens hem centrat en els principals radionúclids alfa del Ra (Taula 1.2.) i de l'U i Th (Taula 1.3.) trobats en la bibliografia i la seva detecció mitjançant els detectors més utilitzats (espectrometria alfa, espectrometria de masses, espectrometria gamma i escintil·lació líquida). També es mostra el rendiment químic i límit de detecció aconseguits en cada mètode per comparar els diferents procediments.

1.3.1. Preparació de mostres ambientals

Depenent del detector a utilitzar el procediment de la preparativa de les mostres requerirà un pretractament més o menys exhaustiu. Generalment, per a aconseguir la determinació individual de radionúclids sense interferències és recomanable

realitzar diversos passos dintre la preparativa partint d'una mostra líquida amb els radionúclids en dissolució.

En primer lloc, diferenciarem entre la preparativa de mostres líquides i mostres sòlides segons la manera habitual de treballar que trobem en la bibliografia. En el cas de mostres líquides és necessari filtrar el volum de mostra líquida a través d'un filtre de 0.45 µm de porus per a treure principalment matèria orgànica en suspensió, etc., i acidificar-la per a ajudar a que es mantinguin els components de la mostra en dissolució. Ara bé, en el cas de partir d'una mostra sòlida ens trobem amb tres tipus principals de matriu on caldria diferenciar entre: mostres minerals com ara un sòl o fangs, mostres amb molta matèria orgànica com ara mostres de biota, i també mostres particulades, és a dir, la partícules ambientals aèries captades a través d'una bomba de succió (volum i temps determinats) i concentrades a sobre d'un filtre. Totes elles es sotmeten a una dessecació a temperatures properes als 90 °C, durant 2 dies aproximadament i després com és necessari posar en dissolució els radionúclids que conté la mostra, es realitza una digestió de la matriu. Hi ha varis tipus de digestions, algunes de les més utilitzades són basades en la digestió per fusió (fusió alcalina, etc.) [46-48] o la digestió àcida segons el mètode descrit per l'Agència de Protecció Ambiental Americana (EPA) [49,50], les quals les trobem descrites en molts treballs. Però a part de que són digestions que consumeixen molt de temps de treball i grans volums de reactius, en alguns casos no digereixen totalment la matriu sòlida. Principalment aquest fet succeeix en mostres amb un elevat contingut en silicats on llavors s'aplica la digestió àcida total amb l'ús de l'àcid fluorhídric (HF) [51,52]. Aquesta digestió no coberta és molt agressiva i tòxica, per això en els últims anys s'ha incrementat l'ús habitual de la digestió assistida per microones on sota altes pressions i temperatures controlades, s'aconsegueixen digestions ràpides i efectives per a mostres inferiors a ~1 g [53-55]. A continuació mitjançant els exemples de les taules explicarem les metodiques més utilitzades en el cas de cada radionúclid escollit, partint de diferents matrius de mostres ambientals.

1.3.2. Radi

En la Taula 1.2. podem veure l'ús de diversos mètodes de preconcentració, purificació i/o extracció del radi, majoritàriament en els casos on la detecció es realitza per espectrometria alfa i per ICP-MS. Hem de tenir en compte que la detecció per espectrometria alfa és la més adient per a la mesura de radionúclids, ja que és capaç de realitzar mesures radioactives de nivells baixos. Però els seus temps llargs de comptatge han donat pas al desenvolupament de mètodes amb l'ús d'una tècnica menys econòmica com ara l'espectrometria de masses. Ara bé, amb les dues tècniques anteriors es requereix obtenir les mostres lliures d'ions d'interferents per a obtenir resultats òptims, ja que en les dues apareix la supressió o distorsió de senyal degut a la matriu de la mostra. Per exemple en el cas de la mesura del Ra amb aquests detectors és primordial l'eliminació dels ions de Ba, d'Sr i de Ca, els quals

són elements amb un comportament químic semblant i interfereixen en la mesura. Tal com explica la bibliografia, la detecció i quantificació del Ra de les mostres ambientals és un punt crític en quant apareixen quantitats baixes de Ba ($10 \mu\text{g}$) en la mostra, principalment en el pas d'electrodeposició de la mostra en espectrometria alfa. D'acord amb aquests fets es necessari dur a terme tractaments de mostra més acurats i selectius possibles.

Un altre factor a tenir en compte en el cas de l'espectrometria alfa, és la possibilitat de l'autoabsorció de la senyal de les partícules alfa per part de la mateixa mostra, ja que aquestes són frenades fàcilment. Per això la mostra ha d'estar dipositada el més llisa i uniformement possible sota el detector. Per aconseguir aquests prerequisits, s'han desenvolupat una sèrie de tècniques de preparació de la font abans de la seva mesura: l'evaporació directa, l'electroesprai, la coprecipitació i l'electrodeposició. Segons bibliografia, els mètodes més utilitzats actualment en el cas del radi i altres són la coprecipitació [56-58] i l'electrodeposició [48,59-61].

La taula presenta diferències a l'hora de plantejar els processos de tractament de la mostra amb l'ús d'altres detectors com el gamma o el d'escintil·lació líquida. Per exemple, en el cas del detector gamma no és necessari realitzar una destrucció de la matriu de la mostra per a la seva mesura, però sí que s'ha de tenir en compte una correcta homogeneïtzació d'aquesta. En l'espectrometria gamma i l'escintil·lació líquida (LSC) trobem majoritàriament tractaments simples amb l'ús de la coprecipitació per tal de concentrar els radionúclids [52,62-64] i amb la necessitat de mesurar volums més grans de mostra [65] ja que la sensibilitat d'aquests equips amb aquests radionúclids resulta baixa. En els dos casos de detecció s'aplica un temps llarg d'espera on s'assoleix l'equilibri secular entre el progenitor (Ra) i els seus descendents de vida mitja curta, resultant mètodes molt poc ràpids.

Un cop anomenades certes característiques a tenir en compte de la mostra segons els diferents detectors utilitzats, s'explicarà de forma general les principals tècniques de pretractament de la mostra. En la taula veiem tècniques de preconcentració i d'extracció diverses i utilitzades de forma variada segons els criteris utilitzats per cada grup d'investigació, sempre buscant millores en la tècnica, ja sigui escurçar els temps, augmentar els rendiments, baixar els nivells de detecció, pensant en una química més verda utilitzant menys volum de reactius i dissolvents, etc. La tècnica de coprecipitació per a preconcentrar i/o separar una sèrie de radionúclids en forma de precipitat o en solució de la resta de matriu és de les més utilitzades. Els mètodes més populars són la coprecipitació amb sulfats ($\text{Ba}(\text{Ra})\text{SO}_4$ i/o $\text{Pb}(\text{Ra})\text{SO}_4$) [48,52,56,60,62-64,66] o bé amb l' MnO_2 [57,67,68]. A més, molts autors destaquen l'addició d'alguna sal, com ara l'EDTA, de citrat, el Na_2SO_4 i el DTPA de sodi [56,60,63,69] a l'hora de realitzar el precipitat o després, amb la qual cosa els components majoritaris interferents (Ca, Mg, etc.) s'agreguen de forma molt nombrosa a aquestes, facilitant la separació del radionúclid d'interès.

També hi han altres tècniques per tal de preconcentrar i extraure els radionúclids de radi com l'aparició de la fibra d' MnO_2 i el Rad Disc on es queda fixat d'una manera selectiva provinent de llargs volums de mostra d'aigua [70-72]. Aquests són bons mètodes per a obtenir la separació d'aquest respecte l'urani i el tori amb una extracció ràpida [59]. Tot i així, sabem que elevades concentracions d'interferents (NH_4^+ , K i Ba) difícils d'eliminar, continuaran provocant interferències significants a la mesura, el que fa que aparegui la necessitat d'afegir més tipus de tractaments d'extracció i/o purificació.

Un dels mètodes més emprats en els darrers anys, són les resines d'intercanvi iònic. Aquestes combinen la selectivitat de les tècniques convencionals (extracció líquid-líquid) amb la versatilitat i simplicitat de les columnes cromatogràfiques. Aquest mètode de separació és molt popular en les anàlisis radioquímiques actuals, pel seu gran estalvi amb reactius i amb temps de tractament de mostra. El seu funcionament es basa en una extracció en fase sòlida (fase estacionària sobre un suport inert) regida principalment per interaccions d'intercanvi iònic. Ara bé segons ens indica la bibliografia es diferencien dos tipus de resines d'intercanvi iònic: les tradicionals (a) i les d'extracció cromatogràfica (b) [51,73].

- a) En aquest cas la retenció dels cations o anions metàl·lics es produeix per un procés d'intercanvi iònic o també hi ha exemples en què s'han format complexos amb els ions metàl·lics i aquests amb la resina.
- b) El mode operatiu s'inicia amb l'addició de reactius per a formar un complex amb l'ió metàl·lic o un complex neutre metall-orgànic, seguit de la extracció en fase sòlida del complex per un extractant.

En el cas del radi tal i com podem observar en la Taula majoritàriament s'utilitzen resines d'intercanvi iònic tradicionals: resines d'intercanvi catiónic fort amb la forma iònica composta pel ió hidrur (H^+), que són la Dowex 50W-X8 i la Bio-Rad AG-50W-X12. Resines d'intercanvi aniònic fort amb la forma iònica composta pel ió clorur (Cl^-), que són la Dowex 1-X8 i la Bio-Rad AG1-X8. I finalment una resina quelatant amb el grup funcional iminodiacetat, la Chelex 100. Hi ha varis autors que defensen com a procediment per a obtenir una separació del Ra i el Ba més efectiva, l'ús d'una o varies resines d'intercanvi iònic. Per exemple, en el cas de treballar amb una mostra complexa s'han aplicat mètodes amb dues resines d'intercanvi iònic de forma seqüencial o bé s'ha afegit un altre tipus de resina [48,58,60,61,68,70].

També s'utilitzen diverses resines d'extracció cromatogràfica per aconseguir la fracció del radi lliure dels principals interferents (Sr i Ba i Pb). Les resines Sr-Spec i Ln (Dipex) en són uns clars exemples. Com a material específic i selectiu utilitzada en alguns estudis trobem la resina d'Sr (Figura 1.7.), la qual té un anell èter corona com a extractant (*4,4'-(5')-di-*t*-butylcyclohexane-18-crown-6*). Els ions de Ba, Sr i Pb queden retinguts a la resina amb una solució d' HNO_3 2-3 M, mentre que el Ra no

queda retingut i s'obté purificat degut a les diferències de mides entre alcalinoterris [67,68,70].

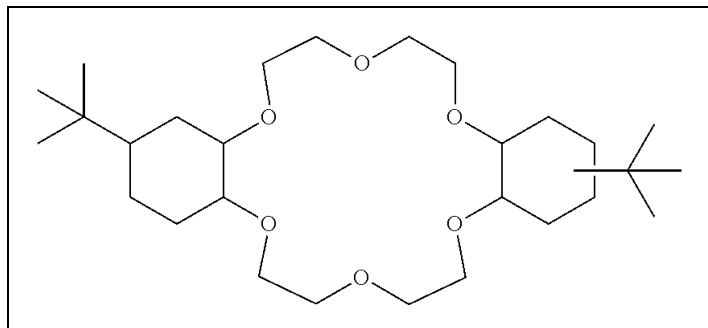


Figura 1.7. Estructura del sistema extractant de la resina Sr-Spec.

L'equilibri d'aquesta resina amb el Sr^{2+} (Pb^{2+} i Ba^{2+}), és el següent:



En els treballs de Thakkar i col. [58] i Benkhedda i col. [74] trobem l'extracció cromatogràfica del radi a partir de la resina Ln-spec amb el grup extractant anomenat *di(2-ethylhexyl)* i *orthophosphoric acid (HDEHP)*). Per exemple en el treball de Benkhedda i col. [74] es va passar la mostra amb EDTA per la resina Ln, aconseguint una elució quantitativa del ^{226}Ra . Seguidament aquesta fracció es va passar a través de la resina Sr-Spec, on es van quedar retinguts el Ba i el Sr. Mitjançant l'ICP-MS es van obtenir unes recuperacions entre el 96 i els 105 % i un MDA de 17 mBq L^{-1} .

En relació a la caracterització individual dels diferents emissors alfa estudiats en mostres ambientals podem destacar el treball realitzat per Jia i col. [61] (Taula 1.2. i 1.3.) en el que es realitza una caracterització completa de tres radionúclids del radi, d'urani i del tori. Per a obtenir la detecció mitjançant espectrometria alfa és necessari la realització de dos mètodes de preconcentració i de separació, un aplicat per a la detecció del radi i l'altre per a l'urani i el tori. Per tant, podem veure en el cas dels actínids d'urani i tori que les extraccions durant el pretractament de la mostra poden realitzar-se en alguns casos mitjançant la mateixa tècnica, per això a continuació els presentem de forma conjunta.

Taula 1.2. Mostra ambiental, tractament de la mostra, detectors emprats, recuperació (η), límits de detecció per al Radi.

Mostres ambientals	Radionúclids	Preconcentració	Separació o purificació	η (%)	Límit de detecció	REF.
Espectrometria α						
Sòl granític (0,5g)	^{226}Ra , ^{223}Ra	$\text{PbSO}_4(\text{Ra})/\text{Ba}(\text{Ra})\text{SO}_4$ EDTA	-	57	5 Bq Kg^{-1}	[56]
Aigua pou/mar (1L)	^{226}Ra , ^{223}Ra , ^{224}Ra	Rad Disc	AG50W-X12	92	0,2 mBq	[59]
Aigua/sòl	^{226}Ra , ^{228}Ra	$\text{Pb}(\text{Ra})\text{SO}_4/\text{EDTA}$	AG1-X8	70 (m. líquid)	0,4 - 3 mBq L^{-1}	[60]
Aigua (2L)/sòl (0,5g)	^{228}Ra , ^{226}Ra , ^{224}Ra , ^{223}Ra	$\text{Ba}(\text{Ra})\text{SO}_4$	AG50W-X12 TOPO/AG50W-X8/ CyDTA	40 (m. sòlid) 86,2	0,7 - 5 Bq Kg^{-1} 0,11 mBq L^{-1} (m. l. **)/ 0,43 mBq kg^{-1} (m. s. **)	[48]
Aigua (0,5-2L)	^{226}Ra	MnO_2/HAc EDTA	-	88 - 98	-	[57]
Aigua (0,5mL-1L)	^{226}Ra , ^{223}Ra	-	AG50W-X8 / Ln	93	3,33 mBq L^{-1}	[58]
A. * embotellada (1 i 2L-100mL)	^{226}Ra , ^{228}Ra , ^{224}Ra	$\text{Ba}(\text{Ra})\text{SO}_4/\text{FeCl}_3$	TOPO / AG50W-X8	86,2	0,11 mBq L^{-1}	[61]
Espectrometria de masses						
Aigua mar (120 - 500 mL)	^{226}Ra , ^{228}Ra	Fibra de Mn/ $\text{Sr}(\text{Ra})\text{SO}_4/\text{Sr}(\text{Ra})\text{CO}_3$	AG50-X8 / Sr-spec	90	~0,1 fg	[70]
Aigua geotèrmica (5L)/ Sediments (0,5g)	^{226}Ra	$\text{Ba}(\text{Ra})\text{SO}_4$	AG50W-X12	60,5 - 85,9	0,02 mBq L^{-1} 0,10 Bq Kg^{-1}	[66]
Aigua mineral (0,2 L)	^{226}Ra	MnO_2	Sr-spec	72	0,02 fg mL^{-1}	[67]
Aigua (20 mL)	^{226}Ra	-	Ln + EDTA / Sr-Spec	96 - 105	17 mBq L^{-1}	[74]
A. * mar (200mL)/Coral (0,4 - 1,8g)	^{226}Ra	MnO_2	(AG50W-X8)*2 / Sr-Spec	80	-	[68]

*Aigua

** Mostra líquida/mostra sòlida

Taula 1.2. Mostra ambiental, tractament de la mostra, detectors emprats, recuperació (η), límits de detecció per al Radi (cont.).

Mostres ambientals	Radionúclids	Preconcentració	Separació o purificació	η (%)	Límit de detecció	REF.
Escintil·lació líquida						
Sediment (5g)	^{226}Ra , ^{224}Ra	Ba(Ra)SO ₄ /H ₂ SO ₄ /BaCl ₂	-	22,7-84,4	<10 Bq Kg ⁻¹	[52]
Aigua (1L)	^{226}Ra	Ba(Ra)SO ₄ /Ba(Ra)CO ₃	-	79,6 - 99,8	4,6-14 mBq L ⁻¹	[62]
Espectrometria γ						
Aigua	^{228}Ra , ^{226}Ra	Ba/Pb(Ra)SO ₄ + citrat	-	85 - 90	-	[63]
Aigua (3L)	^{228}Ra , ^{226}Ra	Ba(Ra)SO ₄ /Fe(OH) ₃	-	<85 - 100	14 - 36 mBq L ⁻¹	[64]
Aigua subterrània/mar (20-150 L)	^{228}Ra , ^{226}Ra	Fibra de Mn	-	<95	-	[71]
Aigua llac	^{226}Ra , ^{228}Ra , ^{224}Ra , ^{223}Ra	Fibra de Mn	-	-	-	[72]
Sediment (200g)	^{226}Ra	-	-	-	-	[65]

1.3.3. Urani i Tori

El mètodes que veiem en la Taula 1.3. ens mostren que la mesura dels radionúclids d'U i de Th majoritàriament es realitza per espectrometria alfa i espectrometria de masses, amb els que es necessita aplicar diverses tècniques de pretractament abans de realitzar la mesura. També trobem algun treball recent com ara el de Antoliu i col. [75] amb una detecció d'U mitjançant LSC després de la seva separació i extracció previ amb la resina d'intercanvi iònic Chelex 100 on s'obtenen límits de detecció més alts (30 mBq L^{-1}) que els obtinguts per espectrometria alfa utilitzant el mateix mètode d'extracció (1 mBq L^{-1}) [76].

Tal i com veiem en la Taula, l'U i el Th es troben majoritàriament preconcentrats en forma de precipitats d'hidròxids de ferro [28,61,77-79]. Altres autors, justifiquen l'ús d'altres agents coprecipitants, ja que en mostres de sòls on hi trobem alts continguts de ferro natural és recomanable eliminar-lo abans d'aplicar els diferents mètodes de separació (resines cromatogràfiques, etc.) [51,80]. És el cas de treballs com ara el de Michel i col. [51] on la preconcentració de radionúclids es va realitzar mitjançant l'oxalat de calci, amb l'adició de $\text{Ca}(\text{NO}_3)_2$ i àcid oxàlic.

Existeixen diferents tipus de tècniques per a realitzar el procés d'extracció i/o purificació de l'urani i el tori de la resta de components d'una mostra. Entre aquests mètodes hi trobem l'extracció amb solvent (extracció líquid-líquid), la cromatografia d'intercanvi iònic tradicional i l'extracció cromatogràfica.

Actualment aquest tipus de separació líquid-líquid on es necessita un volum considerable de solvents orgànics és considera poc respectuós amb el medi ambient i no gaire reproducible. Tot i així, trobem estudis actuals que determinen l'U i el Th mitjançant l'extracció líquid-líquid utilitzant el tri-n-butil fosfat (TBP)/Xilè [28,35,56]. En altres estudis veiem que també és fan servir aquests tipus d'extraccions per a obtenir una fracció lliure d'interferents (sobretot traces de ferro), en el pas previ de la detecció [51].

Recentment s'ha publicat un estudi per Charalambous i col. [76] on s'utilitza una mateixa resina d'intercanvi iònic tradicional, la quelatant Chelex 100, per a realitzar la preconcentració i extracció de l'U en mostres d'aigua subterrània, obtenint generalment recuperacions químiques del 99%, amb MDAs de 1 mBq L^{-1} . Ara bé, en el cas d'ambdós radionúclids les resines d'intercanvi iònic tradicionals s'utilitzen majoritàriament abans o després d'una resina d'extracció cromatogràfica, per tal d'aconseguir una purificació i/ separació completa de la fracció obtinguda [28,51,80]. Per tant, molts cops també trobem una combinació de resines per a obtenir les fraccions a determinar d'urani i tori lliure d'interferents. Per exemple, en el cas de l'estudi realitzat per Michel i col. [51] es va utilitzar en primer lloc una resina d'extracció cromatogràfica, la qual va retenir l'U i el Th deixant passar la resta de interferents. En aquest cas, l'U i el Th és van eluir conjuntament i després es van separar mitjançant la resina d'intercanvi aniònic anomenada Bio Rad AG1-X8. Amb

aquesta resina l'U és eluït en primer lloc i la fracció recuperada del Th és processada una segona vegada per la mateixa resina d'intercanvi iònic per tal de purificar-la.

En el cas de l'urani i el tori s'ha treballat amb una sèrie de resines d'extracció cromatogràfica específiques aplicades a mostres ambientals conegudes com ara l'Uteva, la TRU, o bé d'altres modificades i menys conegudes com ara la Microthene-TOPO, la MCM-41 (*silica mesoporus*) amb un grup fural, la MACE (*crown 2-ethyl-N-benzyl-4,7,10,13,16-pentaoxa-1-azacyclooctadecane*) i la CPMA (*N-(o-carboxyfenyl) maleamic acid*) la qual a la seva superfície té un polímer ió imprès (IIPs).

Segons bibliografia, la resina més utilitzada per a l'extracció d'aquests isòtops és la Uteva (Figura 1.8.), on el material extractant és el *diamyl amylphosphonate* ($(C_5H_{11}O)_2C_5H_{11}PO$ (DAAP) adsorbit sobre un substrat polimèric inert (Amberline XAD-7), la qual es capaç d'extreure actínids hexavalents i tetravalents [51,77-81].

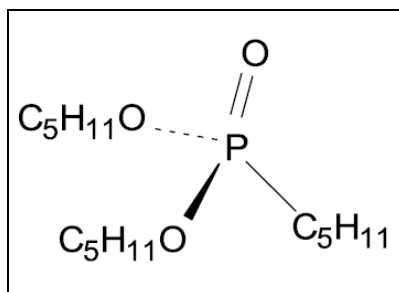
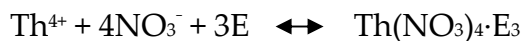
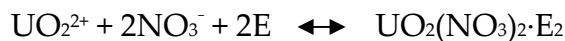


Figura 1.8. Estructura del component extractant de la resina Uteva.

L'origen d'aquesta resina fou solament utilitzada per extraure l'urani, però també s'ha vist que es poden extreure l'U i el Th, de manera conjunta [51] o de manera seqüencial [80].

L'equilibri d'aquesta resina amb el U i el Th és el següent (E=extractant):



Una altra resina específica dels transurànics aplicada en la separació del U en varis tipus de mostres ambientals és la TRU, composta pel sistema d'extracció: CMPO (*octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide* dissolt en tri-n-butyl phosphate (TBP)) [82,83]. En el treball de Rozmaric i col. [82] utilitzant aquesta resina amb mostres d'aigua i sòl es van obtenir unes recuperacions químiques del 97.5 i 92.5 % amb límits de detecció del 0.2 i 0.4 $\mu\text{g L}^{-1}$ per a l'U i el Th, respectivament, mitjançant la detecció per ICP-MS.

També hi ha desenvolupada una altra resina específica d'U i Th, la resina *polyethylene-TOPO (trioctylphosphine oxide)*. Tal i com hem comentat anteriorment, Jia i col. [48] varen desenvolupar una extracció cromatogràfica efectiva en quant a la separació del Ra i el Ba, de l'U i el Th. En els procediments, el precipitat es dissol amb HCl 8 M i temperatura, i es passa a través de la columna d'extracció cromatogràfica *polyethylene-TOPO (trioctylphosphine oxide)*, on l'U i el Th es queden retinguts a la columna i el Ra i el Ba s'elueixen directament. A més, aquesta resina d'extracció cromatogràfica s'utilitza en un altre estudi realitzat pels mateixos autors [61], per tal d'aconseguir la separació entre l'U i el Th, si es condicionada amb HNO₃ 2 M. Finalment, es van obtenir les separacions i després les mesures mitjançant espectrometria alfa amb bones recuperacions i MDAs baixos en els dos casos.

Finalment cal destacar la recent síntesi de noves resines o nous líquids d'extracció en el cas de l'U i/o Th [84-86]. Per exemple, la modificada *silica mesoporus (MCM-41)* utilitzant un grup fural (*5-nitro-2-furaldehyde*) la qual va ser aplicada per tal de realitzar una extracció simultània d'ambdós radionúclids (mesura mitjançant ICP-OES) en mostres d'aigua (100 mL d'aigua dolça i de mar) [84]. En una altre estudi, un monòmer funcional el *N-(o-carboxyphenyl) maleamic acid (CPMA)* va ser sintetitzat per a la preparació d'un polímer específic de Th (IV) imprinat (IIPs), on el Th era acomplexat per grups carboxil. Finalment, es va comprovar el mètode a partir de mostres ambientals com ara, bàlsam de fulles de perera i mostra de sòl [85]. Com podem veure amb aquestes noves resines i mitjançant la detecció amb ICP-OES i ICP-AES, s'obtenen recuperacions químiques de més del 92 % i límits de detecció inferior al ng mL⁻¹. També trobem l'extracció de Th en mostres minerals (Bastnaesite) mitjançant un nou solvent, el MACE (*crown 2-ethyl-N-benzyl-4,7,10,13,16-pentaoxa-1-azacyclooctadecane*) també anomenat monoaza-18-crown-6, amb el qual s'obtenen bones recuperacions i un MDA més elevat de 0.18 µg L⁻¹ [86].

Existeixen més compostos nous per a l'extracció d'aquests radionúclids en l'actualitat (noves fórmules de líquids iònics i resines), però aquests generalment encara no han estat aplicats i comprovats en mostres ambientals [87-89]. Per exemple, en el cas del desenvolupament de líquids iònics es pot destacar el treball realitzat per Srncik i col. [87] on avaluen la capacitat de diferents líquids iònics per a l'extracció d'urani. En general, els treballs relacionats amb aquesta temàtica empenen líquids iònics per a extraure radionúclids dels efluents líquids produïts en el funcionament de les centrals nuclears ja que, aquests poden ser utilitzats en grans volums de mostra i posteriorment poden ser reutilitzats.

Taula 1.3. Mostra ambiental, tractament de la mostra, detectors emprats, recuperació (η), límits de detecció per a l'Uraní i el Tori.

Mostres ambientals	Radionúclids	Preconcentració	Separació o purificació	η (%)	Límit detecció	REF.
Espectrometria α						
Aigua embotellada (2 L, 1 L, 100 mL)	^{238}U , ^{234}U , ^{235}U , ^{230}Th , ^{232}Th , ^{228}Th	BaSO ₄ / FeCl ₃	TOPO / AG50W-X8	74,7 - 75,4	0,0008 (^{230}Th) mBq L ⁻¹ 0,22 (^{234}U , ^{238}U) mBq L ⁻¹	[61]
Aigua subterrània (1L)	^{238}U	-	Chelex 100	99	1 mBq L ⁻¹	[76]
Aigua mar (1L)	^{238}U , ^{234}U , ^{235}U	FeCl ₃	D 1-X8 / Uteva	72	0,7 mBq L ⁻¹	[79]
Sediment (NORM)/ Aigua riu	^{238}U , ^{234}U , ^{230}Th , ^{232}Th	FeCl ₃	TBP/Xilè / AG1-X8	45 - 65	-	[28]
Sediment i sol (5g)	^{238}U , ^{232}Th	CaC ₂ O ₄	Uteva /2*(AG1-X8)/ Di-isopropylether	80 - 95	-	[51]
Aigua pou (500 mL)	^{238}U , ^{232}Th	Nd(NO ₃) ₃ / (Nd(OH) ₃)	Uteva/ D 1-X8	58,4 (U) 23,1 (Th)	0,31 mBq L ⁻¹ (U) 0,19 mBq L ⁻¹ (Th)	[80]
Aigua riu/mar (2L)	^{238}U , ^{234}U	FeCl ₃	Uteva	25 - 67	0,3 mBq L ⁻¹	[77]
Espectrometria de masses						
Mostra mediambiental font radioactiva (1,8g)	^{238}U , ^{235}U	-	TRU	75	1 ng ^{238}U 11,4 pg ^{235}U	[83]
Aigua mar/ dolça (100mL)	U(VI), Th(IV)	-	MCM-41	92 - 97	0,3 $\mu\text{g L}^{-1}$	[84]
Aigua (2 L)/sol (10g)	U, Th	-	TRU	92,5 - 97,5 (U) 77,5 - 92,5 (Th)	0,2 U i 0,4 Th $\mu\text{g L}^{-1}$	[82]
Fulles perera/sol (0,5-1g)	Th (IV)	-	CPMA + (IIPs)	96 - 102,5	0,51 ng mL ⁻¹	[85]
A* mar/riu/carbonats (100mg)	U (VI)	-	Uteva	91 - 99	-	[81]
A* mar gelada (100 - 30 mL)	^{238}U	FeCl ₃	AG1-X8 / Uteva	143	10 pg	[78]
Mineral Bastnaesite (1 g)	Th (IV)	-	MACE	98,5	0,181 $\mu\text{g mL}^{-1}$	[86]
A* riu i mar (2L)	^{236}U , ^{238}U	FeCl ₃	Uteva	-	2,4*10 ⁻⁹ $\mu\text{g L}^{-1}$	[77]

*Aigua

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1.4. Automatismes

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Fins l'actualitat, s'han desenvolupat molts mètodes analítics per tal d'aconseguir la preconcentració i separació de radionúclids individuals de forma manual, aconseguint una font lliure d'interferents per a la seva mesura i quantificació mitjançant equips radiomètrics. Ara bé, aquests mètodes tenen una sèrie de limitacions degudes a la incertesa que apareix al no tenir controlades i fixades de forma acurada i precisa una sèrie de variables, com ara la velocitat de separació i extracció durant el procés, el volum exacte d'eluent i reactius, la precisió de cada tècnic, entre d'altres. Respecte a aquesta última, s'ha de tenir en compte que hi ha una gran manipulació de les mostres i reactius i els temps d'anàlisi es tornen molt llargs.

Per tal de solucionar aquests factors, s'han desenvolupat i utilitzat diferents estratègies amb tècniques de flux amb aplicacions de monitorització i/o analítiques directes *in-situ* trobant solució a les variables esmentades anteriorment.

Dintre de la història de les tècniques de flux veiem l'evolució d'aquestes des de la seva aparició fins els mètodes més actuals. La primera aparició d'aquestes tècniques va ser mitjançant l'anàlisi de flux segmentat (*Segmented Flow Analysis*, SFA) proposat per Skeggs l'any 1957 [90]. A partir d'aquella primera estratègia es va anar evolucionant i van aparèixer altres alternatives com l'anàlisi per injecció de flux (*Flow Injection Analysis*, FIA) proposat per J. Ruzicka i E. H. Hansen l'any 1975 [91], l'anàlisi per injecció seqüencial (*Sequential Injection Analysis*, SIA) proposat per J. Ruzicka i G. D. Marshall l'any 1990 com a alternativa al sistema FIA [92] o l'anàlisi de flux multicommutat (*Multicommutated Flow Injection Analysis*, MCFIA) proposat l'any 1994 per B. F. Reis i col. [93]. Més recentment, han aparegut l'anàlisi per injecció de flux multixeringa (*Multisyringe Flow Injection analysis*, MSFIA) [94,95], proposat l'any 1999 per Cerdà i col. [96], la *lab on valve* (LOV) proposada l'any 2000 per Ruzicka [97] i els sistemes multibomba (*Multipumping flow systems*, MPS) proposat per Lapa i col. l'any 2002 [98].

Aquestes últimes, han anat adquirint importància per a propòsits clínics, industrials i mediambientals, ja que són altament reproduïbles i treballen amb la mínima manipulació de la mostra, sempre tenint en compte l'estalvi econòmic que suposen. La causa d'aquest últim factor, és la simplicitat d'aquests sistemes i la tendència de miniaturització, permetent una reducció de volums tant de reactius, com de mostra. L'automatització i miniaturització dels mètodes durant les anàlisis és un punt molt interessant a tenir en compte per a la realització de tècniques rutinàries, ràpides i eficients [99].

Tal i com hem vist en el tema anterior, a l'hora de realitzar la detecció de radionúclids individuals normalment és necessari aplicar un procés laboriós de pretractament de mostra, que normalment inclou diversos passos com ara la digestió, la preconcentració i la separació. Aquestes tècniques de flux ens permeten obtenir tots o alguns d'aquests passos del pretractament de la mostra d'una forma automatitzada o bé semiautomatitzada [100]. La preparació de la mostra suposa un

70% de temps total d'anàlisi i normalment és el factor més gran que contribueix a la incertesa analítica. A més, l'aplicació de mètodes d'anàlisi automàtics permet a l'analista treballar de forma molt reproducible processant un elevat número de mostres diàries.

L'automatització de la preparativa de mostra genera l'ús de diversos mòduls i peces, fàcilment combinables i reemplaçables entre ells, per tal de realitzar canvis sistemàtics convenients per a cada tipus de radionúclid a determinar. Per tant, estem parlant d'un equip analític molt versàtil, capaç d'adaptar un considerable ventall de possibilitats sense realitzar grans canvis en el sistema, capaç d'introduir diferents materials d'extracció (sòlids i líquids) de formes diferents i utilitzant diverses eines i acoblaments, capaç d'adaptar-se fàcilment de forma automatitzada a alguns detectors.

L'automatització total del procés també depèn dels equips de mesura utilitzats en la detecció dels radionúclids d'interès. Tal i com es mostra a la Figura 1.9., podem observar que per a la mesura d'emissions alfa i beta de radionúclids individuals es necessari un procés de preconcentració i extracció previ i que aleshores, per una banda amb les emissions beta, l'ús de sensors [101] i l'ICP-MS [102,103], ens permeten obtenir el sistema de flux connectat *on-line* amb el detector, obtenint un mètode totalment automatitzat. En el cas del detector d'escintil·lació líquida i el comptador de gas proporcional és molt difícil aconseguir una introducció de fracció líquida en continu en el detector [104,105], per qüestions d'aïllament i disseny del detector per part de les cases comercials. Tot i així, en el cas del detector d'escintil·lació líquida sí que hi ha alguns autors que modificant l'equip, han aconseguit realitzar *on-line* la injecció de mostra [106,107]. Per una altra banda, la detecció d'emissions alfa també es veu totalment automatitzada mitjançant la detecció amb ICP-MS, o bé semiautomatitzada amb la detecció mitjançant l'espectrometria alfa i el comptador de gas proporcional.

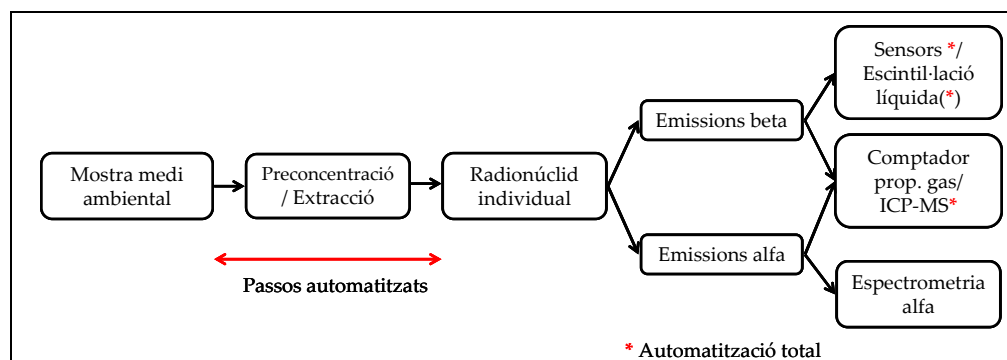


Figura 1.9. Esquema de detecció automatitzada o semiautomatitzada per als isòtops radioactius.

Resulta evident que un mètode completament automàtic és molt difícil d'implementar, especialment en el cas de mostres sòlides. En les primeres etapes de la sistemàtica analítica existeixen poques solucions econòmicament viables per a la seva digestió. En el cas de que les mostres siguin fluids, les solucions per a la seva automatització se simplifiquen per varis motius: són mostres sense excessius problemes d'homogeneïtat i en segon lloc existeix alguna solució per a la seva manipulació mitjançant operacions mecàniques relativament simples, ja sigui mitjançant bombes peristàtiques, de pistó, etc. [108]. Per tant, les mostres sòlides han de passar per un procés de digestió previ i convertir-se en mostres líquides de forma manual.

Tot i així, hi han alguns autors que han automatitzat el procés de digestió de mostres sòlides [109,110]. Per exemple, en el estudi d'Egorov i col. [110] on es va adaptar un sistema de microones seguit d'una columna d'intercanvi aniònic per a l'extracció de ^{99}Tc provinent d'una mostra residual nuclear. A més en aquest mateix estudi també es va realitzar el sistema de la detecció *on-line* mitjançant el detector d'escintil·lació líquida. Per tal de conèixer els diferents sistemes que fan possible aquests pretractaments de mostres de forma automatitzada, explicarem de manera breu en què consisteixen les principals tècniques de flux (materials, sistemàtica, etc.) més utilitzades actualment.

1.4.1. Anàlisi per injecció de flux (FIA)

Degut a que l'anàlisi en flux segmentat (SFA) presentava alguns inconvenients com ara la introducció de bombolles d'aire en el sistema, i la disminució d'eficàcia dels materials de separació, entre d'altres, va ser introduïda com a innovació d'aquesta la tècnica FIA. En FIA la mostra és introduïda mitjançant una vàlvula d'injecció en un canal pel que circula un corrent continu de fluid portador (*carrier*). Durant el transport de la mostra fins el detector s'incorporen els reactius necessaris en el canal del portador o mitjançant canals auxiliars connectats al principal (Figura 1.10.).

En comparació amb altres camps com ara, el farmacèutic amb la detecció de fàrmacs en el medi o l'anàlisi clínic amb la detecció de proteïnes, etc., l'aplicació d'aquesta tècnica en anàlisis radioquímiques és escassa. Això podria ser a causa de la manca de la versatilitat de la tècnica FIA, que fa difícil l'automatització adequada de tot el procés en separacions radioquímiques on són necessaris l'ús de diversos reactius de forma intermitent i amb volums petits i precisos. Altres inconvenients de la tècnica dintre el camp de la radioquímica són: un ús de bombes peristàtiques per a la impulsió de líquids amb tubs especialment vulnerables a reactius agressius, un alt consum d'aquests i de volum de mostra i la dificultat en dissenyar una anàlisi multivariant amb la determinació simultània de diferents paràmetres.

Amb la introducció del flux d'injecció acoblat al ICP-MS (FI-ICP-MS) l'any 1986 [111] es va obrir un camí per a automatitzar els mètodes radiomètrics clàssics usant la

tècnica FIA [112,113]. Per exemple, Dadfarnia and McLeod [114] van utilitzar per primera vegada una columna d'alúmina activada per a preconcentrar U en aigües superficials i de mar de forma *on-line*. Hollenbach i col. [115] varen desenvolupar un mètode molt complex de preconcentració i separació d'U, Tc i Th a través de la combinació de dues columnes de resina d'extracció cromatogràfica, la TRU (^{234}U i ^{230}Th) i la TEVA (^{99}Tc), aconseguint límits de detecció (LOD) de 0.74 (0.003) i 3.7 (0.005) Bq kg⁻¹ (ng g⁻¹) per a l'urani i tori, i més alt de 11 Bq kg⁻¹ (0.02 ng g⁻¹) per al tecneci, en mostres de sòl. Aldstadt i col. [116] varen determinar U en aigües superficials utilitzant una columna amb resina TRU, amb la qual varen aconseguir límits de detecció de 0.30 ng L⁻¹. En tots aquests casos anteriors, el sistema FIA va ser acoblat *on-line* amb l'ICP-MS, aconseguint una automatització completa incloent els passos de preconcentració, separació, i determinació. Més tard, Egorov i col. [117] varen desenvolupar un sistema FIA ràpid per a l'extracció selectiva d'Am i Pu, utilitzant una columna amb resina TRU i acoblat *on-line* a un detector d'escintil·lació líquida, però no es va poder aplicar el procediment a mostres reals degut als mals resultats obtinguts amb mostres més complexes. Un any més tard, aquest mateix procediment va ser desenvolupat amb una altra tècnica automatitzada, el SIA, treballant amb mostres complexes (aigua residual nuclear) a l'obtenir una separació d'ambdós radionúclids molt més efectiva amb l'ajuda d'una optimització multivariant [118].

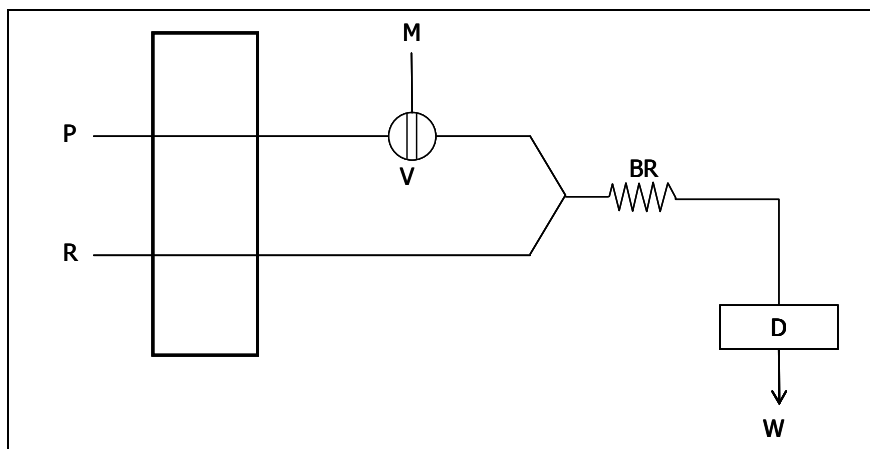


Figura 1.10. Sistema d'anàlisi d'injecció de flux (FIA). P: portador, R: reactiu; D: detector; M: mostra; V: vàlvula de commutació; BR: bucle de reacció; W: residu.

1.4.2. Anàlisi per injecció seqüencial (SIA)

Un sistema d'anàlisi per injecció seqüencial (SIA) està compost bàsicament per una bomba de pistó bidireccional, una vàlvula de selecció, la qual posseeix un port central connectat a la bomba impulsora de líquids i ports laterals connectats als

recipients dels reactius, mostra, columna i detector. El SIA es basa amb l'aspiració seqüencial de volums precisos de mostra i reactius que es condueixen, mitjançant un portador, fins una zona de carga del tub en forma bucle allargat i llavors amb un canvi de canal per part de la vàlvula de selecció es condueixen passant per la columna de separació, fins al detector (Figura 1.11.). Entre els avantatges del SIA s'ha de destacar que el conjunt de tubs és més senzill i resistent a reactius agressius que el del sistema tancat del FIA [119]. A més, les bombes peristàltiques són eliminades i reemplaçades per una bomba de pistó (prevista de 40000 passos) i amb una xeringa de vidre o de PTFE (politetrafluoroetilè) més una vàlvula solenoide adaptada, per on es dispensen o s'aspiren els volums, les quals són resistents a diferents tipus de reactius agressius i treballen amb volums petits. A més, gràcies a aquesta vàlvula solenoide, el portador és tornat al seu dipòsit quan ja no és necessari, sense pertorbar el desenvolupament del mètode.

D'altra banda, la tècnica SIA és idònia per a funcionar de forma multivariant, aquest fet s'afavoreix a l'augmentar els ports laterals, bé utilitzant vàlvules de selecció de fins a 20 ports o connectant un port lateral de la vàlvula principal amb el port central d'altres vàlvules.

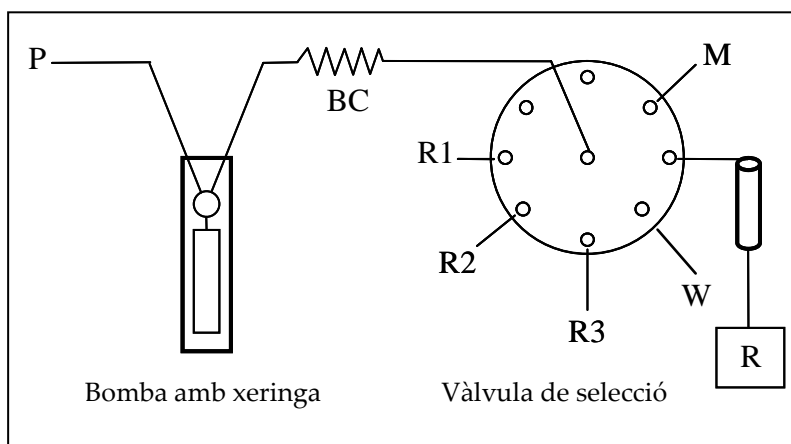


Figura 1.11. Sistema d'anàlisi d'injecció seqüencial (SIA). P: portador; D: detector; M: mostra; BC: bucle de carga; R: reactiu; W: residu. Font: Fajardo i col. [100].

La primera metodologia totalment automatitzada per a una separació radioquímica utilitzant la tècnica SIA, va ser proposada pel grup d'investigació de Grate i col. l'any 1996 [120,121]. Aquests van desenvolupar un sistema SIA per a la separació i determinació d'⁹⁰Sr en residus radioactius (0.25 g de fang deshidratat) provinents de tancs d'emmagatzematge d'una central nuclear a Hanfort (Estats Units) amb activitats molt elevades. La separació es va dur a terme mitjançant una minicolumna (100 mm llargària x 2.1 mm diàmetre, 0.35 mL) que contenia resina Sr-Spec i la detecció es va dur a terme de manera *on-line* mitjançant escintil·lació líquida,

obtenint uns LODs de 2.6 Bq. La principal limitació d'aquest mètode és el requeriment de parar el sistema per a renovar la fase estacionària.

S'han desenvolupat altres sistemes SIA per a determinar activitats més baixes en mostres ambientals, majoritàriament partint de volums més grans de mostra i de resina. Per exemple, una altra aplicació SIA i columna cromatogràfica de resina d'Sr (200 mm llargària x 8 mm diàmetre) amb mostres ambientals (10 g de sòl) i aconseguint la separació del $^{239,240}\text{Pu}$, ^{210}Po i ^{210}Pb va ser realitzada per Kim i col. [122] de forma semiautomatitzada, és a dir mitjançant una mesura *off-line* amb espectrometria alfa ($^{239,240}\text{Pu}$, ^{210}Po) i escintil·lació líquida (^{210}Pb) amb recuperacions superiors al 80% per als tres radionúclids. Altres estudis on també es va determinar $^{239,240}\text{Pu}$ amb unes recuperacions majors del 80% a través del sistema SIA de dues vàlvules de selecció, la vàlvula d'injecció i utilitzant resina TEVA (columna cromatogràfica de 7 cm llargària x 5 mm diàmetre, 0.7 gr de resina) en mostres ambientals, 10-200 g de sòl i sediments, passaren 200 L d'aigua de mar i 20 g de plantes aquàtiques amb un sistema totalment automatitzat (*on-line*) amb l'ICP-MS [123,124].

En altres exemples, aprofitant les propietats adsorbents del diòxid de manganès per separar els ions itri (III), Mateos i col. [125] varen determinar l' ^{90}Sr i l' ^{90}Y simultàniament en aigües termals aconseguint recuperacions elevades a partir del 80% d'itri. L'itri retingut amb el diòxid de manganès va ser eluït amb hidroxilamina i finalment l'activitat beta total va ser mesurada mitjançant el comptador alfa-beta proporcional de gas, assumint que els dos isòtops estaven en equilibri secular i seguint les equacions Bateman. Més tard, aquest mateix autors van dissenyar un mètode també amb fibra de cotó amb diòxid de manganès i la tècnica SIA per a determinar simultàniament el ^{226}Ra i el ^{90}Sr en mostres d'aigua (40 mL) [126]. L'activitat del radi va ser obtinguda directament en el precipitat $\text{Ba}(\text{Ra})\text{SO}_4$, mentre que l'activitat del ^{90}Sr va ser determinada a partir del seu descendent, el ^{90}Y , coprecipitat amb hidròxid de ferro (III).

1.4.3. Anàlisi per injecció de flux multixeringa (MSFIA)

L'anàlisi per injecció de flux multixeringa (MSFIA) va ser desenvolupat amb l'objectiu de combinar en una tècnica els avantatges del FIA, SIA i d'altres no explicats anteriorment pel seu inexistent ús en el camp de la radioactivitat com l'anàlisi per injecció en flux multicommutat (MCFIA). Amb aquesta tècnica obtenim els beneficis que ens proporcionen la versatilitat i robustesa dels sistemes d'injecció seqüencial utilitzant bombes de pistó previstes de diverses xeringues com a impulsores de líquids [127].

Bàsicament, tal i com mostra la Figura 1.12. un sistema MSFIA està compost per un mòdul amb quatre xeringues, mogudes conjuntament per un mateix pistó. Podem veure que cada xeringa té acoblada una vàlvula solenoide de tres vies, això permet

una gran varietat de modalitats d'injecció. També inclou la possibilitat d'un anàlisi multivariant amb un significatiu estalvi de temps i cost per a l'anàlisi.

Aquesta tècnica afavoreix i potencia l'ús de diversos sistemes addicionals, sempre controlats i sincronitzats per ordinador, tant el o els mòduls multixerina que componen el sistema, com altres vàlvules solenoides externes i connectors de PMMA (polimetacrilat) de dos, tres, quatre i fins a cinc vies, més el mostrejador automàtic necessari degut a l'abundància de diverses fraccions de volums obtingudes durant tot el procés. Les vàlvules solenoides (introduïdes amb la tècnica MCFIA), poden canviar de posició sense necessitat de parar el moviment del pistó del mòdul multixerina i el canvi és tant ràpid que no es produeix ninguna sobrepressió.

Com podem veure en la bibliografia aquesta tècnica ha estat recentment aplicada en l'anàlisi de diverses mostres ambientals. Per exemple, en l'estudi de Fajardo i col. [128] varen desenvolupar un mètode semiautomatitzat per a la separació d'estronci mitjançant la resina selectiva de Sr-Spec en mostres d'aigua, llet i sòl. La concentració de l'estronci estable es va determinar *off-line* mitjançant el ICP-AES, mentre que l'activitat beta del ^{90}Sr es va determinar mitjançant el comptador proporcional de gas, el qual, va mesurar activitats de 0.02 Bq (1000 min.) amb un rendiment químic per sobre del 90%. Un altre mètode MSFIA desenvolupat pels mateixos autors va ser aplicat en la separació i determinació de l'itri estable i el radioactiu [129]. Una extracció líquid-líquid (LLE), contenent àcid di-ethylhexilfosfòric (HDEHP) adsorbit sobre un suport inert de C18 dintre de la columna, va ser utilitzada per aïllar el radionúclid. El procediment semiautomàtic va ser aplicat a mostres d'aigua i biològiques aconseguint un LOD de 0.05 Bq per al ^{90}Y i 0.5 mg L⁻¹ en el cas del radionúclid estable amb recuperacions químiques del 97% i desviació relativa estàndard (RSD) del 3%.

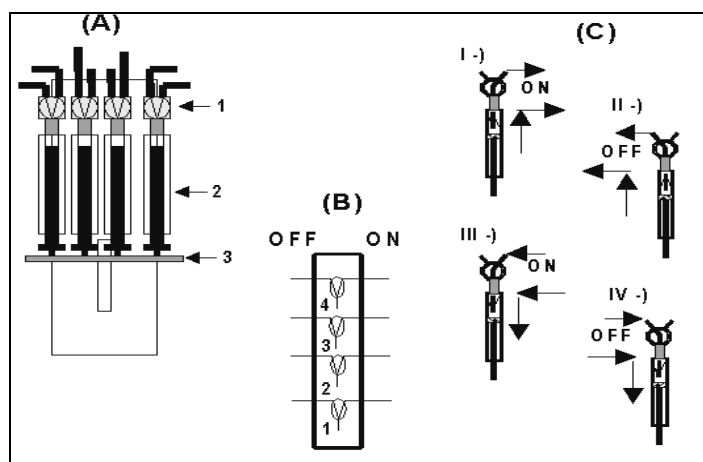


Figura 1.12. Esquema dels modes d'operació utilitzats en el MSFIA. (A) Bureta multixerina. (B) Descripció simbòlica de les vàlvules solenoides integrades en el mòdul de multixerina. (C) Moviment de la bomba peristàltica incloent-hi les quatre direccions en les vàlvules commutades en la xeringa. Font: Cerdà i col. [96].

1.4.4. Mètodes combinats

Les tècniques de flux combinades entre sí, milloren els seus beneficis individuals i són capaces de desenvolupar i adaptar noves aplicacions. Gràcies a la combinació d'aquestes va sorgir una nova generació d'anàlisi en flux, amb noves tècniques com ara: el *lab-on-valve* (LOV) i el multibomba (MPFS). Aquestes tècniques fàcils de combinar amb altres, ens donen un ampli ventall d'opcions per a adaptar diferents tècniques en un mateix sistema de pretractament de mostra.

El sistema de la *lab on valve* (Figura 1.13.) és un sistema concebut per a reduir reactius basat en assajos a nivell microlitre [130], en el qual la manipulació de la mostra i reactius es realitza amb el mode d'injecció seqüencial, permetent la realització d'anàlisi multivariants. La tècnica es basa en un sistema de canals integrat a una cel·la de flux muntada a sobre d'una vàlvula de selecció convencional. Les principals avantatges són la seva compactabilitat i la posició rígida permanent dels canals i el reemplaçament automàtic de la resina des del canal on està en dissolució fins el canal de la columna, de forma que s'ompli i es buida sempre per una obertura d'un mateix canal, assegurant la repetibilitat i reproductibilitat de la manipulació dels fluids i microfluids.



Figura 1.13. Fotografia de la plataforma de *Lab on Valve*.

El sistema de flux de multibomba és una tècnica que es basa en la utilització de diverses bombes solenoides de pistó externes e individuals, on cada pistonada significa la impulsió d'un volum predeterminat de líquid i que juntament amb una elevada freqüència d'aquestes pistonades, s'aconsegueix introduir grans volums en poc temps. Les característiques més destacables del MPFS són, la seva fàcil configuració, la robustesa i el baix cost, ja que cada bomba fa a la vegada de propulsor del líquid i de vàlvula.

Alguns exemples bibliogràfics actuals d'aquestes combinacions són el MSFIA-MPFS (Figura 1.14.), el LOV-MSFIA, el SI-bead injection (BI)-LOV [131], SI-LAV i el MSFIA-SIA amb dues vàlvules de selecció en el mòdul SIA (en el mateix mòdul de vàlvules) desenvolupant dos sistemes SIA millorats simultàniament, sense cost addicional.

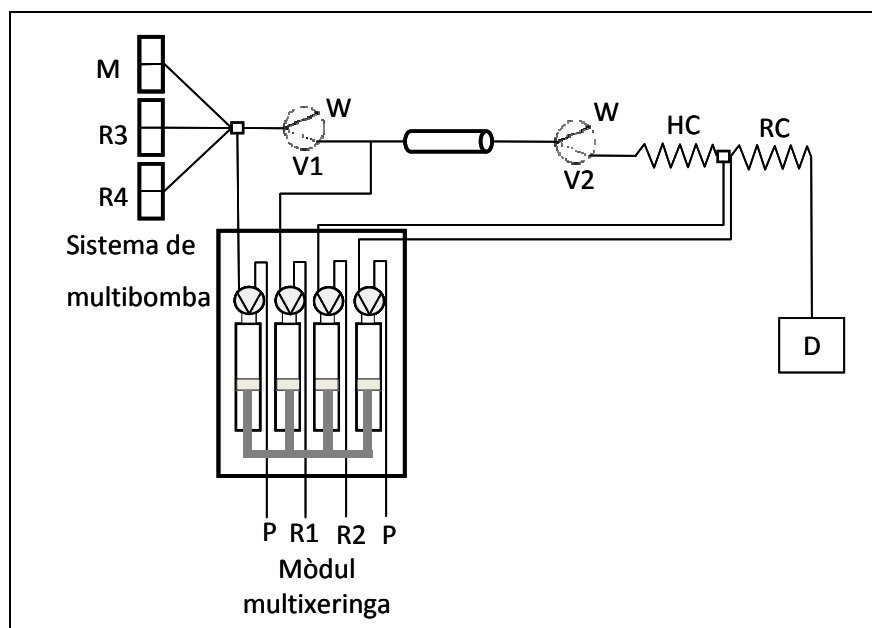


Figura 1.14. Mètode combinat: anàlisi d'injecció multixerina (MSFIA) i sistema de flux multibomba (MPFS). P: portadors; D: detector; R: reactius; M: mostra; W: residu; V: vàlvula de commutació o solenoide externa; HC: bucle de carga, RC: bucle de reacció. Font: Fajardo i col. [100].

En un treball publicat per Fajardo i col. [132] es va establir la combinació del MSFIA-MPFS per a aconseguir la preconcentració i separació del ^{226}Ra en diferents mostres d'aigua (mineral, de botella i de mar). Mitjançant la combinació d'aquestes tècniques es va aconseguir utilitzar volums de mostra grans (0.04 L) amb un temps reduït de treball, aconseguint unes recuperacions més grans del 90 % i una RSD del 0.4 %. Un altre exemple d'aquesta combinació de les tècniques MSFIA-MPFS utilitzant una columna amb resina TRU, va ser desenvolupat per a la preconcentració, extracció i determinació d'ultra traces d'urani total d'una forma *on-line*, per Avivar i col. [133]. La detecció es va dur a terme espectrofotomètricament amb l'ajuda d'una cel·la llarga capil·lar amplificadora de senyal, del complex d'arsenazo-III amb l'urani. Aquest mètode és una alternativa a la detecció clàssica dels mètodes de determinació d'urani (VI) aconseguint LODs similars (12.6 ng L^{-1}) per a un volum de 100 mL de mostra.

Recentment Rodríguez i col. [105] han desenvolupat, utilitzant el LOV-MSFIA conjuntament amb la resina Sr-Spec, un sistema d'extracció automatitzada i/o semiautomatitzada de l'Sr amb el detector ICP-OES (Sr total) i el comptador proporcional de gas (^{90}Sr) de diferents aigües mediambientals d'interès. El sistema proposat va afavorir una reducció de moltes variables, com ara, una reducció considerable del volum de la mostra i de reactius, aconseguint unes recuperacions més grans del 90 % i una reproductibilitat expressada a partir de la RSD va ser del 2.6 %, amb un LOD de 1.8 ng per al Sr total i una activitat mínima detectable (MDA) de 0.008 Bq per a l' ^{90}Sr .

Una de les últimes tendències en automatització *on-line* mitjançant la microextracció en fase líquida, basada en una gota connectada a la injecció seqüencial – *lab at valve* (SI-LAV), ha estat aplicada per a la preconcentració i determinació de metalls, sobretot en el cas del Pb, a través de l'acoblament a l'espectrofotòmetre d'absorció atòmica de flama (FAAS) [134]. Aquest sistema que s'ha aplicat a mostres biològiques com ara l'aigua i l'orina, aconsegueix retenir el complex de plom amb l'amoni pirrolidina ditiocarbamat (ADPC) format *on-line* (es van formar micro-gotes en la fase aquosa) i després s'extreu amb cloroform (extractant). Es va aconseguir un factor de concentració de 125 per a una mostra inicial de 0.01 L on el límit de detecció va ser de $1.8 \mu\text{g L}^{-1}$ i la precisió expressada a partir de la RSD va ser del 2.9 % (amb $50 \text{ Pb } \mu\text{g L}^{-1}$).

1.5. Bibliografia



UNIVERSITAT ROVIRA I VIRGILI
DESENVOLUPAMENT DE TÈCNiques ANALÍTIQUES PER A LA DETERMINACIÓ DE RADIONÚCLIDS
Montserrat Mola Arques
Dipòsit Legal: T.1294-2013

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2. OBJECTIUS

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DESENVOLUPAMENT DE TÈCNIQUES ANALÍTIQUES PER A LA DETERMINACIÓ DE RADIONÚCLIDS
Montserrat Mola Arques
Dipòsit Legal: T.1294-2013

L'objectiu principal de la present tesi doctoral és el desenvolupament de diferents mètodes analítics per a la determinació de radionúclids individuals en mostres ambientals, com són els fangs generats a diferents indústries NORM i també s'inclouen mostres biològiques. Els mètodes desenvolupats inclouen una extracció de forma manual o automatitzada, combinada amb diferents detectors d'emissions radioactives com l'LSC (d'escintil·lació líquida) i l'espectròmetre alfa. Aquests mètodes han de permetre la quantificació de radionúclids lliures d'interferents.

És també un objectiu d'aquesta Tesi Doctoral l'avaluació de la radioactivitat ambiental en l'últim tram de la conca del riu Ebre, dintre de la província de Tarragona, utilitzant els mètodes desenvolupats.

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3. PART EXPERIMENTAL I DISCUSSIÓ

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En aquest capítol s'inclou la part experimental i els principals resultats obtinguts en els diferents estudis realitzats en aquesta tesi. Aquests estan publicats o estan pendent de publicació en diverses revistes científiques de manera que, a continuació es presenten en format article. La part experimental s'ha dividit en dos blocs, el bloc en que es parla de NORM i en aquest s'estudiarà principalment una empresa que es pot classificar com a tal. L'altre bloc s'ha centrat en sistemes d'extracció automatitzats. Prèviament a cada estudi, s'inclou una breu introducció en la que es detallen els principals objectius que es varen establir a l'hora de plantejar-los. Al finalitzar cada bloc es presenta una breu discussió general dels principals resultats obtinguts.

Arran dels resultats derivats d'una tesi doctoral prèviament realitzada en el nostre grup de recerca [1], en què es va observar un possible impacte ambiental provinent de diversos tipus d'indústria NORM a l'estudiar diferents mostres ambientals situades en l'últim tram del riu Ebre, s'ha volgut dur a terme un estudi més exhaustiu i específic sobre aquest tipus d'indústria. Aquesta indústria no nuclear no està subjecta a una normativa referent als nivells permesos de radioactivitat natural en els seus residus. Tot i que existeixen una sèrie de recomanacions provinents de la IAEA [2] sobre els límits de radioactivitat natural que poden contenir aquests residus, és possible trobar-nos amb zones afectades per una sèrie d'abocaments amb nivells elevats de radionúclids d'aquest tipus en el medi.

Concretament, els estudis que s'han dut a terme s'han centrat en diferents zones que contenen o estan influenciades per materials NORM, per exemple l'estudi de diferents tipus de matèries primeres minerals emmagatzemades en el port de Tarragona. També s'ha estudiat la concentració de radionúclids produïda de manera secundària en una planta de tractament d'aigua potable, la qual rep aigua directament del riu Ebre en una localització propera a la seva desembocadura en el mar Mediterrani. Però principalment, ens hem centrat en la indústria de fosfats (DCP), situada en una de les ribes del riu Ebre a Flix, on trobem entre 200.000 i 360.000 tones de fangs acumulats. Aquests fangs s'han originat com a conseqüència del funcionament i producció d'aquesta planta durant més de dues dècades.

En primer lloc es va dur a terme un estudi centrat en la indústria de fosfats de Flix, en el que es pretenia realitzar una caracterització global dels contribuents a la radioactivitat en aquestes mostres de fangs. Per això es van determinar els índex alfa i beta totals i alguns radionúclids individuals com ara el ^{226}Ra i el ^{210}Pb de mostres d'aquesta procedència. Posteriorment, l'objectiu principal que es va plantejar va ser intentar obtenir una caracterització radioactiva més exhaustiva d'aquestes mostres i per això es va ampliar el ventall de radionúclids individuals a estudiar, trobant així els màxims contribuents de la radioactivitat natural en la zona. Per a realitzar aquest estudi també es van incloure altres tipus de mostres relacionades amb la indústria NORM, mostres minerals de fosfats i carbó del port de Tarragona amb l'objectiu de conèixer les activitats de radionúclids que contenen aquests materials minerals

transportats i emmagatzemats sense cap tipus de control. Llavors es van desenvolupar diversos mètodes analítics amb l'aplicació de diferents estratègies per tal d'obtenir diferents radionúclids individuals d'urani i tori lliures d'interferències. Aquestes estratègies elegides es van desenvolupar a partir de l'ús de diversos tipus de digestió (mineralització i microones), de preconcentració de radionúclids (diferents coprecipitats) i d'extracció específica e individual dels radionúclids (diferents tipus de separacions amb intercanvis iònics) [3-5].

Tenint en compte que algunes de les mostres analitzades poden tenir un impacte ambiental important, es va plantejar un altre treball posterior amb una aplicació del mètode analític desenvolupat per a extraure l'urani i el tori, entre d'altres. Però en aquests cas, aplicats a mostres de biota mostrejades als voltants de la indústria de fòsfats esmentada anteriorment. Amb això, es pretenia veure una possible influència dels residus radioactius de Flix sobre diferents espècies d'éssers vius que habiten als voltants d'aquesta zona en el riu Ebre.

Tot i els interessants resultats que es van arribar a obtenir en els estudis realitzats fins aquest punt, cal remarcar que tots els estudis anteriors impliquen una llarga durada d'aquestes analítiques amb l'objectiu d'intentar aconseguir una disminució del temps i una millora del tractament de la mostra, amb una disminució de la manipulació de la mostra i un estalvi considerable del volum de reactius. Aquests fets es poden aconseguir amb una automatització del sistema amb l'ajuda de tècniques de flux. A més cal esmentar que recentment aquestes tècniques han estat aplicades al camp de la radioactivitat per diversos grups d'investigació [6-8], com ara el grup dirigit pel Dr. V. Cerdà de la Universitat de les Illes Balears. En el qual, vaig realitzar una estada durant la realització d'aquesta tesi amb l'objectiu d'aprofundir en el coneixement d'aquest tipus de tècniques d'automatització.

Concretament es van plantejar dos treballs centrats en la utilització d'aquestes tècniques automatitzades, en el primer es va desenvolupar un sistema d'extracció automatitzat mitjançant la tècnica SIA, per a la separació dels radionúclids individuals d'urani i tori. Les mostres estudiades en aquest apartat són alguns dels fangs residuals acumulats en l'embassament de Flix i els fangs obtinguts durant el procés de potabilització de l'aigua en una planta de tractament d'aigua (ETAP). Tal i com es demostra en estudis previs que s'han dut a terme per diferents grups de recerca [9,10] i també en un estudi previ del nostre grup de recerca [11], en aquest tipus de fangs es poden trobar activitats relativament elevades de radionúclids de diferents orígens (sobretot radionúclids d'origen natural), de manera que durant el seu emmagatzematge podrien esdevenir un risc per a la salut dels treballadors de l'ETAP o fins i tot d'altres éssers vius degut a la seva reutilització per exemple, com a material de construcció.

En un segon treball, es va desenvolupar i optimitzar un sistema en que es van combinar les tècniques LOV-MSFIA, per tal de separar de forma seqüencial el contingut d'estronci i plom d'una mateixa mostra mitjançant l'ús de la resina Sr-

Spec. Aquests emissors beta d'origens diferents, van ser escollits per ser uns radionúclids amb elevada toxicitat biològica ja que un cop incorporats en el cos humà s'adapten de manera degenerativa en òrgans i estructura òssia durant molt de temps, degut a les seves vides mitges llargues. En aquest cas es va treballar amb la caracterització de mostres de fangs de l'ETAP, els quals sabem per treballs anteriors del nostre grup mitjançant l'anàlisi per espectrometria gamma, que aquests fangs contenen radionúclids naturals (com ara el ^{40}K , el ^{238}U , el ^{232}Th i el ^{214}Pb , entre d'altres) i també radionúclids artificials (el ^{60}Co i el $^{110\text{m}}\text{Ag}$) [12]. Aquests podrien tenir diversos orígens industrials situats més amunt en la conca del riu Ebre, com ara la central nuclear en Ascó i/o les 300.000 tones de fangs residuals acumulats davant de la planta de fosfat dicàlcic en Flix.

Tots els estudis desenvolupats en aquesta Tesi Doctoral varen ser finançats i recolzats per la Generalitat de Catalunya, Departament d'innovació, Universitats i Empresa a través del projecte 2009 SGR 223, i el Consorci d'Aigües de Tarragona (CAT).

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3.1. NORM i el seu impacte ambiental

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En estudis previs del nostre i d'altres grups de recerca [1,2] s'ha vist clarament un impacte ambiental provinent de la indústria NORM. Dintre d'aquest llistat hi trobem la indústria dels fosfats i fertilitzants [3,4] i concretament, una de les zones estudiades a Espanya, pel que fa als abocaments d'aquest tipus d'indústria NORM es troba situada en l'embassament de Flix en una zona de residus sedimentaris front el complex industrial dintre del curs del riu Ebre [5,6] on hi ha la planta de fosfat dicàlcic (DCP) produït des del 1973 i durant els 25 anys posteriors a partir de la roca fosfòrica del Marroc. A partir d'aquest mineral i mitjançant una reacció química amb l'HCl, es genera el fosfat dicàlcic i com a conseqüència del procés, també es formen subproductes o residus en forma de fangs (Figura 3.1.). Alguns autors sustenten que després del procés de transformació de la roca fosfòrica els residus generats contenen alts nivells de radioactivitat [3,6,7]. Un exemple d'estudi que avalua la concentració de radionúclids naturals en el fosfat dicàlcic i en els fangs produïts per la indústria DCP de Flix és el publicat per Casacuberta i col. [6] en què es van veure activitats màximes de 5000 i 10000 Bq Kg⁻¹ d'²³⁸U i de ²³⁰Th, respectivament, en mostres de fangs. Cal tenir en compte que els residus dipositats dintre del llit del riu són susceptibles a ser remobilitzats i transferits a ecosistemes sensibles o a la cadena alimentària i afectar finalment a la població.

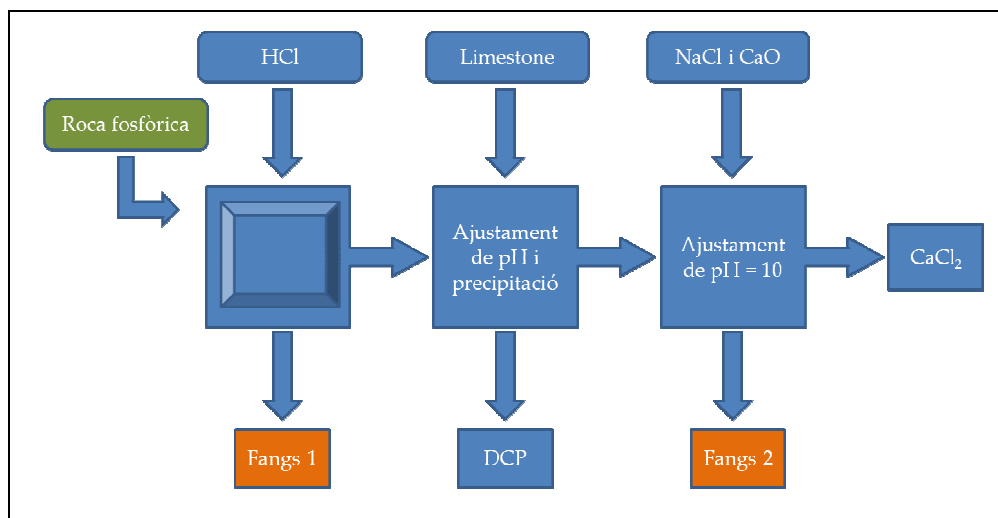


Figura 3.1. Procés de producció del fosfat bicàlcic (DCP) i els fangs residuals basat en la reacció amb l'àcid clorhídric. Fonts: Gafvert et al. [3], Casacuberta [8].

D'acord amb aquestes premisses es va plantejar un primer estudi en què es pretenia obtenir un mostreig global de la zona afectada amb un total de set punts de mostreig i una suma de 46 mostres. Aquest mostreig es va dividir en dues subzones: la Zona I situada davant la planta de fosfat dicàlcic i la Zona II situada davant de la planta de tractament d'aigües residuals (EDAR) inaugurada dintre el complex industrial amb l'aparició de la normativa que dictava el tractament previ dels residus (de la DCP,

entre altres) abans de ser abocats al riu. També es va mostrejar un punt fora de la influència d'aquesta indústria, per comparar les concentracions d'un sòl proper que no ha sofert l'abocament de residus amb les concentracions dels fangs de la zona d'influència de la DCP. Com es volia realitzar un estudi radiològic de tota la zona afectada pels abocaments i veure la distribució de les activitats dels diferents radionúclids, per tal de buscar una relació entre el funcionament de la indústria i la formació dels residus sedimentaris, es va realitzar un mostreig a diferents profunditats. En cada mostra es va mesurar l'índex d'activitat alfa i beta total i certs radionúclids individuals, com ara el ^{40}K , el ^{137}Cs , el ^{226}Ra i ^{210}Pb . Finalment, els resultats obtinguts han estat objecte d'una publicació a la revista *Journal of Hazardous Materials* 198 (2011) 57-64.

Arran dels resultats obtinguts en aquest primer estudi en què es va poder observar que hi havia una distribució diferent dels diferents radionúclids en funció del punt de mostreig i també en funció de la profunditat de la mostra, ja que l'activitat màxima es va veure que es concentrava en la zona de fangs ubicada davant la DCP i concretament en els primers metres de profunditat, vam decidir continuar amb la investigació per determinar més possibles radionúclids individuals majoritaris amb l'objectiu de fer una caracterització radiològica més detallada. Amb aquest objectiu, ens vam centrar en l'estudi dels radionúclids de l'urani i del tori per ser els radionúclids naturals més estudiats segons la bibliografia en casos de presència d'indústria NORM. Al realitzar una cerca bibliogràfica exhaustiva de les tècniques utilitzades per a l'anàlisi d'aquests radionúclids vam poder comprovar la importància d'un pretractament previ a la mostra per tal d'aconseguir els analis lliures d'interferències de la matriu, que impedeixen una mesura més directa per espectrometria alfa [9-12]. Aquest pretractament previ amb mostres sòlides el podem desglossar en tres parts: la forma de digestió, el mètode de preconcentració majoritàriament mitjançant l'ús d'agents coprecipitants i el mètode selectiu de separació i extracció. Finalment, es va plantejar un estudi comparatiu entre diferents formes de pretractament de la mostra, per veure com afecten els diferents mètodes utilitzats en els resultats finals d'U i Th i poder escollir el més òptim. Es van utilitzar, dues formes de digestió (mineralització a cel obert i digestió amb microones), dues formes de coprecipitació dels radionúclids (mitjançant l'adició de FeCl_3 o del $\text{Ca}(\text{NO}_3)_2$) i finalment dues formes selectives d'extracció seqüencial d'aquests radionúclids: una extracció líquid-líquid mitjançant TBP i Xilè [13] i en l'altra es va seleccionar la resina d'extracció cromatogràfica Uteva [14]. Aquests mètodes van ser validats a través de la participació en diversos exercicis d'intercomparació de la IAEA i del CSN. Posteriorment, amb el procediment més reproducible, robust i amb una recuperació dels traçadors més elevada, es va passar a realitzar la quantificació dels radionúclids individuals en mostres reals. Es van analitzar mostres de fangs residuals mostrejats a diferents profunditats front la planta de fosfat dicàlcic en Flix i mostres minerals (diferents matèries primeres industrials) de fosfats i carbó emmagatzemats en unes àrees a l'aire lliure al port de Tarragona. Els resultats

obtinguts en aquest treball han estat publicats a la revista *Journal of Environmental Radioactivity* 115 (2013) 207-213.

Finalment, es va realitzar un darrer treball amb l'objectiu de mostrar l'influència dels fangs acumulats en l'embassament de Flix i que estan en contacte amb l'aigua del riu, sobre les activitats de radioactivitat natural de diferents espècies de biota territorials de la zona. Es van escollir tres tipus d'espècies diferents: l'alga més comuna de la zona (*Cladophora glomerata*), el musclos zebra (*Dreissena polymorpha*) i el tercer, el silur (*Silurus glanis*). El mostreig es va dividir en diverses zones classificades, segons la distància a la que es troba la zona en qüestió respecte de la zona en què hi ha els fangs procedents de la DCP acumulats. Concretament, es van establir les següents zones: la zona 1 fora de la influència de la DCP situada uns kilòmetres més amunt en la presa de Riba-Roja, la zona 2 a l'inici de la zona d'influència, la zona 3 durant la zona d'influència, la zona 4 a pocs metres passat la zona d'influència, la zona 5 a pocs kilòmetres després de la zona d'influència, i la zona 6 en la Badia del Fangar a uns 120 Km de Riba-Roja. Els resultats d'aquest estudi han esta acceptats per a la seva publicació a la revista *Journal of Radioanalytical and Nuclear Chemistry*.

A continuació, tal i com s'ha comentat, s'inclouen els tres treballs que conformen aquest primer bloc d'estudis, introduïts mitjançant una temàtica en comú, la investigació del l'abast del impacte ambiental existent a causa de l'empresa i/o materials NORM.

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**3.1.1. Distribution of naturally occurring radioactive
materials in sediments from the Ebro River
reservoir in Flix (Southern Catalonia, Spain)**

UNIVERSITAT ROVIRA I VIRGILI
DESENVOLUPAMENT DE TÈCNIQUES ANALÍTIQUES PER A LA DETERMINACIÓ DE RADIONÚCLIDS
Montserrat Mola Arques
Dipòsit Legal: T.1294-2013

DISTRIBUTION OF NATURALLY OCCURRING RADIOACTIVE MATERIALS IN SEDIMENTS FROM THE EBRO RIVER RESERVOIR IN FLIX (SOUTHERN CATALONIA, SPAIN)

M. Mola, M. Palomo, A. Peñalver, C. Aguilar, F. Borrull*
Departament de Química Analítica i Química Orgànica
Universitat Rovira i Virgili, Marcel·lí Domingo s/n, 43007 Tarragona, Spain
Unitat de Radioquímica Ambiental i Sanitària (UR AIS), Consorci d'Aigües de Tarragona
(CAT), Ctra Nacional 340, km 1094, 43895 L'Ampolla, Spain

Abstract

Industrial waste containing radioactive isotopes (from U-decay series) was released into Ebro river basin due to the activity of a dicalcium phosphate (DCP) plant for a period of more than two decades. Gross alpha, gross beta, ^{40}K , ^{226}Ra and ^{210}Pb activities were determined in several sludge samples taken at different depths from different points in the area of influence of the DCP plant located in Flix. Samples were collected from two different zones: one in front of the DCP plant and the second in front of a wastewater treatment plant installed several years after the DCP plant. The data obtained verify the influence of industrial DCP production on radioactivity levels present in the area.

Keywords: naturally occurring radioactive materials; dicalcium phosphate plant; industrial waste; sludge.

INTRODUCTION

Natural radionuclides are normally found in the environment in concentrations that seldom become a matter for regulatory concern. However, some human activities can increase the activity concentration of some of these isotopes. Many studies have associated the accumulation of natural radioactivity with the presence of certain industries, such as petroleum extraction, uranium mining and the production of phosphate-based products [1-5]. These natural radioactive elements have been largely unregu-

lated, although different regulatory agencies have become increasingly concerned about their presence in the environment as well as about the possible exposure of workers and the public [6-8]. Specific legislature regarding the limits of contamination of natural radioactive waste has not been introduced, however, guidelines have been published, such as the IAEA Draft Safety Guide DS161 [9], that provide recommendations about radioactivity limits in solid waste, mainly derived from non-nuclear industries [10]. In Spain, Naturally Occurring Radioactive Materials

(NORM) were not subject to regulation until the publication of Royal Decree 783 in 2001 [11], which was recently modified in 2010 through Royal Decree 1439 [12] approved as a result of the transfer of European Council Directive 96/29 [13]. These regulations apply directly to those responsible for activities involving natural sources of radiation, making it mandatory to conduct studies to determine whether such activities contribute to a significant increase in the radiation exposure of workers or members of the public.

As mentioned above, the production of phosphate-based products is considered a NORM activity [14-16]. Using sedimentary phosphate rocks as a raw material in an industrial process leads to the input of several different radionuclides, mainly ^{238}U and its decay chain daughters, resulting in increased natural radioactivity in the immediate environment. The products obtained through these processes can be used for several different processes, and it is important to highlight that the results of these industrial processes should be evaluated and regulated, as they can be of radiological concern to workers and the public.

Various Spanish studies have verified natural radionuclide accumulations resulting from phosphoric acid production, for example in Huelva (southern Spain) and in Flix (north-eastern Spain) [17-21]. For instance, Villa et al. [19] studied an area of the Estuary of the Tinto and Odiel rivers (Huelva) and evaluated the ^{226}Ra and ^{210}Pb activities in bottom sediment

samples collected from 1999 to 2005, the influence of the waste dumped by the phosphate industry and its temporal evolution. In conclusion, the authors observed that the activities decreased considerably due to the self-cleaning and dilution of this contamination after direct releases into maritime areas ceased in 1998 [22,23].

Our study focuses on the dicalcium phosphate (DCP) plant located in Flix. The production process of DCP from Moroccan phosphate rock started in 1973 and continued for about 25 years. Several studies have focused their attention on this process and some authors have concluded that it leads to the presence of large amounts of radioactivity in both end products and by-products [4,14]. One of the primary problems with the Flix plant is that it released its waste streams into a reservoir of the River Ebro without any prior treatment until the late nineties, when Spanish Royal Decree 11 [24] was approved.

Some of the published studies carried out in the Flix reservoir area have shown the problem of accumulated residues resulting from DCP production. These studies had two basic aims: to evaluate the concentration of different radioisotopes accumulated in the sludge and to evaluate the possible influence of the DCP industry on the River Ebro ecosystem. In relation to the former, Costa [20] measured the concentrations of ^{238}U , ^{226}Ra and ^{210}Pb and found values approximately 308, 92 and 38 times higher than the natural levels of these isotopes in the bed of the same river. Another study by

Casacuberta et al. [21] demonstrated the influence of the industrial activity of the DCP plant on increased radioactive levels in the surrounding area.

Several studies published previously by our group [25,26] have looked at the second objective mentioned above – the effect of the DCP industry on the ecosystem. In one such study, radioactivity levels in two different species of algae were evaluated (*Cladophora glomerata* and *Cynodon dactylon*) [26] from samples taken at different points along the course of the River Ebro. Our results showed that the presence of the DCP plant has had a significant influence on levels of radioactivity, as the highest activity values were observed in algae samples taken from the area surrounding the plant (Flix).

These studies, as well as others focusing on different types of contaminants such as PCBs, heavy metals and others derived from similar industries, make it clear that the early extraction of this contaminated sludge is crucial in order to prevent a possible environmental problem in the river course. In this respect, it is important to point out that as this article is being written a project is underway to remove the sediment sludge from the Ebro area [27,28].

The main goal of this study is to evaluate the radiology of the sludge accumulated in the Flix reservoir at different depths. In particular, our purpose was to establish a possible relationship between our results and the industrial activity conducted at the

DCP plant. Since most of the research published to date has studied sediments taken at a superficial level, one of our main aims is to evaluate whether the radioisotopes in the area located in front of the DCP plant are distributed uniformly.

2. Sampling details and methods

2.1. Samples

In this study, sludge samples were collected from different points within the area of influence of the DCP plant in Flix. Figure 1 shows the area of study close to the DCP factory where the emerging sludge samples from that factory were released into the Ebro River (Catalonia, Spain).

Figure 2 shows the sampling area, which was near the plant and in the River Ebro. Specifically, the figure shows two different zones where sludge had accumulated. Zone I is located in front of the DCP plant, where sludge samples were collected from a single sampling point at different depths (A1). Zone II is situated in front of a wastewater treatment plant (WWTP) for the plant and sludge samples were collected from five different sampling points at different depths (B2, B3, B4, B5 and B6) here as well. Finally, we also took sludge samples from a sampling point (C7) which is theoretically not affected by DCP emissions since it is located out of the area where the DCP plant released its waste streams. For all the sampling points, sludge samples were collected at different depths ranging between 1 and 11 m. Therefore, a total

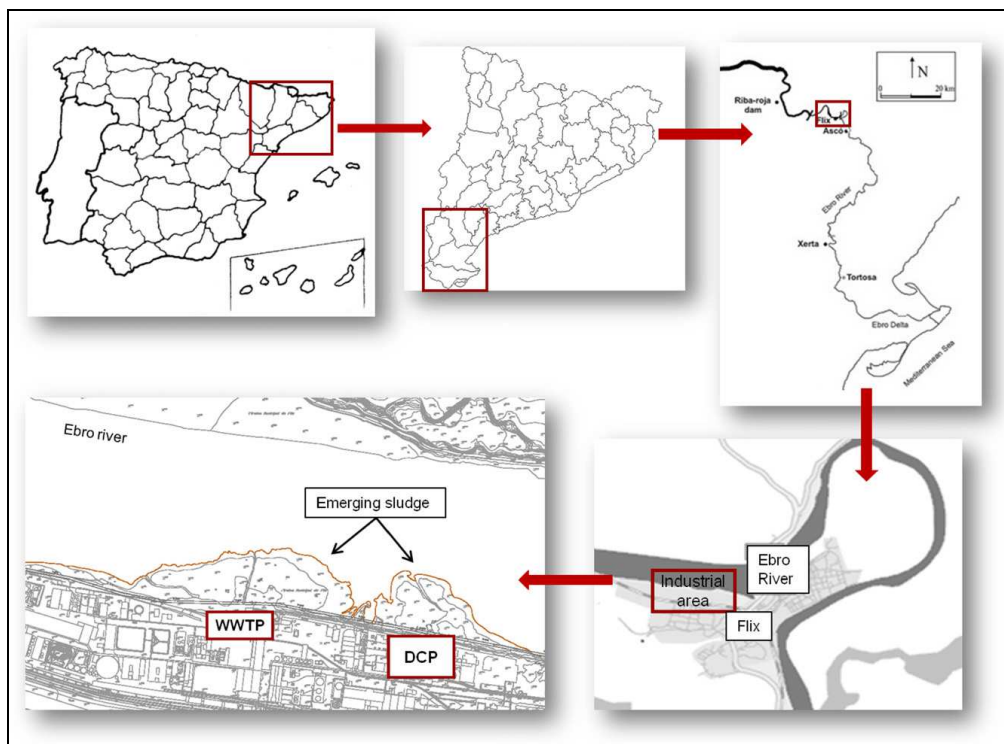


Figure 1. Area of study close to the DCP factory in which the emerging sludge samples were deposited in the Ebro River is shown (South-Western Catalonia, Spain).

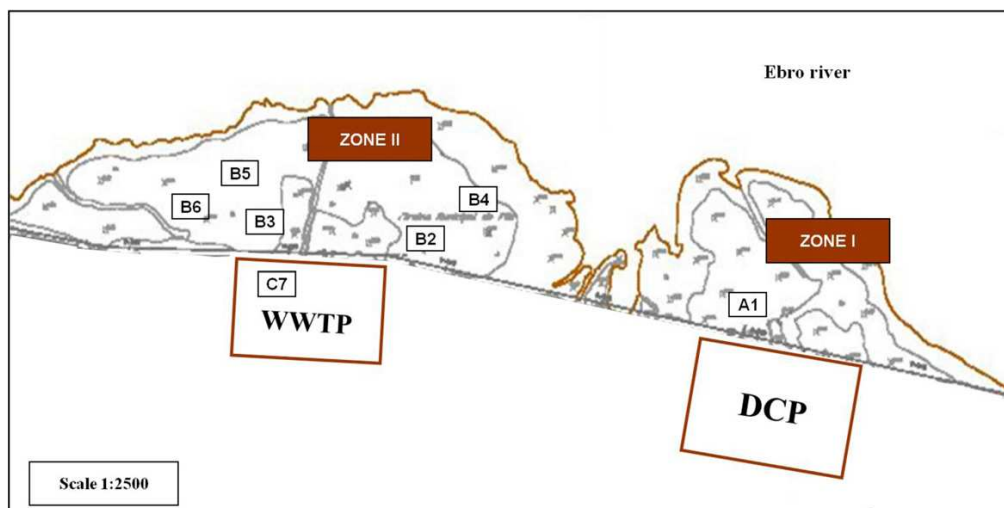


Figure 2. Location of the seven different sampling points included in this study in front of the area of influence of the DCP plant. Sludge samples were collected from seven different points: A1 is located in the zone called Zone I (in front of the DCP plant) and sampling points B2, B3, B4, B5 and B6 are located in Zone II (in front of the WWTP). C7 is a sampling point located outside of the area of influence of the plant. For each sampling point, sludge samples were collected at different depths ranging between 1 and 11 m.

of 46 sludge samples were taken. Approximately 750 g of damp sludge sample was taken at each sampling point and placed in a plastic container. Samples were transported to the laboratory where they were transferred to a tray and dried in an oven at a temperature of 110 °C. The samples were then crushed in a ball mill and sifted in a 250 µm sieve.

2.2. Detectors and preparation of samples

To measure gross alpha activity, a zinc sulphide (ZnS) scintillator counter (photo multiplier tube and base preamplifier, model 2000, Canberra, USA) with a voltage of 0.76 kV was used. A certified solution of ^{241}Am with a nominal activity concentration of $4.7 \pm 0.4 \text{ KBq}\cdot\text{g}^{-1}$ provided by Amersham International plc. (Buckinghamshire, England) was used to determine the alpha detection efficiency. A planchet containing ^{241}Am with an activity of 100 Bq was prepared from the standard certified solution, and this was used for monthly calibration. The background of each detector was determined by counting an empty planchet for 5000 minutes.

Gross beta activity was measured with a 10 channel low level alpha/beta counter detector type (Model Berthold LB770, Germany), with a voltage of 1650 V. The background of each detector was determined by counting an empty planchet for 900 minutes and monthly calibration was performed by using one planchet containing ^{241}Am with an activity of 100 Bq and another planchet of $^{90}\text{Sr}/^{90}\text{Y}$ with an activity of

100 Bq. These planchets were prepared from certified solutions of ^{241}Am ($4.7 \pm 0.4 \text{ KBq}\cdot\text{g}^{-1}$) and $^{90}\text{Sr}/^{90}\text{Y}$ ($4.7 \pm 1.5 \text{ KBq}\cdot\text{g}^{-1}$), both provided by Amersham International plc. (Buckinghamshire, England). Source thickness is important in the determination of gross alpha and beta activities in soil and also water samples due to the self-absorption and energy losses. In this sense, we have prepared different planchets containing ^{241}Am and ^{90}Sr standards and increasing amounts of sodium nitrate provided by Merck (Darmstadt, Germany), ranging from 0 to 100 mg for gross alpha determination and from 0 to 700 mg for gross beta determination. The obtained thicknesses in the self-absorption planchets ranged between 0 and 5 mg cm^{-2} and between 0 and 25 mg cm^{-2} for gross alpha and gross beta determination, respectively. Afterwards, in the measurement of the different samples, we applied the corresponding correction factor.

Gamma emitters were measured with a high-resolution germanium detector (HPGe) (model 2020 Canberra Industries, Meriden, USA), equipped with a standard multi-channel analyser. The operating conditions were a voltage of 4500 V, negative polarity and a relative efficiency of 20%. Genie 2000 software (Canberra Industries, Meriden, USA) was used to acquire and subsequently analyse the information provided by the gamma spectra. The background of the detector was determined by counting a 60 mL plastic beaker containing milliQ water for 20 h and monthly calibration

was performed by using a standard certified solution which was spiked with a known activity concentration of Pb-210 to cover the entire energy range. Both solutions were provided by the *Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas* (CIEMAT) (Madrid, Spain).

For gross alpha and gross beta activity measurements, 0.05 g of dry sludge sample was weighed into a striated stainless steel planchet supplied by Tecnasa (Madrid, Spain), 2 mL of distilled water was added and dried at a temperature not exceeding 150 °C, in accordance with the procedure stipulated by national laboratories [29]. The samples were then measured using two cycles of 1000 minutes in each case.

For the measurement of gamma spectra, 60 g of each sample were placed in a 60 mL beaker, which was introduced in the spectrometer and then measured for 20 hours. In the case of ^{226}Ra , each beaker was sealed and stored for three weeks prior to its measurement in order to ensure secular equilibrium between ^{226}Ra and its short-lived daughters (^{214}Pb and ^{214}Bi). ^{226}Ra activity values were determined from the photopeaks of its daughter nuclides in secular equilibrium.

3. Results and discussion

In this study the gross alpha and gross beta activity indexes, and the activities of some natural (^{226}Ra and ^{210}Pb) and artificial (^{137}Cs) gamma emitters were measured in sediments of the Ebro

river reservoir near the town of Flix. Most of the samples were taken from the area of influence of a DCP plant. Our main aim was to establish a possible relationship between the uniformity in the distribution of radioactive content found in the samples analysed and the industrial activities undertaken at the plant. In the following subsections we discuss the primary results yielded by our study.

We would like to stress that for the purpose of improving and ensuring the quality of the results of all the procedures carried out in our laboratory we participate periodically in both national and international proficiency/ inter-comparison exercises with mineral samples such as soil and phosphogypsum.

3.1. Special cases: C7 profile and the presence of ^{137}Cs

Sampling point C7 was included as a reference. This point, as mentioned earlier, is not affected by the emissions resulting from the industrial activity carried out in the evaluated area, so the sludge samples taken from C7 should, in theory, not contain any contributions resulting from DCP or WWTP dumping.

Figure 3 shows the different values obtained for gross alpha, gross beta and ^{226}Ra activities for the samples taken at different depths for C7 and their error bars (corresponding to counting uncertainties). We obtained values of between 103 and 309 Bq·kg⁻¹ for gross alpha, between 448 and 876 Bq·kg⁻¹ for gross beta and between 28

and $63 \text{ Bq}\cdot\text{kg}^{-1}$ for ^{226}Ra . We compared these results with others reported in the literature in which sludge samples from different areas not influenced by an industrial activity such as a DCP plant were analysed for their radiological content. For instance, Spain has a monitoring program for supervising the radiological quality of the environment called the *Programa de Vigilancia Radiològica Ambiental (PVRA)* which is established under the regulations of the Nuclear Safety Council (CSN) [30]. We selected the results obtained for soil samples from Zaragoza, a city located upstream on the River Ebro, outside of the area of influence of the Flix DCP plant, for comparison purposes. We found that the activity values published by the CSN (between 480 and $670 \text{ Bq}\cdot\text{kg}^{-1}$ for gross beta) were similar to those obtained for C7, and to those reported by United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) (values between 6 and $250 \text{ Bq}\cdot\text{kg}^{-1}$ for ^{226}Ra) [31]. Therefore, we concluded that C7 could be used as good reference, as it is not influenced by DCP. The measurement of an artificial isotope, ^{137}Cs , was also considered as a reference because its activity profile can be very useful in understanding the temporal distribution of the radionuclides in the sediments taken from the area of influence of the DCP plant in Flix. The presence of this artificial radionuclide at certain depths can be related to the nuclear weapons testing carried out in the atmosphere between 1950 and 1960 as well as to the fallout produced by

the Chernobyl accident in 1986, and it has been used to date different sediments [32,33].

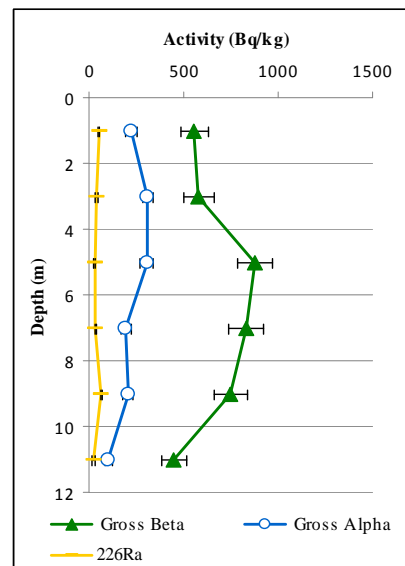


Figure 3. Vertical profiles for gross alpha, gross beta and ^{226}Ra activities (Bq/kg) vs. depth for the sludge sample collected in sampling point C7. Error bars are derived from counting uncertainties at $k=2$.

Figure 4 shows the different profiles obtained for ^{137}Cs activity and the corresponding uncertainties for some of the sampling points examined to illustrate the behaviour of this artificial isotope. Specifically, the figure shows the profiles obtained for sampling points A1 (located in Zone I) and B2 (in Zone II). A similar behaviour has been found with regard to the distribution of ^{137}Cs in the two sampling points. In both cases this artificial radioisotope could be quantified starting at a certain depth, at approximately 3 metres, and up to 5 metres in A1 and 7 metres in B2. This confirms that this radioisotope was introduced into the environment

from a certain date, probably in the fifties, when this specific radionuclide was released into the atmosphere because of the nuclear weapons testing performed between 1950 and 1960. Moreover, due to the Chernobyl nuclear accident in 1986 it was an additional input of this isotope. The activity values obtained ranged from 5 to 20 Bq·kg⁻¹. It is important to note that the data we obtained also allows us to establish, by comparison, when the main releases from the DCP industrial plant occurred.

3.2. Gross alpha activity index

One of the parameters measured for all the samples was the gross alpha activity index, which is likely influenced by the DCP plant. Our results are shown in Figure 5, which gives the profiles of the six different sampling points in the two different testing zones. A different distribution was found at all these sampling points than at C7 (see Figure 3), with higher activity values for gross alpha obtained at these six sampling points, mainly in the upper layers (between 1 to 2 metres), followed by a general decrease in activity values. Error bars corresponding to the uncertainties we encountered are also shown in the figure.

The results yielded by sampling point A1 (Figure 5a), which is located just in front of the DCP plant, reveals some interesting data. A maximum concentration of gross alpha activity was found in this sample at 1 m (11118 ± 234 Bq·kg⁻¹) followed by a marked decrease up to a depth of 5 m (339 ± 44

Bq·kg⁻¹). At that depth and deeper, activity remained more or less constant. Therefore, it can be concluded that the influence of the DCP plant decreased as depth increased, since the results obtained were similar to those found at sampling point C7. This behaviour in site A1 might be explained by the profile obtained for ¹³⁷Cs and through some bibliographic data regarding the historical evolution of the DCP plant [34]. We can attribute the higher values of activity in the upper layers to the higher productivity of the DCP industry during the period from 1992 to 1997. So the main contribution to the radioactivity in these sludge samples took place after the Chernobyl nuclear accident. This assessment was reached by comparing the profiles for this sampling point (Fig. 4a and 5a), which demonstrated the prior introduction of ¹³⁷Cs.

Samples from five different points (B2, B3, B4, B5 and B6) were collected in Zone II, which is located in front of the WWTP. Figure 5 (b to f) shows the results obtained from those samples. For instance, in the B3 profile, maximum activity was found at a depth of 1 m (12992 ± 275 Bq·kg⁻¹), while at 3 m activity was determined at 303 ± 30 Bq·kg⁻¹. These values suggest that the measured activity remained more or less constant over time. A very similar behaviour was found in sampling point B2. The other three sampling points (B4, B5 and B6) yielded activity values in the upper layer that were approximately three times lower than in B2 or B3.

In the activity profiles for some

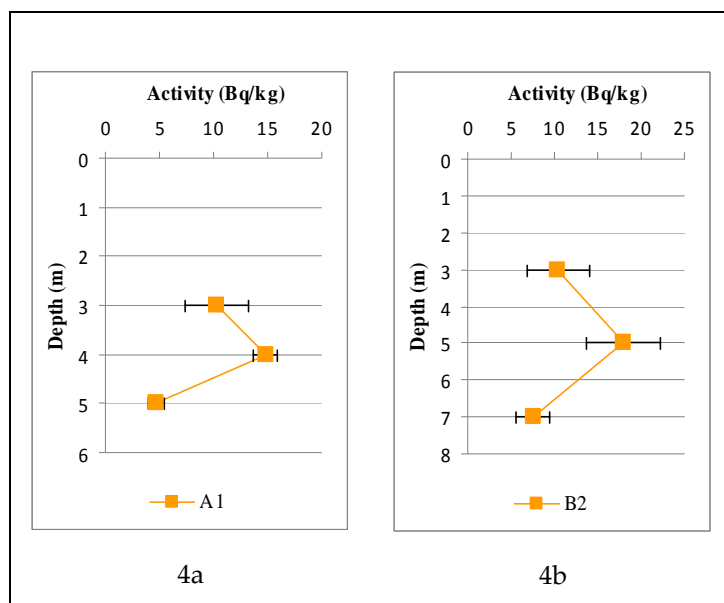


Figure 4. Vertical profiles for ^{137}Cs (Bq/kg) vs. depth from sludge samples collected in sampling points A1 (Figure 4a) and B2 (Figure 4b). Error bars consider counting uncertainties at $k=2$.

sampling points, such as B4, a pronounced increase in measured activity was found at a certain depth, for example, between 7 and 9 metres. Taking into account the evolution of the industrial activity at the site, this might be attributed to a sporadic release of waste.

3.3. Gross beta activity index

We also measured gross beta activity for all the sludge samples. The corresponding values obtained are also presented in Figure 5, which shows that the trend for gross beta activity is very similar to that obtained for gross alpha activity. One of the main contributors to gross beta activity in different soils is ^{40}K [31] and we believe that this isotope also plays a relevant role in the different samples analysed in this case. However, due to the DCP

industrial activity, other beta isotopes may have also contributed to gross beta activity. To verify this, the relationship between ^{40}K activity and gross beta activity with their error bars is shown in Figure 6. Specifically, the graphs obtained for C7 and A1 are shown as examples to illustrate this behaviour. Data for C7 are primarily shown because this sampling point is out of the area of influence of the DCP plant, so a linear correlation between the two measured parameters is expected. This trend is shown in the figure corresponding to sample point C7 (Figure 6a). However, in sampling point A1 (Figure 6b) no linear correlation between the two parameters was found in the upper layers (the first 1 to 3 metres of depth in the profile), which suggests that other beta isotopes from the ^{238}U chain apart from

^{40}K have contributed to gross beta activity. According to various previous studies reported in the bibliography, such as those by Martínez et al. [35] and Azouazi et al. [36], low levels of ^{40}K in the sedimentary material are indicators of the presence of high levels of the other isotopes, mainly ^{210}Pb and other ^{238}U descendants and point to the intrusion of NORM from industries which use phosphate rocks as a raw material in the production of fertilizer.

Also, according to UNSCEAR [31] and the study published by Khater et al. [37] the raw material used in the phosphate industry is very poor in ^{40}K . This leads us to conclude that apart from ^{40}K , other contributors have played a role in the gross beta activity measured in this study, such as ^{210}Pb and ^{214}Pb , which are derived from the ^{238}U decay series.

3.4. Gamma emitters

Gamma activity was measured to verify the presence of some of the main individual isotopes that may have contributed to the gross alpha and gross beta activities measured previously. To this end, we measured activity resulting from ^{226}Ra , ^{210}Pb and ^{40}K . The resulting values are shown in Table 1 along with the corresponding uncertainty values. In the case of ^{210}Pb (46.5 KeV) the uncertainties were higher than the other radionuclides due to the Compton effect and the high background, which is characteristic of the low energy spectrum in which this

radionuclide emits. Comparing the values reported in Table 1 with the corresponding profiles for gross alpha and gross beta activities (see Figure 5), the same trend emerges higher activity values for such isotopes (^{226}Ra and ^{210}Pb) were obtained in the upper layer (at a depth of 1 metre). Specifically, results comparable to those published in Costa's study [20] were obtained in terms of the values determined in the upper layers.

The results from sampling point A1 also lead to several important conclusions. Maximum concentrations of ^{226}Ra and ^{210}Pb activity in this sample were found at 1 m ($5847 \pm 97 \text{ Bq}\cdot\text{kg}^{-1}$ and $2499 \pm 606 \text{ Bq}\cdot\text{kg}^{-1}$, respectively) and then dropped off considerably until a depth of 5 m ($34 \pm 3 \text{ Bq}\cdot\text{kg}^{-1}$ of ^{226}Ra and $<\text{MDA}$ for ^{210}Pb). These values are not significantly different from those measured at sampling point C7. Therefore, we can conclude that ^{226}Ra and ^{210}Pb contribute to a great extent to the gross activity measured and their origin can be related to the industrial activity carried out in the testing area. In the case of B4, B3, B5 and B6, higher concentrations of these isotopes were obtained at a depth of 1 metre. Moreover, for some sampling points such as B4, a pronounced increase in the measured activity was obtained at a certain depth in the corresponding activity profiles. This was in accordance with the profiles obtained for gross alpha and gross beta activity values.

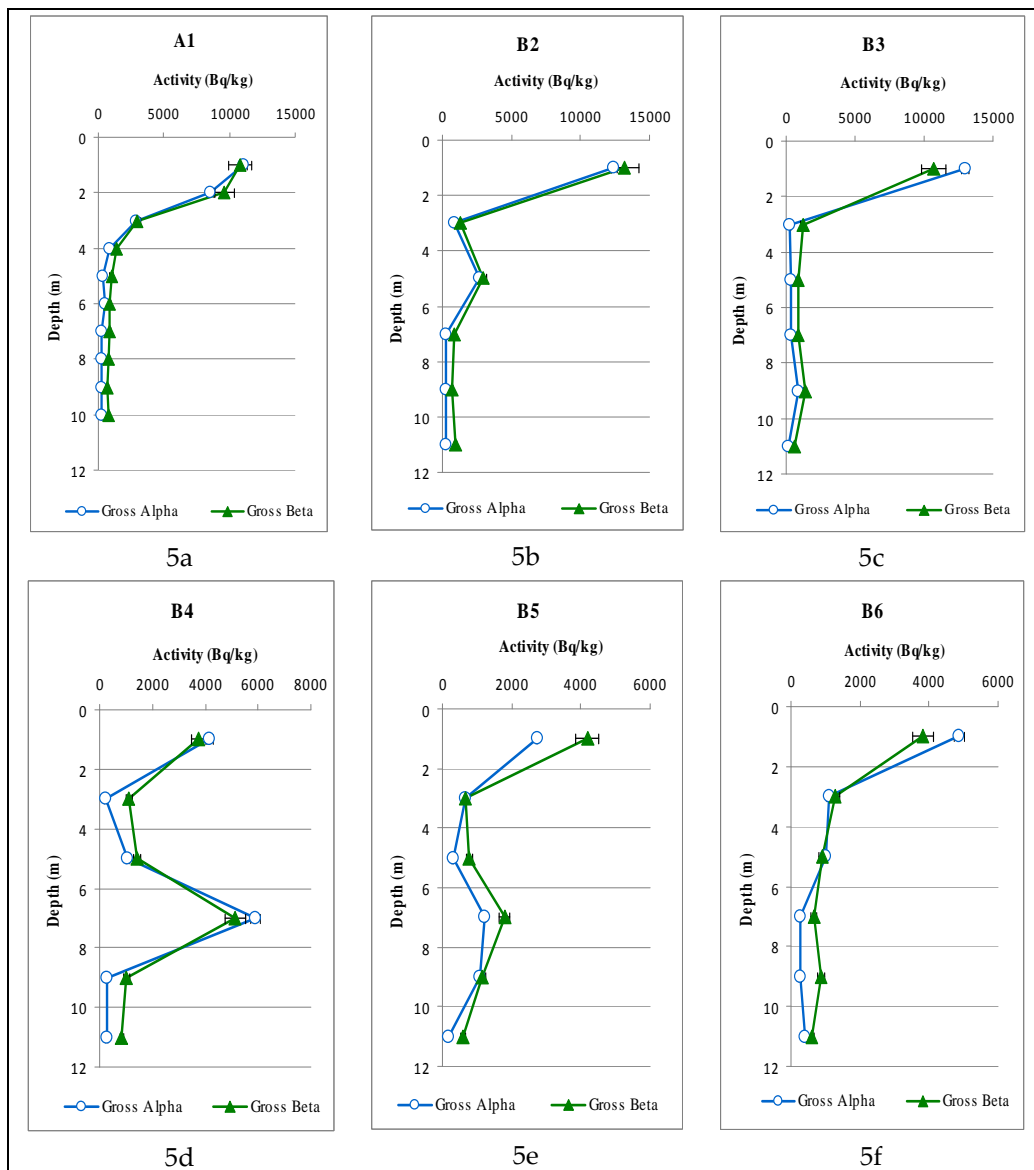


Figure 5. Vertical profiles for gross alpha and gross beta activities (Bq/kg) vs. depth obtained for the sludge samples collected in the different sampling points: A1 (Figure 5a), B2 (Figure 5b), B3 (Figure 5c), B4 (Figure 5d), B5 (Figure 5e) and B6 (Figure 5f). Error bars consider counting uncertainties at $k=2$.

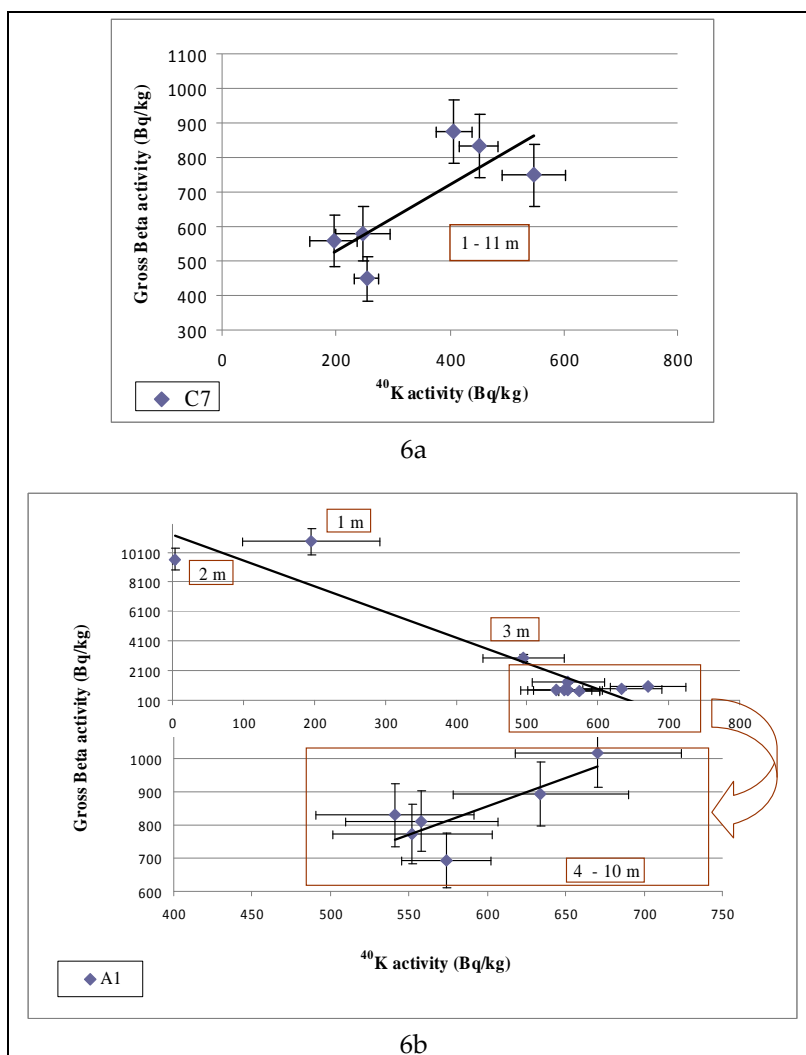


Figure 6. Gross beta activities (Bq/kg) vs ^{40}K activities (Bq/kg) for sludge samples from sampling point C7 (Figure 6a) and A1 (Figure 6b). The corresponding depths are also indicated in the figure.

4. Conclusions

Sludge samples in two different zones within the area of influence the DCP industry in Flix were measured for their radiological content. Samples closer to the surface were found to have higher activity values and this trend was more pronounced in Zone I (located in front of the DCP plant) than

in Zone II (located in front of the WWTP).

The individual evaluation of different isotopes from the ^{238}U chain led us to conclude that ^{226}Ra and ^{210}Pb contributed to a great extent to the gross activity measured and their origin is related to the industrial activity carried out in the testing area. The distribution of the radioactivity

Table 1. Activity concentration and uncertainty (K=2) of ^{226}Ra , ^{210}Pb and ^{40}K (Bq/kg) in different depths from sludge samples.

Code	A1			B2			B4		
	^{226}Ra (Bq kg $^{-1}$)	^{210}Pb (Bq kg $^{-1}$)	^{40}K (Bq kg $^{-1}$)	^{226}Ra (Bq kg $^{-1}$)	^{210}Pb (Bq kg $^{-1}$)	^{40}K (Bq kg $^{-1}$)	^{226}Ra (Bq kg $^{-1}$)	^{210}Pb (Bq kg $^{-1}$)	^{40}K (Bq kg $^{-1}$)
1	5847 ± 97	2499 ± 606	196 ± 97	2760 ± 53	1118 ± 277	164 ± 22	566 ± 15	356 ± 97	323 ± 61
2	2479 ± 48	1127 ± 272	<69	—	—	—	—	—	—
3	341 ± 11	259 ± 8	495 ± 57	242 ± 10	125 ± 64	561 ± 66	38 ± 3	<55	883 ± 64
4	114 ± 4	86 ± 38	558 ± 51	—	—	—	—	—	—
5	34 ± 3	<55	671 ± 53	687 ± 20	319 ± 99	624 ± 78	185 ± 9	129 ± 67	600 ± 36
6	40 ± 6	<18	541 ± 50	—	—	—	—	—	—
7	43 ± 5	<54	634 ± 56	31 ± 5	<18	641 ± 52	996 ± 25	820 ± 208	411 ± 84
8	35 ± 3	<19	552 ± 51	—	—	—	—	—	—
9	30 ± 5	<53	574 ± 29	30 ± 3	<19	597 ± 54	42 ± 6	<56	712 ± 33
10	34 ± 5	<55	558 ± 49	—	—	—	—	—	—
11	—	—	—	26 ± 5	<18	534 ± 28	39 ± 5	<54	645 ± 54

Code	B3			B5			B6		
	^{226}Ra (Bq kg $^{-1}$)	^{210}Pb (Bq kg $^{-1}$)	^{40}K (Bq kg $^{-1}$)	^{226}Ra (Bq kg $^{-1}$)	^{210}Pb (Bq kg $^{-1}$)	^{40}K (Bq kg $^{-1}$)	^{226}Ra (Bq kg $^{-1}$)	^{210}Pb (Bq kg $^{-1}$)	^{40}K (Bq kg $^{-1}$)
1	4182 ± 77	1337 ± 330	285 ± 28	896 ± 21	312 ± 83	200 ± 29	1034 ± 28	433 ± 115	332 ± 53
2	—	—	—	—	—	—	—	—	—
3	50 ± 7	<22	440 ± 34	131 ± 8	67 ± 26	<40	172 ± 9	<29	291 ± 58
4	—	—	—	—	—	—	—	—	—
5	48 ± 6	<19	557 ± 5	38 ± 6	<18	549 ± 48	172 ± 10	<29	301 ± 25
6	—	—	—	—	—	—	—	—	—
7	93 ± 6	44 ± 34	441 ± 25	301 ± 10	82 ± 38	336 ± 52	29 ± 5	<18	531 ± 98
8	—	—	—	—	—	—	—	—	—
9	134 ± 8	54 ± 35	543 ± 53	150 ± 8	53 ± 40	438 ± 44	30 ± 5	<19	606 ± 52
10	—	—	—	—	—	—	—	—	—
11	27 ± 4	<18	398 ± 45	22 ± 6	<22	490 ± 29	30 ± 5	27 ± 21	471 ± 49

over time and in relation to the industrial activity might be explained through the data obtained by ^{137}Cs measurement. We found concordance in the accumulation of radionuclides and the activity carried out in the DCP plant.

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DESENVOLUPAMENT DE TÈCNiques ANALÍTIQUES PER A LA DETERMINACIÓ DE RADIONÚCLIDS
Montserrat Mola Arques
Dipòsit Legal: T.1294-2013

**3.1.2. Comparative study of different analytical methods
for the determination of ^{238}U , ^{234}U , ^{235}U , ^{230}Th i
 ^{232}Th in NORM samples (Southern Catalonia)**

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COMPARATIVE STUDY OF DIFFERENT ANALYTICAL METHODS FOR THE DETERMINATION OF ^{238}U , ^{234}U , ^{235}U , ^{230}Th AND ^{232}Th IN NORM SAMPLES (SOUTHERN CATALONIA)

M. Mola, M. Palomo, A. Peñalver, F. Borrull, C. Aguilar*
Departament de Química Analítica i Química Orgànica
Universitat Rovira i Virgili, Marcel·lí Domingo s/n, 43007 Tarragona, Spain
Unitat de Radioquímica Ambiental i Sanitària (UR AIS), Consorci d'Aigües de Tarragona (CAT), Ctra Nacional 340, km 1094, 43895 L'Ampolla, Spain

Abstract

Uranium and thorium isotopes from sludge samples taken from an area of influence of a dicalcium phosphate factory, located close to the Ebro River reservoir in Flix, and from mineral raw materials (coal and phosphate) which were deposited in Tarragona Harbour (Catalonia) have been measured. To do that, several procedures to determine these isotopes have been applied and compared in terms of accuracy, precision and total analysis time. In particular, digestion procedures, such as one based on conventional acidic digestion or another based on the use of microwave digestion (MW), have been tested. Moreover, different radiochemical separation procedures have been applied. In this regard, one method based on liquid-liquid extraction using TBP/xylene and another based on the use of extraction chromatography using UTEVA resins have been compared. Firstly, the different proposed methods were tested by analyzing a phosphogypsum sediment and a moss-soil sample from two different intercomparison exercises. The MW-UTEVA method provided the best results (recoveries higher than 82% for uranium and thorium isotopes) and was then applied to the NORM samples. The obtained results showed that the higher uranium and thorium activities values were found in phosphate raw material and in the more superficial samples located in sludge sediments next to the dicalcium phosphate factory.

Keywords: UTEVA resin, alpha spectrometry, microwave digestion, naturally occurring radioactive material, dicalcium phosphate factory, phosphate, coal.

INTRODUCTION

Recent studies have shown that the main sources of technologically enhanced natural radioactivity are phosphate industrial activities (Ashraf Khater et al., 2001; Abril et al., 2009;

García-Talavera et al., 2011) and coal-fired power plants (Cevik et al., 2008; Mahur et al., 2008; Papastefanou, 2010), among others. Phosphate industry uses, as a raw material, phosphate rocks which contain several radionuclides, mainly ^{238}U and its

decay chain daughters (up to $5 \text{ Bq}\cdot\text{g}^{-1}$) (Casacuberta et al., 2009). Generally, if the industrial waste is released to the environment, an uncontrolled enhancement of the natural radioactivity is observed (Villa et al., 2009). On the other hand, coal-fired power plants, which play an important role in electric power generation, need fossil fuels such as coal that also contain traces of naturally occurring radionuclides such as ^{238}U , ^{226}Ra , ^{210}Pb , ^{232}Th and ^{40}K (Tsikritzis et al., 2008; Janković et al., 2011). Usually, the coal is extracted from mines and then it is transported to intermediary storage areas such as industrial parks, harbours, etc. before the industrial processes that involve the use of that material.

The environmental impact of these activities dealing with naturally occurring radioactive materials (NORM) is important. In this sense, the evaluation of the potential environmental radiological significance, through the measurement of concentrations of uranium and thorium isotopes in different input and output materials as mineral raw materials (phosphate and coal) or waste sub-products, can provide important information. For this purpose, several steps previous to the measurement of these isotopes by alpha-spectrometry in mineral matrices are required. First it is necessary the conversion of the isotopes associated with the matrix into their soluble form, and then their radiochemical separation. In particular, the complete dissolution of the

samples has mainly been performed using acidic digestion, but this procedure is time consuming and implies the use of hazardous reagents (Lee et al., 2005; Mihai, 2005). More recently, alternative procedures that simplify the digestion processes have been introduced, such as the use of microwave digestion (MW) or fusion digestion (Mihai, 2005; Michel et al., 2008; Singhal et al., 2010). After the sample digestion, there are different alternatives for the radiochemical separation of the different radioisotopes (Eikenberg et al., 2009; Palomo et al., 2010; Reis et al., 2011). The most widely used methodologies are based on the use of liquid-liquid extraction (LLE) and, in the case of uranium and thorium separation, one of the most commonly used strategies is performing the extraction with tri-n-butyl phosphate (TBP) and xylene and then a purification process by using an ion-exchange material (Kiliari and Pashalidis, 2010; Lozano et al., 2010; Palomo et al., 2010). However this approach has some disadvantages, such as the use of large amounts of organic solvents, which can be harmful. Moreover, the recoveries reported by some authors are rather limited. For instance, Lozano et al. (2010) obtained recoveries between 40% and 70% for uranium and thorium isotopes in soils and vegetables and almost 70% in water samples. Other strategies reported in the bibliography for the radiochemical separation including the use of extraction chromatography have been spread intensively over the last few

years due to the availability of different commercial and specific resins, such as UTEVA, TEVA or TRU (Horwitz et al., 1992; Pilviö and Bickel, 2000; Maxwell and Culligan, 2006; Tosheva et al., 2006; Tsai et al., 2008; Casacuberta et al., 2012). For instance, in the study from Tosheva et al. (2006) the obtained recovery values for uranium and thorium isotopes were between 78% and 87% in environmental waters, using the combination of 3M RAD™ disks (for isolating Pb) and UTEVA resins.

The present study aims to assess the natural radioactivity, through the measurement of thorium and uranium isotopes, in raw and waste sub-products materials from two different areas. The first area is located in front of a dicalcium phosphate (DCP) factory in Flix where between 200.000 and 360.000 tones of sludge containing relatively high levels of radioactivity are accumulated. The second area is located in Tarragona Harbour which manages the entrance and storage in uncovered zones of 1.100.000 tons-year⁻¹ of coal and 2.000 tons-year⁻¹ of phosphates. To be able to perform this radiological characterization, different methodologies have been compared by the analysis of two different samples from intercomparison exercises organized by the Nuclear Safety Council (CSN) and the International Atomic Energy Agency (IAEA), in order to find the best conditions to determine uranium and thorium isotopes.

2. Methods and sampling details

2.1. Instrumentation

Speedwave four microwave digestion system with built-in, non-contact temperature and pressure measurement supplied by Berghof (Eningen, Germany) as used for the digestion of solid samples.

The alpha-spectrometer (EG&G ORTEC, Model 676A, USA) includes an ion-implanted silicon detector (ORTEC, size: 450 mm²; alpha resolution: 25 keV FWHM at 5.48 MeV of ²⁴¹Am) in a vacuum chamber through a vacuum pump (Edwards, Model E2M8), a detector bias supplier, a preamplifier, a linear amplifier and a multichannel pulse height analyzer. The calibration was carried out using a stainless steel planchet with certified activities for ²³³U, ^{239,240}Pu and ²⁴¹Am obtaining efficiencies (6 different detectors) oscillated between 16.8% and 17.6%. During the measurement, the pressure of the chamber was maintained at 13.328 Pa. The electro-deposition apparatus was supplied by Tecnasa (Madrid, Spain).

2.2. Reagents and materials

All chemical reagents used in this study were of analytical grade. Hydrochloric acid (38%), nitric acid (65%), hydrogen peroxide (30%), ammonia solution (25%), iron chloride (III), phenolphthalein (1% solution in ethanol), oxalic acid dehydrate (99.5%) and xylene were all supplied by J.T. Baker (Deventer, Holland). Ascorbic

acid (99.7%) was supplied by Merck (Darmstadt, Germany). Calcium nitrate tetrahydrate ($\geq 99\%$), ammonium hydrogenphosphate (98%) and aluminum nitrate nonahydrate p.a., were supplied by Sigma-Aldrich (St. Louis, MO, USA). Tri-n-butyl phosphate (TBP) was supplied by Fluka (Steinheim, Germany). Columns (20 cm length and 10 mm internal diameter) which contained 7.5 g of BIO-RAD AG1-X8 resin (100-200 mesh chloride form) were supplied by Bio Rad Laboratories (El Prat de Llobregat, Spain). Uteva resin was purchased from Triskem Inter. (Bruz, France) as a 2 cm³ packed column. Digested samples were filtered with 0.45 μm filters supplied by Whatman (Maidstone, England). Uranium and thorium were electroplated onto stainless steel planchets (25 mm diameter and 0.63 mm thickness) supplied by Tecnasa (Madrid, Spain). To determine the recovery of tested methods, ²³²U and ²²⁹Th certified solutions with well-known activity concentration values were used, both provided by Ciemat (*Centro de Investigaciones Energéticas, Medio-ambientales y Tecnológicas*) (Madrid, Spain).

2.3. Samples

To test the proposed methods, we used two reference materials from different intercomparison exercises. One was organized by the Nuclear Safety Council (CSN) in 2008 and the sample was a phosphogypsum sediment from Huelva (Spain). The second one was from an international

intercomparison exercise organized by the International Atomic Energy Agency (IAEA) in 2009. The sample submitted was a moss-soil from an old red marble mine in Hungary. Coal and phosphate samples were taken from the storage area in Tarragona Harbour, where, as it is shown in Figure 1, there are two subareas where coal (which are stored an uncovered zone of 212.420 m²) and phosphate (stored an uncovered zone of 2.580 m²) are deposited. In particular samples of 300 g were collected at five different points distributed uniformly in the corresponding mountains of material stacked, and then the coal and phosphate samples were mixed and homogenized in a plastic container.

Sludge samples from an industrial area of Flix reservoir were analyzed. In particular, we analyzed samples from sediments originating from a DCP factory's industrial activity located beside the Ebro River. The location of the different sampling points is shown in Figure 2. It is possible to distinguish two different zones: zone I, which is located in front of the DCP factory and zone II, which is located in front of the wastewater treatment plant (WWTP). Sampling point A1 is located in zone I and sampling points B1, B2 and B3 are located in zone II. At each sampling point, sludge samples were collected with a specific extraction crane at different depths between 1 m and 11 m, taking approximately 750g of the damp sludge at each depth and sampling point. After collection, samples were introduced into plastic

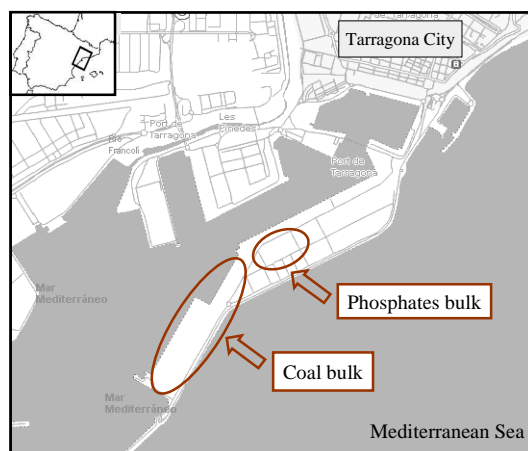


Figure 1. Area of Tarragona Harbour close to the Tarragona city. Location to the mineral raw material deposits of coal and phosphate.

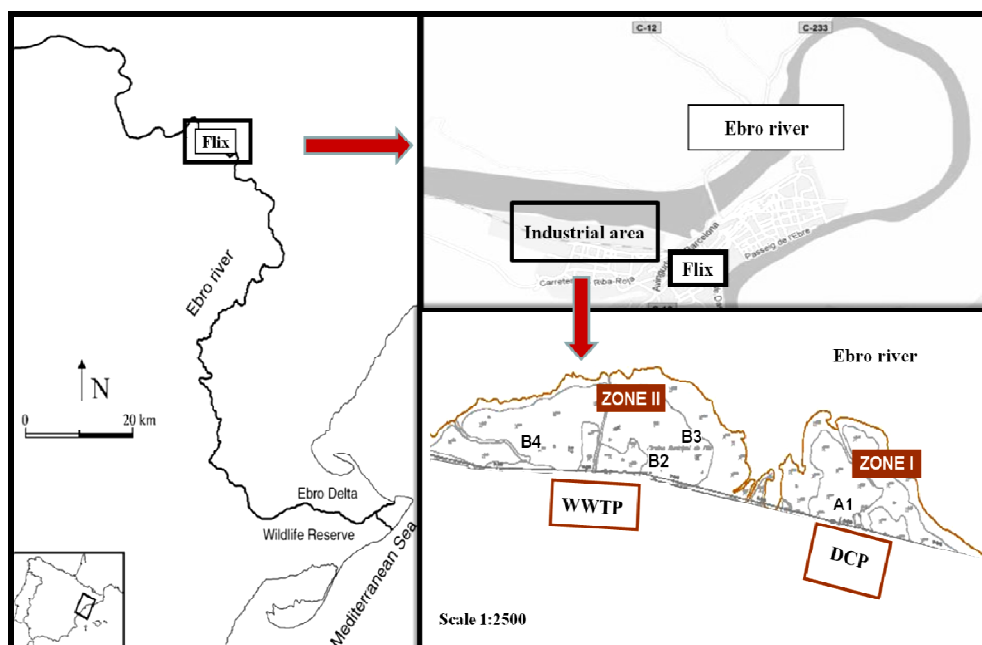


Figure 2. Area of study close to the DCP factory from which the emerging sludge samples were deposited in the Ebro River (Southwest Catalonia, Spain) showing the sampling points.

containers. Therefore, a total of 28 sludge samples were taken.

2.4. Initial treatment

Initially, samples were dried in a stove at 110 °C and then crushed in a ball

mill and sifted in a sieve of 250 µm. Afterwards, about 20 g of dry sample was introduced in a muffle furnace at 550 °C for 12 hours and, after cooling, samples were transferred into a vessel. The samples were spiked with the

tracers, in particular with 1 mL of ^{232}U ($42.4 \text{ Bq}\cdot\text{L}^{-1}$) and 1 mL of ^{229}Th ($61.0 \text{ Bq}\cdot\text{L}^{-1}$) to evaluate the radiochemical yield and were dried under an IR lamp.

The amount of sample taken was dependent on the subsequent digestion process. As such, 2.5 g of sample was taken when the acidic digestion was performed and 0.5 g was the sample weight for the microwave digestion.

2.5. Mineralization of the solid samples

Two different procedures were applied for the mineralization of samples from intercomparison exercises. The first of these consisted of an acidic digestion following the EPA Method 3050B (1996). For this, 2.5 g of ashing sample were transferred to a Teflon beaker and then leached with aqua regia (3:1 HNO_3/HCl). The final solution was evaporated to dryness. Afterwards, 10 mL 8M HNO_3 were added and successive additions of 5 mL H_2O_2 were performed until no further reaction was observed. This solution was evaporated to dryness and repeats the digestion but left none evaporated solution in the end.

The second procedure was based on the use of microwave-assisted digestion following the procedure described in EPA Method 3051A (1998). In this case, 0.5 g of ashing sample was transferred to a Teflon-PFA (perfluoroalkoxy) closed vessel and then 8 mL of aqua regia were added (3:1 HNO_3/HCl). The mixture was introduced into the microwave

system for 30 minutes under high pressure and high temperature conditions (about at $215 \text{ }^\circ\text{C}$).

After cooling the sample in both cases, the solution was filtered through a $0.45 \text{ }\mu\text{m}$ pore-size syringe filter to remove the insoluble particles and then it was brought to a final volume of 50 mL with deionized water.

2.6. Radiochemical separation procedure

We tested two different procedures for the precipitation of uranium and thorium. In the first, 30 mL of iron chloride (III) solution ($30 \text{ mg}\cdot\text{mL}^{-1}$) were added and then the pH was adjusted to 8 by slowly adding a concentrated ammonia solution in order to co-precipitate uranium and thorium with iron ($\text{Fe}(\text{OH})_3$). The pH was controlled using pH test strips. In the second procedure, the precipitate was obtained after adding 0.5 mL of calcium nitrate solution ($1.25 \text{ mg}\cdot\text{mL}^{-1}$) and 200 μL of ammonium hydrogen-phosphate ($3.2 \text{ mg}\cdot\text{mL}^{-1}$). The pH was then adjusted (using also pH test strips) about 6 by slowly adding a concentrated ammonia solution in order to co-precipitate uranium and thorium with calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) (Thakkar, 2001). In both procedures, the co-precipitate was recovered by a centrifugation process, discarding the supernatant. Precipitate was then dissolved with 10 mL of $3 \text{ mol}\cdot\text{L}^{-1} \text{HNO}_3$ and $1 \text{ mol}\cdot\text{L}^{-1}$ aluminum nitrate ($\text{Al}(\text{NO}_3)_3$) solution. After the preconcentration step, it is necessary to separate uranium and thorium isotopes. In our study, we tested two

different procedures. The first was based on a liquid-liquid extraction procedure using TBP/xylene and ion-exchange material (BIO-RAD AG1-X8 resin) for a final purification process (Palomo et al., 2010). The second was based on an extraction chromatography procedure by using an UTEVA resin, following the method described by Horwitz et al. (1992) with some further modifications as proposed by Oliveira and Carvalho (2006). When the uranium and thorium had been extracted by the UTEVA resin, in order to clean-up the resin for future extractions, 20 mL of oxalic acid 0.1 mol·L⁻¹ were used.

2.7. Electrodeposition and sample counting

In all the procedures previously described, the uranium and thorium fractions obtained after separation were evaporated in the bath sand. When almost dry, the residues, which contain uranium or thorium, were reconstituted by adding 1 mL of 0.3 M Na₂SO₄. This solution was then dried, the residue treated with 0.3 mL of concentrated H₂SO₄ and then 5 mL of desionized water were added, along with two drops of thymol blue. This solution was heated and its pH was adjusted until the change of indicator was a yellow colour by the addition of concentrated NH₄OH drop by drop. The solution was then transferred to an electrodeposition cell (Talvite, 1972) and submitted to electrolysis for 2 hours, under current density of 1.5 A/cm². Just before the end of the electrolysis, 1 mL of concentrated

NH₄OH was added in order to assure uranium and thorium deposit attachment on the stainless steel disk (Zarki et al., 2001). The electrodeposition apparatus was used to accumulate uranium and thorium in the form of a uniform film deposited on stainless-steel disks of 20 mm in diameter. The anode was a polished platinum spiral wire. Following the deposition, the disc was counted for 72 hours to determine the activity of uranium and thorium isotopes using an alpha-spectrometer (ORTEC Plus).

3. Results and discussion

The present study is conducted to characterize the NORM waste generated from a dicalcium phosphate factory production, and also some materials temporarily deposited in Tarragona Harbour, in particular some mineral raw materials (phosphate and coal). From a radiological protection point of view, it is important to know which the individual radiological contributors to the possible high activity level of these kind of samples. For that purpose, uranium and thorium isotopes from different samples taken from both areas of study have been determined. Previously to that, and in order to find the best method in terms of accuracy and precision, we tested different experimental conditions by the analysis of two samples from different intercomparison exercises. In the following subsections we discuss the main results obtained through this study.

3.1. Determination of uranium and thorium in intercomparison samples

To find out the optimum conditions to perform the determination of uranium and thorium isotopes, different experimental conditions were tested by the analysis of two intercomparison samples. In particular uranium and thorium were determined in a phosphogypsum sample from an exercise organized by CSN in 2008, and for the other sample, a moss-soil sample submitted by the IAEA in 2009 uranium was determined.

Table 1 shows the main differences between the four procedures followed to analyse these intercomparison samples. The variations could be

attributed to the digestion method by acidic digestion or by microwave assisted digestion, the reagent used for the precipitation of actinides, FeCl_3 or $\text{Ca}(\text{NO}_3)_2/(\text{NH}_4)_2\text{HPO}_4$, and the separation procedure followed in each case, LLE followed by a purification process using an ion-exchange resin or by extraction chromatography by using Uteva columns. Tables 2 and 3 show the main results obtained when the four different procedures included in this study were applied to the analysis of the intercomparison samples. For each method three replicates were performed. In the tables, the reference activity values (in the case of CSN for uranium and thorium isotopes or only for uranium in the case of IAEA)

Table 1. Evaluated procedures for the determination of uranium and thorium.

Method	Sample amount (g)	Dissolution method	Precipitate	Separation
1	2.5	Mineralization	$\text{Fe}(\text{OH})_3$	TBP / Xylene
2	2.5	Mineralization	$\text{Fe}(\text{OH})_3$	Uteva
3	2.5	Mineralization	$\text{Ca}_3(\text{PO}_4)_2$	Uteva
4	0.5	Mineralization with MW	$\text{Ca}_3(\text{PO}_4)_2$	Uteva

according to the organizers of each intercomparison exercise are included as A_{ref} . The recovery values obtained for each procedure for the corresponding tracer (^{232}U and ^{229}Th) are also included. Event that the minimum detectable activities (MDA) for uranium and thorium isotopes were not listed in the tables, the corresponding values ranged between 0.2 and 0.7 $\text{Bq}\cdot\text{Kg}^{-1}$.

In the case of the phosphogypsum sample from CSN, as can be observed

in Table 2, the recovery value obtained for uranium when the procedure 1 was used was rather low. This can be explained by losses during the liquid-liquid extraction step or by the incomplete separation between both isotopes. In contrast, the highest recoveries for the tracer were obtained for procedures 3 and 4, which presented also similar values. In both cases, co-precipitation of uranium and thorium was performed with $\text{Ca}_3(\text{PO}_4)_2$ followed by concentration

and separation with UTEVA columns, so it can be concluded that Fe^{+3} has a negative influence on the process. This has been previously reported in the bibliography. For example Missana et al. (2003) and Santos et al. (2002) demonstrated that the presence of Fe^{3+} ions contribute to the formation of colloidal species with uranium ions or that the Fe^{+3} ions are stronger in competition to placed in the ion-exchange selective resin. On the other hand, for all the tested methodologies the obtained values were close to the reference activity provided by the organizers of each intercomparison exercise, with Z-score values between 0.1 and 0.7.

Table 2 also shows the results obtained for thorium isotopes (^{230}Th and ^{232}Th). As can be observed, in this case, the highest recovery value was obtained for the procedure 4 ($82 \pm 17\%$). Again, these results can be attributed to the interference due to the presence of Fe^{3+} ions (Santos et al., 2002). When we compared the results for thorium isotopes with those provided by CSN, we could verify that for all the tested conditions, the obtained values were close to the reference activity values with Z-score values between 0.1 and 2. In the case of the other intercomparison sample from IAEA, method 2 was not tested due to the previous results that showed the high interference by Fe^{+3} ions with UTEVA columns. So for this sample, only methods 1, 3 and 4 were tested for uranium determination. According to the data presented in Table 3, we could observe that even that with the

acidic digestion and using $\text{Ca}_3(\text{PO}_4)_2$ as coprecipitating agent, the recovery was around 94%, the measured activities for uranium isotopes were far from the reference activity (trueness ranged between 53% and 57%). The differences between the sample matrix compositions of both intercomparison samples could be the reason of such behaviour. However, using microwave assisted method, the obtained recovery was similar ($87 \pm 7\%$) and the activities of the uranium isotopes were close to the reference activity. So considering all these results we can affirm that as it happens for the other intercomparison sample, the best results were obtained for the procedure 4 that does not involve an acidic digestion.

3.2. Determination of uranium and thorium in sediment sludge, coal and phosphate samples

Under the optimum conditions established, different mineral raw materials and waste sludge samples from different NORM industries were measured following the procedure numbered as 4 in Table 1. In the case of the coal samples and the phosphate samples taken from Tarragona Harbour, the average activities obtained for uranium and thorium isotopes with their respective uncertainties are shown in Table 4. In this case, the minimum detectable activities ranged between 0.4 and 1.2 $\text{Bq}\cdot\text{kg}^{-1}$.

For the coal samples, the obtained activities for ^{238}U and ^{234}U isotopes were similar and around 180 $\text{Bq}\cdot\text{kg}^{-1}$.

Table 2. Average of ^{234}U , ^{238}U , ^{230}Th and ^{232}Th specific activity values (A) and associated uncertainties obtained when a reference phosphogypsum sample (CSN 2008) was processed with the different tested methods. The table also includes the test Z-score, the relative bias and the exactitude. Uncertainties are expressed at $k=1$.

Method	PG (g)	*n	**η %	^{234}U					^{238}U				
			^{232}U	A (Bq/Kg)	A ref	Z score	Precision (%)	Trueness (%)	A (Bq/Kg)	A ref	Z score	Precision (%)	Trueness (%)
1	2.5	3	50 ± 5	51 ± 6	56±10	0.5	22	9	48 ± 6	55±10	0.7	22	13
2	2.5	3	75 ± 6	55 ± 8		0.1	22	2	53 ± 7		0.2	23	4
3	2.5	3	95 ± 6	54 ± 7		0.2	22	4	52 ± 6		0.3	22	5
4	0.5	3	98 ± 2	59 ± 7		0.3	22	5	59 ± 8		0.4	23	7
			^{229}Th	^{230}Th					^{232}Th				
1	2.5	3	55 ± 18	282 ± 34	332±66	0.8	23	27	3.8 ± 0.9	6.1±1.2	2.0	29	38
2	2.5	3	27 ± 6	357 ± 41		0.4	23	12	5 ± 1		1.4	37	26
3	2.5	3	61 ± 4	311 ± 35		0.3	23	11	5.6 ± 0.8		0.4	24	8
4	0.5	3	82 ± 17	354 ± 42		0.3	23	10	6 ± 1		0.1	30	2

*n = number of samples analyzed

**η = chemical recovery (obtained from ^{232}U tracer and ^{229}Th tracer)

In the case of thorium, the measured activities were higher: $474 \pm 103 \text{ Bq} \cdot \text{kg}^{-1}$ for ^{230}Th and $275 \pm 24 \text{ Bq} \cdot \text{kg}^{-1}$ for ^{232}Th . In both cases, these values were higher than the natural radionuclide concentrations in soil according to the United Nations Scientific Committee

on the Effects of Atomic Radiation (UNSCEAR) (2000) which average values were $35 \text{ Bq} \cdot \text{kg}^{-1}$ for ^{238}U and $30 \text{ Bq} \cdot \text{kg}^{-1}$ for ^{232}Th , so the reported values in our study can be indicative of enhanced radioactive levels. In the bibliography, there are different

Table 3. Average of ^{234}U and ^{238}U specific activity values (A) and associated uncertainties obtained when a reference moss-soil sample (IAEA 2009) was processed with the different tested methods. The table also includes the test Z-score, the relative bias and the exactitude. Uncertainties are expressed at $k=1$.

Method	Moss soil (g)	*n	**η %	^{234}U					^{238}U				
			^{232}U	A (Bq/Kg)	A ref	Z score	Precision (%)	Trueness (%)	A (Bq/Kg)	A ref	Z score	Precision (%)	Trueness (%)
1	2.5	3	63 ± 7	10 ± 1	21.8±0.8	5.3	14	53	10 ± 1	22.2±0.8	5.9	15	56
3	2.5	3	94 ± 4	10 ± 2		5.7	16	57	10 ± 2		5.5	17	55
4	0.5	3	87 ± 7	24 ± 2		1.0	9	10	22 ± 2		0.1	9	1

*n = number of samples analyzed

**η = chemical recovery (obtained from ^{232}U tracer and ^{229}Th tracer)

studies that show that uranium and thorium activities in coal are strongly influenced by its origin (Mahur et al., 2008; Papastefanou, 2010; Janković et al., 2011). In Table 4 we also summarize the results obtained for the phosphate samples, as we can see the obtained activities for ^{238}U and ^{234}U isotopes were around $1600 \text{ Bq}\cdot\text{kg}^{-1}$. In the case of ^{230}Th , the measured activity was $2061 \pm 507 \text{ Bq}\cdot\text{kg}^{-1}$. These results are comparable with the reported in the bibliography for several authors who have measured the same isotopes from phosphate rocks samples from different origins (Ashraf Khater et al., 2001).

Table 4. Uranium and thorium isotope activities and associated uncertainties of the measurement for coal and phosphate samples analyzed by alpha-spectrometry. Uncertainties are expressed at $K=1$.

Radioisotope (Bq/kg)	Sample	
	Coal	Phosphate
^{230}Th	474 ± 103	2061 ± 517
^{232}Th	275 ± 24	34 ± 11
^{234}U	182 ± 23	1637 ± 67
^{235}U	6 ± 2	73 ± 5
^{238}U	187 ± 16	1574 ± 63

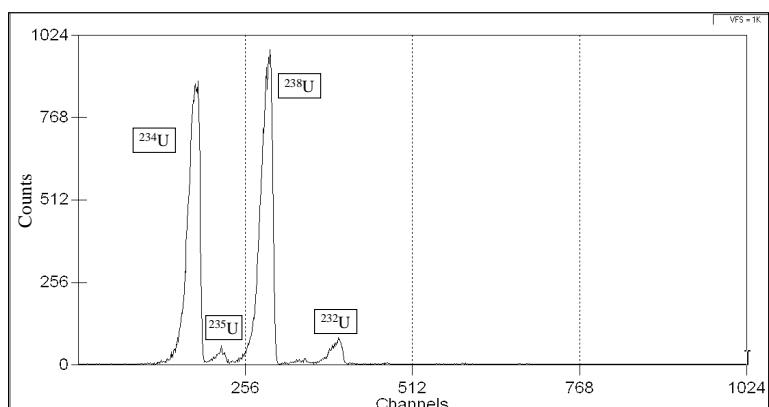
Moreover, it is well known that when this kind of materials is used as raw materials in DCP plants, this produces an enhancement of the radioactive levels in its area of influence. To verify this, we also take samples for the area

of Flix where a DCP plant is located and where it has been demonstrated that there is an environmental radiological impact (Casacuberta et al., 2009). Currently, the Ebro River reservoir in front of this industry is affected by the accumulation of wastes from the DCP plant and, for this reason, different sampling points in this contaminated area were selected (see Figure 2). In particular, we selected one sampling point in zone I (sample A1) and three different samples in zone II (samples B2, B3 and B4).

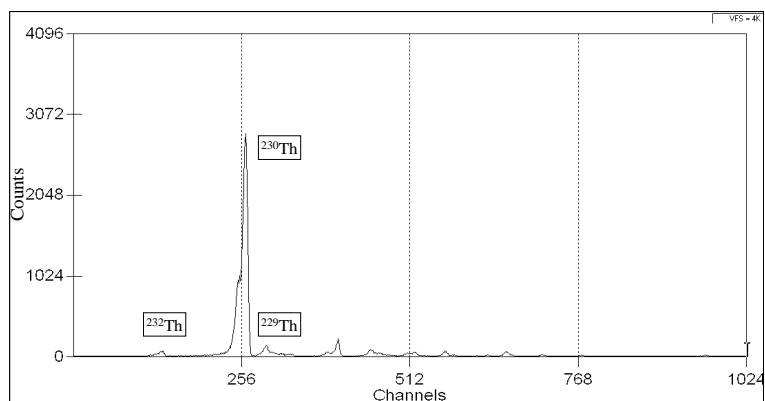
Table 5 shows the activity values obtained for uranium and thorium isotopes for the samples taken in the DCP area of influence using the selected methodology. Minimum detectable activities were between 0.1 and $1.5 \text{ Bq}\cdot\text{kg}^{-1}$ with average recoveries values for the tracers of $91 \pm 9\%$ for ^{232}U and $79 \pm 18\%$ for ^{229}Th . For these samples it is important to highlight that the higher activity values for ^{230}Th and uranium isotopes were obtained at the superficial levels. For example, in sampling point A1 (zone I), the higher activity values were found between 1 and 4 meters of depth and from that depth it remains more or less constant. As an example, Figure 3 shows the spectra obtained for the sample taken at a 1 meter depth for sampling point B3. In particular, Figure 3a shows the spectra obtained for uranium isotopes and Figure 3b shows the spectra for thorium isotopes. The obtained results are comparable to those obtained in a recent study by Casacuberta et al.

(2012) who used MW digestion and UTEVA columns for the analysis of uranium and thorium in NORM samples from the same DCP plant (phosphate rock input and phosphate rock output by the industry). In contrast, in our study for deeper samples the activity values were found to be very similar (between 24 and 43 Bq·kg⁻¹) to the natural

radionuclide content in soil (“natural background”), according to the UNSCEAR report (2000). In fact, the large difference between the activities of ²³⁰Th, ²³⁴U and ²³⁸U and the activity of ²³²Th and ²³⁵U can be attributed to the DCP industrial activity, which contributes to the enhancement of the activity concentrations of the isotopes belonging to the ²³⁸U decay series.



3a



3b

Figure 3: Uranium (3a) and thorium (3b) spectra of sampling point B3 at a depth of 1 m.

Table 5. Uranium and thorium isotope activities and associated uncertainties of the measurement for sludge samples analyzed by alpha-spectrometry. Uncertainties are expressed at K=1.

Sample	Depth (m)	²³⁰ Th (Bq/kg)	²³² Th (Bq/kg)	²³⁴ U (Bq/kg)	²³⁸ U (Bq/kg)	²³⁵ U (Bq/kg)
B4	1	2217 ± 377	51 ± 13	1399 ± 217	1310 ± 205	187 ± 40
	3	460 ± 95	15 ± 5	349 ± 67	357 ± 68	30 ± 7
	5	570 ± 117	20 ± 6	396 ± 77	393 ± 76	8 ± 2
	7	40 ± 9	16 ± 4	26 ± 7	25 ± 7	1.2 ± 0.6
	9	35 ± 9	22 ± 6	23 ± 6	19 ± 5	1.3 ± 0.6
	11	48 ± 11	17 ± 5	26 ± 7	28 ± 7	0.5 ± 0.3
B3	1	1737 ± 281	39 ± 9	1103 ± 205	990 ± 185	58 ± 12
	3	31 ± 9	31 ± 9	25 ± 7	23 ± 6	15 ± 4
	5	533 ± 93	37 ± 9	310 ± 62	295 ± 59	9 ± 3
	7	3331 ± 456	71 ± 14	2235 ± 410	2329 ± 428	0.8 ± 0.4
	9	74 ± 16	30 ± 7	47 ± 11	45 ± 11	0.3 ± 0.2
	11	32 ± 11	20 ± 7	24 ± 7	22 ± 6	0.5 ± 0.3
B2	1	5513 ± 999	57 ± 23	3762 ± 653	3344 ± 584	103 ± 22
	3	298 ± 61	22 ± 6	199 ± 41	173 ± 37	8 ± 3
	5	1163 ± 191	47 ± 11	690 ± 129	635 ± 119	17 ± 5
	7	29 ± 8	26 ± 7	24 ± 7	22 ± 6	0.8 ± 0.4
	9	28 ± 8	26 ± 7	23 ± 6	21 ± 6	0.5 ± 0.3
	11	32 ± 8	22 ± 6	29 ± 8	28 ± 7	0.8 ± 0.5
A1	1	3520 ± 586	48 ± 13	2599 ± 401	2476 ± 384	188 ± 35
	2	3624 ± 558	39 ± 10	2713 ± 439	2636 ± 428	129 ± 26
	3	1668 ± 235	37 ± 8	1040 ± 166	956 ± 153	39 ± 9
	4	339 ± 62	30 ± 8	234 ± 46	207 ± 42	5 ± 2
	5	34 ± 8	29 ± 7	33 ± 8	30 ± 8	1.2 ± 0.6
	6	38 ± 9	25 ± 7	41 ± 10	35 ± 9	1.0 ± 0.5
	7	43 ± 10	26 ± 6	33 ± 9	34 ± 9	0.6 ± 0.4
	8	39 ± 9	26 ± 7	29 ± 8	28 ± 8	0.5 ± 0.2
	9	32 ± 8	32 ± 7	26 ± 7	25 ± 7	0.8 ± 0.3
	10	32 ± 13	34 ± 8	26 ± 7	24 ± 6	0.5 ± 0.4

4. Conclusions

In this research, we have been tested different methods for the determination of uranium and thorium isotopes in mineral samples. The method based on UTEVA columns with a previous microwave digestion presented the highest recoveries and

the best results in terms of precision and trueness obtained when intercomparison samples were analyzed so it was used for NORM samples analysis. By using that method, it has been possible to determine uranium and thorium isotopes in mineral raw samples and sludge samples taken from Tarragona

Harbour storage zones and in the area of influence of a DCP factory in the Ebro River reservoir. The highest concentrations were found in the first meter of depth from B2 and A1 samples with activities between 2500 and 5500 Bq·kg⁻¹ for isotopes from ²³⁸U chain. These samples were located nearer to the DCP factory than the rest.

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DESENVOLUPAMENT DE TÈCNiques ANALÍTIQUES PER A LA DETERMINACIÓ DE RADIONÚCLIDS
Montserrat Mola Arques
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RADIONUCLIDES IN BIOTA COLLECTED NEAR A DICALCIUM PHOSPHATE PLANT, SOUTHERN CATALONIA, SPAIN

M. Mola, M. Palomo, A. Peñalver, C. Aguilar, F. Borrull*
Departament de Química Analítica i Química Orgànica
Universitat Rovira i Virgili, Marcel·lí Domingo s/n, 43007 Tarragona, Spain
Unitat de Radioquímica Ambiental i Sanitària (URAI), Consorci d'Aigües de Tarragona
(CAT), Ctra Nacional 340, km 1094, 43895 L'Ampolla, Spain

Abstract

Industrial waste containing radioactive U-decay series isotopes was released into the Ebro River, Spain, over a period of >20 years from a dicalcium phosphate (DCP) plant. This release raised activities of several natural radionuclides (e.g. ^{238}U , ^{234}U , ^{230}Th , ^{232}Th and ^{226}Ra) in biota taken from the area near the DCP plant. Plants and animals selected for this study included the green algae (*Cladophora glomerata*), the blue mussel (*Mytilus edulis*), the zebra mussel (*Dreissena polymorpha*) and the scavenger catfish (*Silurus glanis*) because they are all common in the area. Multiple sampling points were chosen for this study: 1) a site in the Riba-Roja Reservoir, above the DCP plant's area of influence, 2) four sites in the area surrounding the DCP plant, close to the town of Flix, and 3) a location in the Ebro Delta Estuary in Fangar Bay. Significant differences in the activities (in $\text{Bq}\cdot\text{kg}^{-1}$ of dry weight) for the radioisotopes included in this study among samples were attributed to sample location and the species evaluated. For instance, relatively high activities for uranium and radium were obtained in algae collected around the DCP plant, compared to results obtained for algae samples taken from the unimpacted Riba-Roja Reservoir. In contrast, for zebra mussels, enhanced activities were observed for all radionuclides and, in particular, for thorium and radium isotopes within the area of influence. Among catfish samples, activity values from different locations were not significantly different, though slightly higher activities were observed at the sampling point just downstream of the DCP factory.

Keywords: naturally occurring radioactive materials; dicalcium phosphate plant; biota; radioactivity; bioaccumulation

INTRODUCTION

Currently, production plants using dicalcium phosphate (DCP) are considered NORM (naturally occurring radioactive material)

industries in accordance with two reports of the International Atomic Energy Agency (IAEA) [1, 2]. Various studies have demonstrated that the use of sedimentary phosphate rock as a raw material in industrial processes

leads to release of several radionuclides into the environment. For instance, studies of the DCP factory in Flix, Spain, demonstrated that $>700,000 \text{ m}^3$ of toxic residues (metals, organic compounds and radionuclides) have been released from that plant since the 1960s and have accumulated in the Ebro River [3-5]. Disposal of these sediments into the environment may lead to chemical and radiochemical contamination. Moreover, there are several studies which have been focused on the biological impact of this type of NORM industry [6-9].

River biota such as mussels, fish and algae are capable of concentrating toxic substances, including radionuclides, in their tissues [10-17]. For example, Vera Tomé et al. [12] studied the activities of natural uranium and thorium isotopes and ^{226}Ra in the aerial fraction of vegetation collected near a uranium mine located in the Extremadura region of SW Spain. The activity concentrations in the zone downstream from the mine were $1050 \text{ Bq}\cdot\text{kg}^{-1}$ for ^{238}U , $1060 \text{ Bq}\cdot\text{kg}^{-1}$ for ^{234}U , $768 \text{ Bq}\cdot\text{kg}^{-1}$ for ^{230}Th and $1141 \text{ Bq}\cdot\text{kg}^{-1}$ for ^{226}Ra in a homogenous mixture of grass-herb pasture samples. Palomo et al. [17] demonstrated the ability of different biota to absorb radionuclides present in the environment. In that study, algae samples taken along the course of the Ebro River were evaluated as bioaccumulators of radioisotopes. High ^{214}Bi and ^{214}Pb activities, $105\pm 43 \text{ Bq}\cdot\text{kg}^{-1}$ and $100\pm 58 \text{ Bq}\cdot\text{kg}^{-1}$, respectively, were found in the algae *Cladophora glomerata*

collected near the area of influence of the DCP factory in Flix, whereas activities were much lower at more distant sampling points.

Other studies highlight how fauna such as mussels or fish species have been used to evaluate the bioaccumulation of pollutants such as radioisotopes. For instance, Martin and Ryan [16] published a review in which mussels (*Velesunio angasi*) were used for monitoring and assessment of mining impacts along the Northern Territory Creeks. They determined that ^{238}U and ^{226}Ra were the most commonly evaluated isotopes to correlate natural radiological enhancement to mining activities. Various studies have focused on *Mytilus* mussels [8, 18-20], as well as the zebra mussel (*Dreissena polymorpha*) [21-23], and demonstrated the capacity of these organisms to concentrate several radionuclides present in their environment. With respect to fish, Haridasan et al. [24] concluded that enhanced ^{226}Ra concentrations in fish (*Thalassinus sp.*) in some bodies of water were caused by a nearby phosphogypsum disposal area.

This study was undertaken to evaluate the biota storage of several natural radionuclides (^{238}U , ^{234}U , ^{230}Th , ^{232}Th , ^{226}Ra) in samples of biota collected in an area that is influenced by a DCP plant. The isotopes were measured in samples of green algae (*Cladophora glomerata*), blue mussels (*Mytilus edulis*), zebra mussels (*Dreissena polymorpha*) and scavenger catfish (*Silurus glanis*). These kind of samples were selected as possible

sensitive target species and because they are common in the Ebro River area. It was of particular interest for us to evaluate the correlation between radioactivity levels in these samples and the accumulated sediments derived from the industrial activity of the DCP plant.

2. Methods and sampling details

2.1. Study area and samples

The studied segment of the Ebro River in southern Catalonia, Spain, is approximately 109 km long and extends from the Riba-Roja Reservoir to the Ebro Delta Estuary (Fig. 1). This study focused on the zone around the DCP plant located in Flix (41.2 Lat/0.6 Long). Samples from three types of aquatic biota, a green algae, a catfish, and two species of mussels, were collected in September and October 2012. Sampling point 1 was outside the area of influence of the DCP plant and was used as a control site. Sampling points 2 to 5 were located above (2), in front of (3) and below (4 and 5) the DCP plant on the river. Point 6 corresponds to a mussel farm located in Fangar Bay (40.8 Lat/0.7 Long) located on the Mediterranean coast sea, which receives constant water flow from the river.

2.2. Reagents and materials

All chemical reagents used in this study were of analytical grade. Hydrochloric acid (38%), nitric acid (65%), hydrogen peroxide (30%), ammonia solution (25%), and oxalic acid dehydrate (99.5%) were all

supplied by J.T. Baker (Deventer, Holland). Ascorbic acid (99.7%) was supplied by Merck (Darmstadt, Germany). Calcium nitrate tetrahydrate ($\geq 99\%$), ammonium hydrogenphosphate (98%) and aluminum nitrate nonahydrate p.a., were supplied by Sigma-Aldrich (St. Louis, MO, USA). uteva resin was purchased from Triskem Inter. (Bruz, France) as a 2-cm³ packed column. Digested samples were filtered with 0.45- μ m filters supplied by Whatman (Maidstone, England). Uranium and thorium were electroplated onto stainless steel planchets (25 mm diameter and 0.63 mm thick) supplied by Tecnasa (Madrid, Spain).

To evaluate the plating efficiency of the alpha spectrometry procedure, certified solutions of ²³²U and ²²⁹Th with activity values of 15.01 ± 0.15 Bq g⁻¹ and 20.91 ± 0.29 Bq g⁻¹, respectively, were used. Both were supplied by Ciemat (*Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas*, Madrid, Spain).

The calibration of the zinc sulphide (ZnS) scintillation counter was performed using a certified solution of ²⁴¹Am with a nominal activity concentration of 4.7 ± 0.4 KBq g⁻¹ supplied by Amersham International plc. (Buckinghamshire, England) and determined alpha detection efficiency. A planchet containing ²⁴¹Am with an activity of 100 Bq was prepared from the standard certified solution, and was used for monthly calibration. The calibration of the high-resolution germanium detector (HPGe) was performed using a standard certified

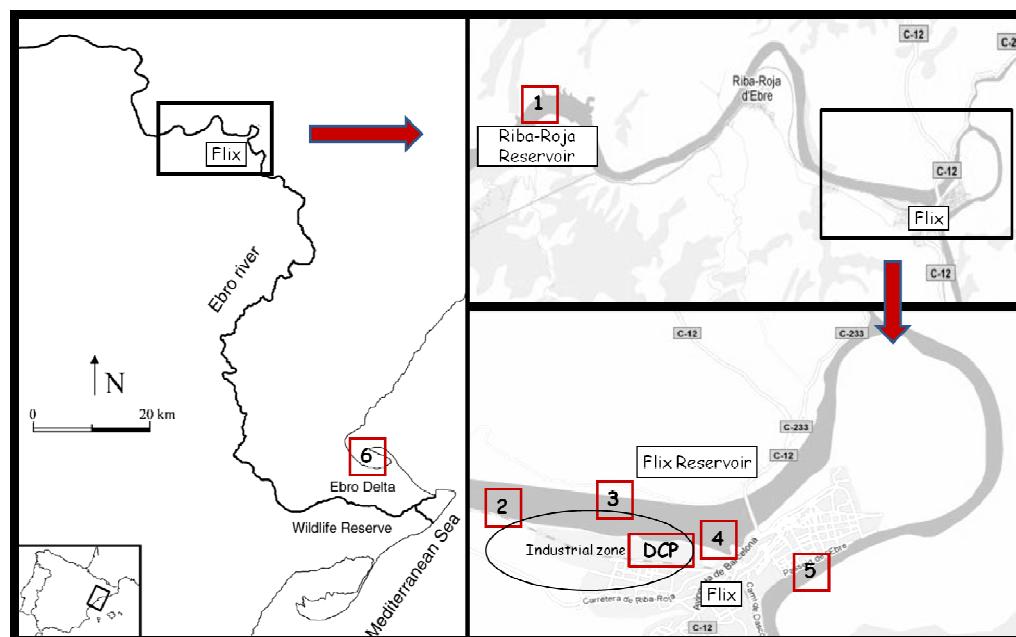


Figure 1. Map showing the location of the town of Flix, SW Catalonia, Spain, and the course of the Ebro River to the Ebro Delta, including the six sampling points in this study, from the Riba-Roja Reservoir, through the area influenced by the DCP plant, to the estuary in Fangar Bay. Biota were collected from point 1 in the Riba-Roja Reservoir, points 2, 3, 4 and 5, in an area surrounding the DCP plant, and point 6, in Fangar Bay, where there is a mussel farm.

solution supplied by Ciemat (Madrid, Spain), which covered the energy range between 59 and 1836 KeV.

2.3. Instrumentation

A Pressurized Microwave Decomposition System supplied by Anton Paar (PFA vessel digestion closures, Graz, Austria) was used for sample digestions.

The alpha spectrometer (EG&G ORTEC, Model 676A, USA) includes an ion-implanted silicon detector (ORTEC, size: 450 mm²; alpha resolution: 25 keV FWHM at 5.48 MeV of ²⁴¹Am) in a vacuum chamber evacuated with a vacuum pump (Edwards, Model E2M8), a detector bias supplier, a preamplifier, a linear amplifier, and a multichannel pulse

height analyser. During measurement, the pressure in the chamber was maintained at 10⁻² Torr.

To measure ²²⁶Ra, a zinc sulphide (ZnS) scintillation counter (photo multiplier tube and base preamplifier, model 2000, Canberra Industries, USA) with a voltage of 0.76 kV, was used. The background was determined by counting an empty planchet for 5,000 minutes.

Gamma emitters were measured with a high-resolution germanium detector (HPGe) (model 2020 Canberra Industries, Meriden, USA), equipped with a standard multi-channel analyser. The operating conditions were set at a voltage of 4500 V, negative polarity and a relative efficiency of 20%. Genie 2000 software

(Canberra Industries, Meriden, USA) was used to acquire and subsequently analyse the information provided by the gamma spectra.

2.4. Sample treatment

Between 2 and 3 kg wet weight of mussels and algae samples were collected. Catfish with wet weights between 6 and 9 kg were also collected. Samples were immediately transferred to plastic bags. In the laboratory, the mussel clumps were disaggregated. In the case of the blue mussels, individuals with shell lengths between 6 and 9 cm were selected. For zebra mussels, the shell length selected was between 2 and 3 cm. The analysis of shells with similar range of age of each specimen was established since this fact can have an influence on the activity concentrations which can be found in mussels. The flesh and the shells were separated and only the soft tissues were analysed. Mussel tissues (soft part), algae and catfish muscle samples were dried at 110°C and then ashed at 550°C for 12 hours in a furnace. After cooling, samples were crushed and sifted through a 250- μm sieve.

2.5. Analytical methods

For ^{226}Ra determination two different methods were used, one for algae and fish samples, and the other one for mussels. That was due to the different available amount of sample. In the case of algae and catfish samples, an amount of 40 g or 60 g was put into 60 mL sealed plastic beakers that were

placed in the gamma spectrometer and measured for 20 hours. Each beaker was sealed and stored for three weeks prior to measurement. The ^{226}Ra activity was determined from the photopeaks of its short-lived daughters (^{214}Pb and ^{214}Bi), with which ^{226}Ra was assumed to be in secular equilibrium.

In the case of mussel samples, and due to the limited amount of sample available, we used the method described by Vallés [25] to isolate radium. The method consists of a preconcentration step with $(\text{Ra-Ba-Pb})\text{SO}_4$ of a sample previously digested of 0.5 g, followed by separation of lead from radium using EDTA and glacial acetic acid (CH_3COOH). The precipitate obtained was then transferred to a striated stainless steel planchet (5 cm diameter) with 2 mL of distilled water, and dried at a temperature $<150^\circ\text{C}$. After the separation process, the planchets were stored in a desiccator for two days and then measured using 2 cycles of 400 minutes in a $\text{ZnS}(\text{Ag})$ solid scintillation detector. The measurement was repeated after 10 days to determine ^{226}Ra and ^{224}Ra activities.

For uranium and thorium determination, 0.5 g of ash was placed into a Teflon-PFA (perfluoroalkoxy) closed vessel for the mineralization process. Before microwave-assisted digestion, the ashes were spiked with the tracers, 1 mL of ^{232}U (42.4 Bq L^{-1}) and 1 mL of ^{229}Th (61.0 Bq L^{-1}) for uranium and thorium radiochemical yield determination or 1 mL of BaCl_2 (25 g L^{-1})

and 1 mL $\text{Pb}(\text{NO}_3)_2$ (30 g L^{-1}) for radium radiochemical yield determination in the mussels case. Next, 8 mL of aqua regia (3:1 HNO_3/HCl) was added and solid samples were digested for 30 minutes under high pressure and high temperature conditions (215°C). After cooling, the solution was filtered through a 0.45- μm -pore syringe filter to remove the insoluble particles and then brought to a final volume of 50 mL with deionized water.

For the radiochemical separation of uranium and thorium, the method described by Mola et al. [5] was followed. This method involves a preconcentration step with calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$). Alpha isotopes are then extracted with a Uteva resin column and finally electroplated. The last step consists of activity measurement with an alpha spectrometer for 260,000 seconds.

3. Results and discussion

As we have stated before, our main aim was to evaluate the ability of different biota species, collected in an area which is influenced by a DCP, to accumulate different radioisotopes which can be present in the environment. With this in mind, we tested different procedures to determine uranium, thorium and radium isotopes in the collected samples first with the analysis of an intercomparison sample, and then, under the optimum conditions, we focused on the analysis of the different biota samples. In the following

subsections we present the main results obtained.

3.1. Digestion of samples

To evaluate the digestion method used for the studied biota samples, a sample from an intercomparison exercise organized by the Spanish Nuclear Safety Council (CSN) in the year 2005 (vegetal matrix), which contained 7.5 ± 1.5 Bq kg^{-1} of ^{238}U , 6.4 ± 1.3 Bq kg^{-1} of ^{230}Th and 17.3 ± 2.6 Bq kg^{-1} of ^{226}Ra , was analysed with two different microwave-assisted digestion procedures, and then the obtained results were compared with those reported by the CSN. Regarding the digestion procedures, a comparison was made between the conventional digestion procedure with aqua regia and with another specific procedure for biological samples that used H_2O_2 , in line with the EPA Method 3052 [26].

Results showed high recovery values (between $87 \pm 4\%$ and $90 \pm 13\%$) for the uranium tracer (^{232}U), using both digestions described above, whereas recoveries for the thorium tracer (^{229}Th) varied considerably, depending on the reagent digestion method used. Recovery using aqua regia was $95 \pm 6\%$ compared to the value of $50 \pm 30\%$ obtained with the other procedure (H_2O_2). Moreover, as a consequence of the comparison with the results reported with the organization responsible for the intercomparison exercise, it was concluded that obtained values were close to the certified activity values (Z-score values between 0.7 and 1.7). Precision

values were similar, ranging between 21% and 28%. However, accuracy was better (12-14%) using aqua regia than H_2O_2 (27-34%). For the radium separation procedure, aqua regia microwave-assisted digestion was used. The recovery of Ba^{2+} tracer ($88 \pm 7\%$), the precision (30%), the trueness (11%) and the value of the Z-score (0.7) were in concordance with previous uranium and thorium values.

3.2. Biota samples from the areas near Flix and Fangar Bay

After selecting the best digestion method, samples of biota collected from the six localities (Figure 1) were analysed. Table 1 shows the sampling points, the average activity values (Bq kg^{-1} dry weight) of ^{238}U , ^{234}U , ^{230}Th , ^{232}Th and ^{226}Ra , and the uncertainty associated with each sample. It has to be highlighted that the different biota samples were selected according its different expected behaviour. Moreover, we have to take into account that previously to this study we have measured gross alpha activities in river water samples, in particular in samples from Ebro River, where the DCP is located close by and also from the Ter River which does not have the influence of this kind of industry. The results obtained when these water samples have been analysed clearly show an influence of the industrial activity carried out in the area of Ebro River, since higher values for the gross alpha activity were obtained (with a mean value of $0.11 \pm 0.02 \text{ Bq L}^{-1}$ ($n=11$)) in comparison with the corresponding

values obtained for Ter River samples (with a mean value of $0.03 \pm 0.01 \text{ Bq L}^{-1}$ ($n=11$)). So it is expected that biota samples taken in the area of the DCP plant can have a higher activity for those alpha emitting isotopes which are present in the water.

In the case of algae samples, they are in close contact with water, so it is expected that the possible radioisotopes which can be quantified in those samples are the more soluble as it is the case of uranium or radium isotopes. In the case of mussel and catfish samples, as they are living more closely to the sediment samples, it is expected that these organisms could accumulate less soluble radionuclides such as thorium. Results for each kind of biota are presented and discussed in detail below.

3.2.1. Algae samples

Cladophora glomerata is the most common fresh-water alga of the Ebro River and it is found in large amounts along the entire course of the river. Green algae samples were collected in the area surrounding the DCP plant, specifically at sampling points 1, 2, 4 and 5.

The influence of the presence of the on-site waste derived from the DCP industrial activity on uranium isotopes and ^{226}Ra activity in the algae samples is clearly demonstrated (Table 1). Figure 2 shows activity values for ^{234}U , ^{226}Ra and ^{230}Th measured at the different sampling points. The location of the DCP is indicated. Samples taken at points upstream of the factory show similar

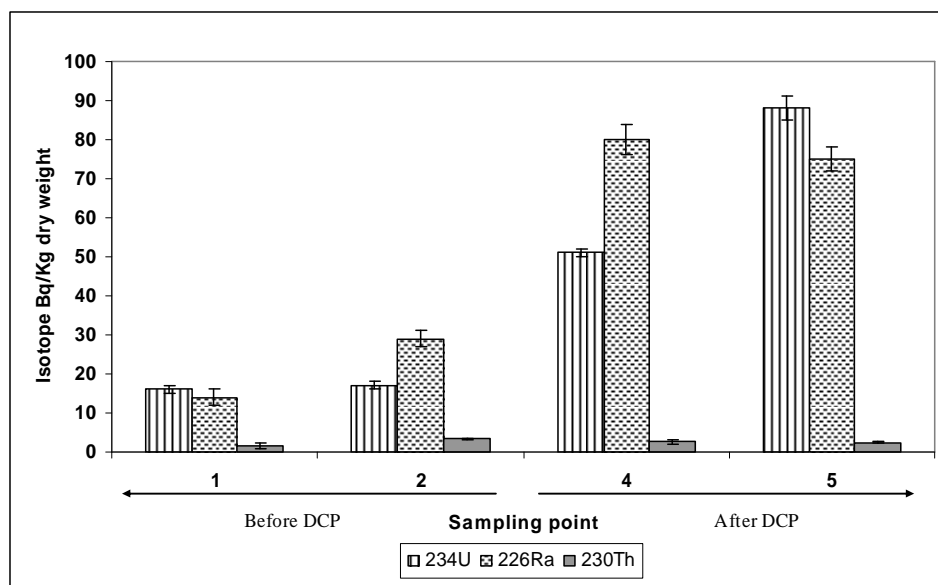


Figure 2. Graphic showing ^{234}U , ^{230}Th and ^{226}Ra activities (Bq/kg) from sampling points 1, 2, 4 and 5. Sampling points 1 and 2 are located upstream of the DCP plant, whereas sampling points 4 and 5 are located downstream of the plant. Error bars show counting uncertainties at $k=2$.

values. For uranium and radium, the influence of the industry is clear, as activity levels, especially for uranium, are much higher at sampling points 4 and 5, whereas in the case of thorium no differences were observed in the overall evaluated area. We can conclude, from all these results that the algae samples have the capacity of absorbing those radionuclides soluble in water which is their living media, this is uranium and radium; but on the other hand, the low solubility of thorium in water could explain its low absorption for the algae samples. These results are in agreement with the reported by other authors, who demonstrated by several studies the capacity of such kind of samples for bioremediation purposes [7, 13, 27, 28]. The ability of aquatic plants such as algae to remove uranium from mining wastewater is explained by the

reduction of U(VI) aqueous complexes to U(IV) stable precipitates on the cell surface and then later, internal incorporation of U in different forms [13]. In the case of radium, García-Talavera et al. [28] reported that the absorption capacity for this isotope was related to the introduction of $^{226}\text{RaCl}_2$ into algae tissue as a soluble compound.

3.2.2. Mussel samples

Mussels are demonstrated to be bioaccumulators because of their ability to concentrate several environmental contaminants in their tissues [11, 16, 21, 29]. For example we can highlight the study of Martin and Ryan [16] who demonstrated the ability of mussels to accumulate high ^{226}Ra levels and their potential as indicators of NORM-type industry. In our case we studied the behaviour

of zebra mussel, a non-native species from Eastern Europe which has been introduced as an invasive species in the area under study. Zebra mussel samples were collected at sampling points 1 and 5, from zones with high concentrations of particulate matter in the river. On the other hand, samples from another mussel specie (blue mussel) were also analysed in order to verify if the environmental impact of the DCP plant reaches the area where this kind of biota samples are cultivated, perhaps by river transport of radionuclides in the sediments near the DCP factory. In particular blue mussels were taken from sample point 6 (Figure 1).

In the case of zebra mussels, regarding uranium, thorium and radium, higher activities were obtained in the area close to the DCP. For example, in the case of thorium $7.1 \pm 0.3 \text{ Bq kg}^{-1}$ for ^{230}Th , $2.3 \pm 0.2 \text{ Bq kg}^{-1}$ for ^{232}Th were obtained at sampling point 5 in contrast to the $0.6 \pm 0.1 \text{ Bq kg}^{-1}$ for ^{230}Th , $0.3 \pm 0.1 \text{ Bq kg}^{-1}$ for ^{232}Th at sampling point 1. This indicates that natural uranium is more abundant in not influenced point 1 than the other thorium and radium radionuclides. Even though there is a DCP factory between the two sampling points, this species has more affinity for thorium than does the green alga and this can be related to the different behaviour of both biota samples. In the case of algae samples, they are in close contact with river water (where uranium and radium isotopes are present due to their solubility), whereas for mussel samples their

habitat is close to the sediment samples where thorium is expected to be present at higher activities.

Blue mussel activities were compared with values from other studies of the genus *Mytilus* [20, 30]. Blue mussels in our study were non influenced by the sludge river containing in front to the DCP (Flix) since their ^{238}U activity was lower ($1.3 \pm 0.2 \text{ Bq kg}^{-1}$ dry weight) than 3 Bq kg^{-1} dry weight, the normal ^{238}U activity for consumed mussels, reported by Barisic and Kniewald [31]. Moreover radium activities were lower to <MDA (minimum detectable activity). Kiliç and Çotuk [20] analysed samples from the Golden Horn Estuary, outside the zone of influence of a NORM industry. The ^{238}U activities in the soft parts of mussels ranged between 0.4 Bq kg^{-1} and 1.38 Bq kg^{-1} dry weight, whereas the ^{232}Th activities ranged slightly higher, between 0.49 and 3.58 Bq kg^{-1} , showing that ^{238}U and ^{232}Th values obtained in our study were found between these ranges of activities.

3.2.3. Catfish samples

The scavenger catfish is a non-native species imported from Danube River, between Germany and Romania. It adapts its feeding habits easily and is a successful invasive species in the Ebro River, thanks to its territorial character.

Catfish samples were collected at sampling points 1, 3 and 5. A slight increase in mean uranium, thorium and ^{226}Ra activities was observed at sampling point 3, after the DCP plant on the river (Table 1). For instance,

Table 1. Uranium, thorium and radium isotopes activities (Bq/Kg dry weight) and associated uncertainty of the measurement for biota samples analyzed by alpha-spectrometry, gamma spectrometry and ZnS detector.

Sample	Sampling point	²³⁴ U		²³⁸ U		²³⁰ Th		²³² Th		²²⁶ Ra	
		A ± U*	AMD**	A ± U*	AMD**	A ± U*	AMD**	A ± U*	AMD**	A ± U*	AMD**
Green algae (<i>Cladophora glomerata</i>)	1	16 ± 1	0.1	14.6 ± 0.1	0.1	1.6 ± 0.8	0.1	0.8 ± 0.1	0.1	14 ± 2	1.3
	2	17 ± 1	0.2	15.5 ± 0.4	0.1	3.3 ± 0.3	0.1	1.0 ± 0.1	0.1	29 ± 2	1.1
	4	51 ± 1	0.6	46 ± 2	0.4	2.6 ± 0.6	0.1	1.5 ± 0.2	0.1	80 ± 4	1.5
	5	88 ± 3	0.4	77 ± 3	0.1	2.5 ± 0.1	0.3	1 ± 0.1	0.1	75 ± 3	1.7
	1	5.4 ± 0.1	0.05	4.9 ± 0.1	0.03	0.6 ± 0.1	0.06	0.3 ± 0.1	0.05	1.9 ± 0.1	0.2
Zebra mussel (<i>Dreissena polymorpha</i>)	5	14.0 ± 0.1	0.07	12 ± 1	0.08	7.1 ± 0.3	0.13	2.3 ± 0.2	0.09	14.4 ± 6.1	0.3
	6	1.4 ± 0.3	0.11	1.3 ± 0.2	0.08	0.8 ± 0.4	0.09	0.5 ± 0.1	0.07	<AMD	0.4
Scavenger catfish (<i>Silurus glanis</i>)	1	0.2 ± 0.1	0.06	0.2 ± 0.1	0.01	0.3 ± 0.1	0.03	0.03 ± 0.02	0.01	<AMD	0.2
	3	0.5 ± 0.1	0.03	0.4 ± 0.1	0.01	0.5 ± 0.1	0.01	0.03 ± 0.01	0.02	1.6 ± 0.2	0.3
	5	0.4 ± 0.1	0.03	0.3 ± 0.1	0.01	0.3 ± 0.1	0.01	0.04 ± 0.01	0.02	0.4 ± 0.2	0.2

*U is the expanded uncertainty (k=2)

** AMD is the minimum detectable activity

activities increased from $<0.2 \text{ Bq kg}^{-1}$ (MDA) to $1.6 \pm 0.2 \text{ Bq kg}^{-1}$ for ^{226}Ra . In general, however, no significant differences were observed among sampling points and this can also be related with the conditions under which this fish is living.

4. Conclusions

We conclude that sludge waste around the industrial zone (mainly from the DCP plant) can have an influence on the radionuclide content of biota near to the town of Flix. The impact on the mussels in the Delta Estuary is less significant. Differences in activity concentrations among the biota are a consequence of differences in their food intake patterns and metabolism. The radioactivities are also related to the sampling location and anthropogenic activities in the area generate effluents that may increase concentrations of naturally occurring radiation in the environment.

The activity concentrations of ^{230}Th , ^{232}Th and ^{226}Ra in zebra mussels from Flix and ^{234}U , ^{238}U and ^{226}Ra for the green alga from Flix and downstream of the toxic zone, showed enhancement as a consequence of the sludge accumulated by the DCP plant in the river. Estuary blue mussels along the 109 km length of the affected area showed uranium and thorium results similar to those in unaffected areas, but slightly higher uranium concentrations. Our results suggest that the green alga, zebra mussels and blue mussels can be used as bio-indicators

of the changes of radioactivity concentration in the medium.

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3.1.4. Discussió de resultats

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Encara que en la part experimental de cada article estan discutits individualment els resultats derivats d'aquests, en aquesta secció discutirem els aspectes més importants a destacar.

En relació a la part de comprovació i validació dels diferents mètodes analítics utilitzats en tots aquests treballs, sempre s'ha treballat mitjançant l'ús de patrons o mostres d'exercicis d'intercomparació com a mostres de referència. En les quals, es coneixen d'una forma certificada les activitats dels diferents radionúclids. Llavors s'ha garantit en totes les analítiques un bon ús dels mètodes de tractament de la mostra i una detecció òptima de les activitats dels índex beta i alfa total i els diferents radionúclids individuals.

Per a la determinació dels radionúclids d'urani i tori s'han aplicat mètodes radioquímiques amb diferents tipus de digestió, preconcentració i extracció. Mitjançant una comparativa dels resultats del rendiment químic, el factor *Z-score*, entre altres paràmetres obtinguts en l'anàlisi de diferents mostres d'intercomparació, s'ha escollit l'òptim. En el segon treball podem observar que amb l'extracció clàssica líquid-líquid amb TBP/xilè es varen registrar les recuperacions químiques més baixes en ambos traçadors (^{232}U i ^{229}Th). També hem obtingut valors de rendiments més baixos en quant a l'ús de l'agent coprecipitant, com ara amb el FeCl_3 , degut a que el ió Fe^{+3} s'associa fàcilment amb els ions del Th^{+4} [1,2]. Cal destacar, la forma en que es digereix la mostra, ja que en una mineralització amb el microones la temperatura i la pressió estan sota control durant tot el procés i aquest fet ens ha proporcionat una digestió uniforme i reproduïble i a més, molt més còmoda i ràpida. Podem concloure que amb el mètode de la digestió amb microones, la precipitació amb $\text{Ca}_3(\text{PO}_4)_2$ i l'extracció cromatogràfica amb resina Uteva s'han obtingut els millors rendiments químics i valors satisfactoris de *Z-score* en totes les mostres de referència aplicades i per a tots els radionúclids individuals de l'urani i del tori quantificats. Per tant, ha estat el mètode elegit per a treballar amb les mostres reals amb diferents matrius sòlides (fangs residuals i biota).

En els dos primers treballs basats en la caracterització dels fangs residuals acumulats en l'embassament de Flix, es van mesurar elevades concentracions de radioactivitat mitjançant els índex alfa i beta total i els radionúclids individuals analitzats (descendents de la cadena del ^{238}U). Els perfils de profunditat ens han mostrat que aquestes activitats estan majoritàriament localitzades entre els tres primers metres. Més concretament, estem parlant d'activitats entre els 10.000 i 15.000 Bq Kg^{-1} d'índex alfa i beta total. En el cas de la majoria de radionúclids individuals analitzats (^{226}Ra , ^{210}Pb , ^{238}U , ^{234}U , ^{230}Th), varem trobar activitats màximes entre els 6000 i 1000 Bq Kg^{-1} , principalment en el primer metre de profunditat. Després, en majors profunditats (generalment, a partir dels 7 metres de profunditat) trobem un decreixement d'aquestes activitats fins a valors amb una mitjana de 30 Bq Kg^{-1} , mantenint-se constants en profunditats superiors.

S'ha pogut veure un comportament diferent entre els perfils del mostreig com ara l'obtenció d'activitats més baixes amb l'augment de la distància a la DCP. També, s'ha vist en la majoria de perfils situats davant de la EDAR del polígon un increment d'activitats sobtat en profunditats elevades. Gràcies a l'estudi i la datació amb el ^{137}Cs trobat en algun d'aquests perfils a concentracions destacades (oscil·lant entre els 5 i 20 Bq Kg^{-1}), s'ha relacionat la profunditat d'aquests increments d'activitats, anomenats anteriorment, amb alguns abocaments puntuals en els primers anys de producció de la DCP sobre l'any 1973 (any temporalment proper a la primera aparició d'aquest radionúclid artificial a l'atmosfera terrestre, degut a les primeres proves d'armament nuclear).

Un altre punt a destacar en aquest treball ha estat el mostreig d'un perfil de sòl proper a la zona tòxica dels fangs residuals sedimentats, però fora de la seva influència, el perfil control anomenat C7. Les activitats obtingudes de ^{226}Ra en aquest perfil de control entren perfectament dintre del interval de les dades reportades per la UNSCEAR [3] amb valors entre els 6 i 250 Bq Kg^{-1} de ^{226}Ra . És considerat llavors, com a sòl espanyol amb activitats normals sense estar sota la influència de la indústria NORM. Al comparar els valors d'activitats d'índexs alfa i beta i radionúclids individuals del perfil de control amb la resta de punts del mostreig, veiem que en profunditats elevades dels fangs tòxics s'observen els mateixos valors d'activitats, mostrant que en aquestes profunditats no hi ha influència de la DCP. És necessari doncs, que per a la l'extracció de les tones de fangs acumulats es tingui en compte la informació obtinguda en aquests treballs, per tal de tenir una referència i saber on es concentren els fangs amb més activitat radioactiva i per tant destinar-los a tractaments més específics i la resta de fraccions sòlides més netes es conduiran directament a l'abocador.

Arran dels resultats que s'han obtingut en l'anàlisi dels fangs tòxics procedents de la DCP, també s'han estudiat mostres minerals de fosfats i carbons utilitzades com a matèria primera en indústries NORM. Segons la UNSCEAR i la IAEA, aquestes mostres minerals es poden considerar en alguns casos (segons l'origen geogràfic, etc.) mostres NORM [3-5]. En general els valors trobats dels radionúclids d'U i de Th referents al carbó no haurien de ser preocupants però per altra banda, els valors obtinguts en el cas dels fosfats sí que mostren concentracions elevades. Per tant, s'hauria de planificar un futur treball amb l'estudi de dosis que reben els treballadors i el medi ambient que està en contacte amb aquests minerals. Per exemple, realitzar diverses mesures de dosis com ara durant el seu emmagatzematge, durant la seva manipulació i tractament industrial, per tal de saber si aquests valors d'activitat superen o no la dosi indicativa total de 0.1 mSv/any per persona.

Una forma de comprovar la influència i/o transferència de la radioactivitat continguda en aquests fangs tòxics, caracteritzats en els estudis anteriors, en el medi, va ser a través d'un mostreig i anàlisi de diferents espècies de biota que habiten les aigües en aquest tram del riu. En general hi ha dues tendències que revela l'estudi de

biota, per una banda la clara influència de la radioactivitat distribuïda en els fangs tòxics a l'embassament de Flix i meandre de Flix sobre les espècies de biota. Per una altra banda, també revela una diferent absorció dels radionúclids naturals en els diversos tipus de biota estudiats. Tot això es degut a la diferent distribució geogràfica d'aquestes espècies de biota, a la seva capacitat de bioacumulació i el comportament de certs radionúclids acomplexats a nivell superficial i/o cel·lular en aquestes. Per exemple, en aigües superficials amb menys material en suspensió hi trobem les algues amb una gran capacitat d'adsorció dels isòtops d'urani i el ^{226}Ra dintre les cèl·lules vegetals. En canvi, en mostres com ara el músculo zebra ubicats en forma de colònies agregades sota roques i conductes metàl·lics en zones més profundes i amb un tant per cent elevat de matèria en suspensió, hi trobem concentracions a destacar de tori. En altres espècies, com ara els silurs, no hem vist aquest efecte acumulatiu tant pronunciat.

Tots aquests resultats obtinguts en aquests treballs mostren la necessitat de realitzar una extracció d'aquests fangs. Tot i que, aquesta retirada pot afectar en un increment de la radioactivitat natural en els ecosistemes del riu, s'han realitzat diferents projectes per a evitar la problemàtica. Finalment, cal comentar que durant el 2011 - 2012 es van iniciar les obres per a la retirada dels residus acumulats a l'embassament de Flix amb el tancament progressiu de la zona tòxica mitjançant uns discs de contenció i que actualment mantenen la zona tòxica aïllada del curs natural del riu Ebre. S'ha començat amb la retirada d'aquests residus, els quals s'han d'analitzar i tractar abans de ser traslladats a una altra zona d'emmagatzematge (el Racó de la Pubilla) i allà ser continguts en un dipòsit controlat.

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3.2. Automatització



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En els darrers anys, han sorgit noves tècniques de flux que constitueixen una bona alternativa als mètodes clàssics per tal d'aconseguir separacions radioquímiques on apareix principalment la preconcentració i extracció de radionúclids individuals de forma automàtica. Analíticament, hi ha la necessitat de disposar de mètodes que ofereixin resposta ràpida, que tinguin cura amb el medi, que siguin sensibles i precisos, econòmics i si és necessari, que siguin portàtils. Un altre factor molt important segons les mostres amb que es treballi, per exemple en el nostre cas amb mostres amb concentracions elevades de radionúclids naturals o bé en altres casos amb mostres de residus procedents de centrals nuclears, és l'opció de minimitzar la manipulació d'aquestes i també dels volums de reactius químics necessaris per al procediment.

En aquest sentit, en aquest bloc es plantegen estudis encaminats al desenvolupament de tècniques analítiques automàtiques, per tal de continuar treballant amb diferents mostres NORM de forma segura i reproduïble. Els coneixements necessaris per a desenvolupar aquests mètodes de forma automatitzada van ser adquirits durant l'estada realitzada en el grup de recerca de Química Analítica, Automatització i Mediambient de la Universitat de les Illes Balears dirigit pel Dr. V. Cerdà. Un grup amb molta experiència amb aquests tipus de mecanitzacions amb sistemes de flux, per al desenvolupament de mètodes analítics diversos.

En el primer treball es va desenvolupar un sistema automatitzat per a la separació i extracció seqüencial de l'U i el Th mitjançant tècniques de flux. En aquest es va continuar treballant amb les mostres de fangs residuals de Flix amb elevades concentracions dels radionúclids descendents de ^{238}U i matrius complexes. També es van introduir mostres de fangs produïts durant la depuració de l'aigua del riu Ebre en l'ETAP, els quals s'ha vist en treballs anteriors del nostre grup de recerca [1] que contenen de forma concentrada radionúclids de diferents orígens. Aquestes mostres que resideixen en el medi considerades mostres NORM juntament amb una mostra de fosfoguix de la IAEA (necessària per validar el mètode un cop optimitzat), se'ls realitza la digestió amb microones optimitzada en treballs anteriors.

Abans però, a partir d'un blanc amb traçadors (^{232}U i ^{229}Th) es treballa per tal d'optimitzar el mètode de flux automatitzat amb la tècnica SIA. Aquesta es compon per una xeringa impulsora de flux connectada mitjançant el tub bucle de carga a la vàlvula de selecció, i aquesta a la vegada, connectada per un dels ports perifèrics a una columna amb dimensions fixades (4.5 mm i.d./55.0 mm longitud) amb una capacitat de resina Uteva de 400 mg. El sistema elegit i sobretot la part de la columna és diferent que el desenvolupat en un altre treball realitzat per Avivar i col. [2] on varen desenvolupar un sistema d'extracció d'ambos radionúclids en mostres d'aigua enriquides amb patrons mitjançant la combinació LOV-MSFIA i l'ús d'un volum fixat de 30 mg de resina Uteva en un dels canals de la LOV. Aquest fet és degut a que en el nostre treball es va desenvolupar i optimitzar un sistema d'extracció que ens permetés treballar amb més volum de resina, per tal d'evitar que els grups extractors

de la resina es saturin abans d'extraure el total de les activitats contingudes en mostres tant concentrades i complexes com ara els fangs de Flix.

La detecció es va realitzar mitjançant l'espectrometria alfa després de l'electrodeposició de les fraccions obtingudes al final del procés, per a poder quantificar els diferents radionúclids individuals (^{238}U , ^{234}U , ^{232}Th i ^{230}Th). Finalment, es va realitzar una comparativa de resultats entre dos mètodes, l'extracció manual estudiada en un treball previ i l'extracció automatitzada mitjançant la tècnica de flux SIA, ambdós amb la resina d'extracció cromatogràfica Uteva.

A través d'un altre treball anterior del nostre grup de recerca, sabem que les mostres de fangs produïts en l'ETAP contenen radionúclids d'origen natural i artificial, a causa de la geografia i diversificació industrial de la zona [3]. Per tant, en un segon treball es volia desenvolupar un sistema de flux automatitzat per a l'extracció seqüencial de dos radionúclids molt biotòxics i acumulables en el cos humà, l' ^{90}Sr d'origen artificial i el ^{210}Pb d'origen natural. Per una banda, el fet d'obtenir més informació dels radionúclids que contenen aquestes mostres ens permet tenir un control més exhaustiu d'aquestes activitats, ja que no es disposa de normativa que reguli els límits en continguts de concentracions de radioactivitat. Per una altra banda, aquesta informació ens pot servir d'ajuda a l'hora de planificar diversos fets de gestió d'una planta de tractament d'aigües com ara l'emmagatzematge, el tractament o la reutilització d'aquestes mostres, ja que no és estrany l'ús d'aquests fangs per a la producció de materials de construcció o bé per a la recuperació de terres afectades per explotacions mineres.

En relació al sistema utilitzat, s'ha elegit la combinació de les tècniques LOV-MSFIA amb la columna de resina Sr-Spec integrada en un canal perifèric de la LOV amb dimensions fixades (1.5 mm i.d./16.0 mm longitud) amb capacitat de 30 mg de resina. La decisió d'utilitzar aquesta tècnica combinatòria va ser deguda a la tendència de miniaturització que trobem en la bibliografia més actual en disminuir els volums de reactius i resina necessaris, per tal d'obtenir un sistema més econòmic afavorint una química més verda. A més, aquesta tècnica també presenta una gran reproductibilitat, gràcies al sistema de reemplaçament automàtic de resina, des del canal de l'emmagatzematge de la resina fins el canal perifèric de la columna [4,5]. La seva optimització es va realitzar mitjançant un blanc amb traçadors d'estronci i plom no radioactius (Sr^{+2} i Pb^{+2}) mesurats amb l'ICP-MS. Després es va realitzar la validació del mètode mitjançant dues mostres d'exercici de intercomparació, una mostra de cendres vegetal del CSN i un sòl de l'àrea de Txernòbil de la IAEA.

La detecció dels radionúclids d'aquestes mostres de intercomparació i dels fangs de l'ETAP es va realitzar mitjançant un detector d'escintil·lació líquida (LSC) on per a la mesura del ^{210}Pb , el qual és un emissor beta però amb descendència tant d'emissió alfa com de beta, es va utilitzar un mode de mesura "*Alpha/Beta*" on és necessari optimitzar un paràmetre denominat PSA (*Pulse shape analysis*) que permet minimitzar les interferències alfa en les mesures beta i les beta en les mesures alfa. En

aquest cas es va agafar un valor de PSA de 95, que va ser optimitzat en un treball anterior del nostre grup [6]. La mesura de l'altre emissor beta, ^{90}Sr , es va realitzar a partir del seu descendent ^{90}Y una vegada s'ha assolit l'equilibri secular entre ambdós.

A continuació, tal i com s'ha comentat, s'inclouen els treballs d'automatismes esmentats.

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3.2.2. Uranium and thorium sequential separation from NORM samples by using a SIA system

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URANIUM AND THORIUM SEQUENTIAL SEPARATION FROM NORM SAMPLES BY USING A SIA SYSTEM

M. Mola, A. Nieto, A. Peñalver, F. Borrull, C. Aguilar*

Universitat Rovira i Virgili

Marcel·lí Domingo s/n, 43007 Tarragona (Spain)

Unitat de Radioquímica Ambiental i Sanitària (UR AIS)

Consorci d'Aigües de Tarragona (CAT), Ctra Nacional 340, km 1094, 43895 L'Ampolla

Abstract

This study presents a sequential radiochemical separation method for U and Th isotopes using a novel SIA system with an extraction chromatographic resin (Uteva). After the separation, uranium and thorium isotopes have been quantified by using alpha spectrometry. The developed method has been tested by analyzing an intercomparison sample (phosphogypsum sample) from International Atomic Energy Agency (IAEA) with better recoveries for uranium and thorium than the obtained by using a classical method (93% for uranium using the new methodology and 82% with the classical method, and in the case of thorium the recoveries were 70% for the semi-automated method and 60% for the classical strategy). Afterwards, the method was successfully applied to different NORM samples, in particular sludge samples taken from a drinking water treatment plant (DWTP) and also sediment samples taken from an area of influence of the dicalcium phosphate (DCP) factory located close to the Ebro river reservoir in Flix (Catalonia). The obtained results have also been compared with the classical method and from that comparison it has been demonstrated that the presented strategy is a good alternative to existing methods offering some advantages as minimization of sample handling, reduction of solvents volume and also an important reduction of the time per analysis.

Keywords: Uteva resin; alpha spectrometry; sequential injection analysis; naturally occurring radioactive material.

INTRODUCTION

There are some industrial activities that can cause increased concentrations or exposures to naturally occurring radioactive materials (NORM). Raw materials, products and wastes from NORM facilities contain

significant concentrations of natural radionuclides, mainly from the ^{238}U and ^{232}Th decay series. The interest in such kind of activities has increased in the last years since these radionuclides can reach the environment (Palomo et al., 2010a; Casacuberta et al., 2012; Moharram et al., 2012) and in this

sense, several approaches involving the determination of the most common radionuclides involved in those processes have appeared (Bolívar et al., 2009; Casacuberta et al., 2011; Hrichi et al., 2013). Previous studies carried out by our research group have been focused in the presence of ^{238}U and ^{232}Th and decay products in the surroundings of a dicalcium phosphate factory (DCP) or in the sludge produced in a drinking water treatment plant (DWTP) (Palomo et al., 2010b; Mola, et al., 2013). In general, in these applications, uranium and thorium isotopes have been determined by alpha spectrometry and the used procedure required tedious and time-consuming radiochemical separations before the activity measurements of these isotopes.

Up to date, the main strategies used to determine those radionuclides are based in multistep procedures focused in the isolation from matrix and also in the radiochemical separation of these radionuclides of interest, which is necessary prior to the measurement by alpha spectrometry to avoid the presence of possible interfering alpha emitters which can degrade the obtained spectra. In the last years, the use of extraction chromatography has a widespread use due to its advantages in comparison with traditional separation methods as for example the commercial availability or also it is worth to mention that the use of large amounts of reagents is also minimized (Osváth et al., 2009; Guérin et al., 2010;

Sadi et al., 2010; Gautier et al., 2013; Taddei et al., 2013). Even that the advantages of extraction chromatography with selective resins, still there are some important drawbacks as the high level of sample manipulation by a skilled analyst. In this sense, over the past few decades, an enormous effort has been focused to the development of new methods which involve a certain degree of automation with minimal manipulation of sample (Miró et al., 2002; Horstkotte et al., 2005; Mitani and Anthemidis, 2013). For that purpose, there are different strategies and among them the flow closed systems such as flow injection analysis (FIA), multipumping flow systems (MPFS) and lab on valve (LOV) systems are relatively simple, cheap and they are considered as green chemistry techniques. In the literature there are different studies which applied these techniques in methods focused to the determination of different radionuclides (Kim et al., 2008; Fajardo et al., 2010; St-Amant et al., 2011; Rodríguez, et al., 2012; Mola et al., 2013). It is worth to mention the review of Fajardo et al. (2010) in which it is given an overview of the different used approaches concerning automation in the determination of radioisotopes using flow systems. In that review, it is clearly demonstrated by the different discussed strategies that automation of the analytical methods allows the precise control of sample and reagent volumes and flow rates, what leads to improvement in reproducibility.

The main aim of this work is the

development of a method which allows the sequential separation of uranium and thorium isotopes prior to their measurement in waste sludge samples from different origins with the minimal manipulation of the sample. In particular we focused in sludge samples from two kinds of NORM industrial activities: from a drinking water treatment plant and from a dicalcium phosphate factory. The automated method was based on the sequential injection analysis (SIA) technique using an Uteva resin to separate uranium and thorium isotopes from sludge samples and afterwards, their measurement using alpha spectrometry. In the literature there are other previous works by Avivar et al. (2010, 2012) in which uranium and thorium have been determined by using a fully automated LOV-MSFIA system, but in those cases the applicability was focused to the determination of the total content of uranium and thorium in water samples and using ICP-MS as detection system. Moreover, we also have compared the obtained results with the developed method with the results obtained with a traditional method previously developed in our laboratory.

2. Methods and sampling details

2.1. Reagents and materials

All chemical reagents used in this study were of analytical grade. Hydrochloric acid (38%), nitric acid (65%), ammonia solution (25%), oxalic acid dehydrate (99.5%) were all

supplied by J.T. Baker (Deventer, Holland). Aluminum nitrate nonahydrate (puriss. p.a.), was supplied by Sigma-Aldrich (St. Louis, MO, USA). Uteva resin as spheres of 50 – 100 μm and as a 2 cm^3 packed columns were purchased from Triskem Inter. (Bruz, France). Glass fibre prefilters were supplied by Millipore (Madrid, Spain). Digested samples were filtered with 0.45 μm filters supplied by Whatman (Maidstone, England). Uranium and thorium were electroplated onto stainless steel planchets (25 mm diameter and 0.63 mm thickness) supplied by Tecna (Madrid, Spain).

To evaluate the alpha procedure recovery, ^{232}U and ^{229}Th certified solutions with well-known activity concentration values were used, both provided by Ciemat (*Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas*) (Madrid, Spain).

2.2. Instrumentation

Speedwave four microwave digestion system with built-in, non-contact temperature and pressure measurement supplied by Berghof (Eningen, Germany) was used for the digestion of solid samples. Twelve pressure vessels made of TFM fluoropolymer were located in a rotor with a gas collection system where 1.450 W of microwave power can be obtained.

The SIA system, which is shown in Figure 1, was based in the design used in previous studies (Avivar et al., 2011; Rodríguez et al., 2012) with some modifications. As can be

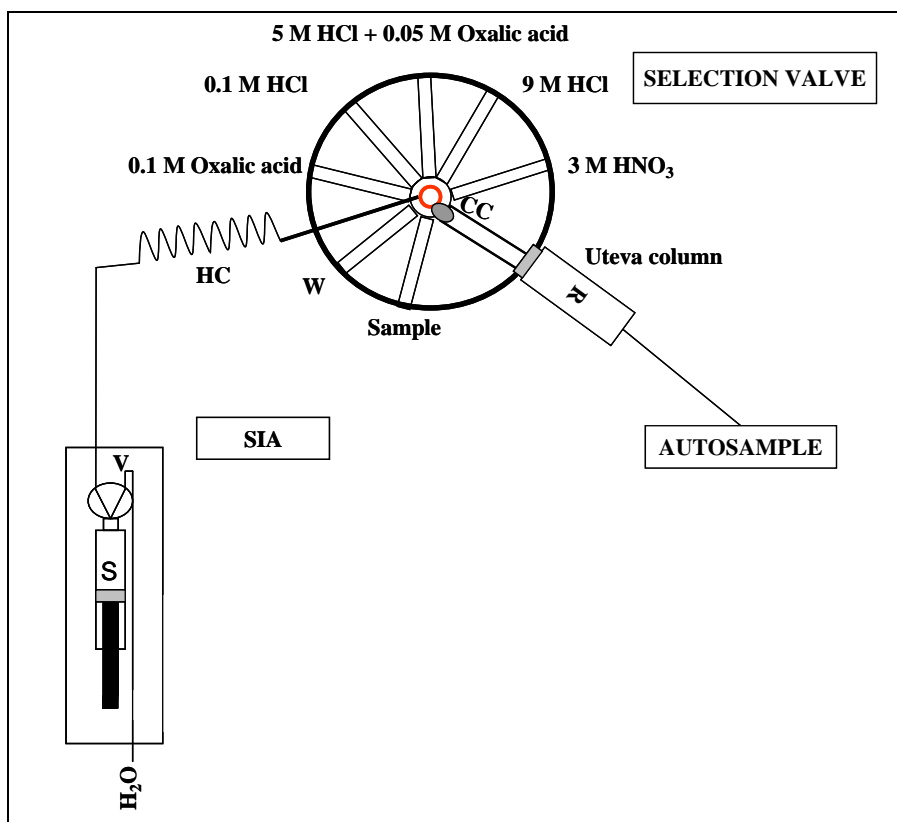


Figure 1: SIA system for U and Th isolation and preconcentration: S: syringe, HC: Holding Coil, V: Solenoid Valve, R: resin, CC: Central conduit.

observed in the Figure 1, the different integrating parts of this system are: a multisyringe burette (BU4S; Crison Instruments, Barcelona, Spain) equipped with a syringe of 10 mL (S) (Hamilton, Switzerland), a eight-port multiposition selection valve (Crison Instruments, Barcelona, Spain) and connected through the central port to S via a holding coil (HC). In one position of the valve an external methacrylate column with 5,5 mm internal diameter (i.d.) and 45 mm length was connected (R), enclosing the bead column channel (Sciware, Palma de Mallorca, Spain). This column was also connected to an

autosampler. All the system was automatically controlled by the software package AutoAnalysis 5.0 (Sciware Systems).

The alpha-spectrometer (EG&G ORTEC, Model 676A, USA) includes an ion-implanted silicon detector (ORTEC, size: 450 mm²; alpha resolution: 25 keV FWHM at 5.48 MeV of ²⁴¹Am) in a vacuum chamber through a vacuum pump (Edwards, Model E2M8), a detector bias supplier, a preamplifier, a linear amplifier and a multichannel pulse height analyzer. During the measurement, the pressure of the chamber was maintained at 10⁻² Torr. The electrodeposition apparatus

was supplied by Tecnasa (Madrid, Spain).

2.3. Samples

A sample from an intercomparison exercise organized by the International Atomic Energy Agency (IAEA, 2008) was used to validate the developed method. This sample was a phosphogypsum from a processing plant located in Gdansk (Poland) with known activities of different isotopes, among them uranium and thorium as it is shown in Table 1.

Several samples from two different origins were analyzed in order to apply the developed method. On one hand, three sludge samples from a DWTP located in L'Ampolla (Tarragona) were taken in three different months (from January to March 2013) from dry bulks of sludge accumulated in an established area of the DWTP. Each monthly sample (named as DWTP1, DWTP2 and DWTP3, respectively) was composed from the combination and homogenization of six sub-samples taken from dry bulk. On the other hand, three sludge samples from the industrial area of Flix reservoir, taken from the area located in front of a DCP plant were also analyzed. In that case, we selected three samples from three different sampling points all located in the area of influence of the DCP plant. In this case samples were identified as DCP1, DCP2 and DCP3.

Afterwards, they were transferred 200 g to a Pyrex glass tray and dried in a stove at a temperature of 110 °C. After that, the samples were crushed in a

ball mill and sifted in a sieve of 250 μm to be finally stored in a plastic bag in the laboratory.

2.4. Initial treatment

4 g of dry samples were introduced in a muffle furnace at 550°C for 12 hours and, after cooling, 0.3 g of the total amount of sample was transferred into a porcelain vessel. Then samples were spiked with the tracers to evaluate the radiochemical yield, in particular with 1 mL of ^{232}U (42.4 Bq L⁻¹) and 1 mL of ^{229}Th (61.0 Bq L⁻¹) and the samples were dried under an IR lamp. The digestion procedure of the solid samples is based in a mineralization process with 9 mL of aqua regia (3:1 HNO₃/HCl) during 30 min under high pressure and high temperature conditions (about at 215 °C) by microwave-assisted digestion following the procedure described in EPA Method 3051A (1998). After cooling the sample, the solution was filtered through a 0.45 μm pore-size syringe filter to remove the insoluble particles. The resulting solution was evaporated until dryness in a bath sand and then redissolved using 10 mL of solution composed by 3 mol L⁻¹ of HNO₃ – 1 mol L⁻¹ of Al(NO₃)₃.

2.5. Radionuclide separation

The SIA manifold was used for uranium and thorium isolation and separation. The flow system can be observed in Figure 1, and it is composed by different eluents and cleaning solutions reservoirs that are attached to selection valve ports as follows: 3 (3 mol L⁻¹ HNO₃), 4 (9 mol

Table 1. Results obtained for the reference material (IAEA 2008). Uncertainties are expressed at K=1, n=4.

		Recovery (%)		A (Bq/kg dry weight) ± u		
Radionuclide		²³² U	²²⁹ Th	²³⁸ U	²³⁴ U	²²⁹ Th
Aref (Bq/kg) ± u				120,0 ± 5,5	120,0 ± 4,5	211 ± 4,5
CLASSICAL	A (Bq/kg) ± u	82±10	60±2	94,0 ± 5,0	109,2 ± 2,0	203,7 ± 8,9
	MDA* (Bq/Kg)			1,1	1	0,5
	Z score			2,2	0,9	0,4
	Trueness (%)			21,8	9,0	3,5
	Precision (%)			7,0	4,2	4,9
	Desvest			6,3	2,4	11,1
	RSD (%)			6,7	2,2	5,5
AUTOMATED	A (Bq/kg) ± u	93±5	70±3	134,0 ± 5,0	129,2 ± 6,5	214,0 ± 1,6
	MDA* (Bq/Kg)			1	0,8	0,5
	Z score			1,2	0,8	0,1
	Trueness (%)			11,7	7,7	1,4
	Precision (%)			6,0	6,3	2,3
	Desvest			4,3	4,1	2,3
	RSD (%)			3,2	3,2	1,1

* MDA (minimum detectable activity)

L⁻¹ HCl), 5 (5 mol L⁻¹ HCl – 0.05 mol L⁻¹ oxalic acid), 6 (0.1 mol L⁻¹ HCl) and 7 (0.1 mol·L⁻¹ oxalic acid), ports 1 and 8 are employed for sample disposal and waste, respectively.

First, the Uteva resin located in a methacrylate column (0.4 g) which was connected to the port 2 is conditioned with 2 mL of 3 mol l⁻¹ HNO₃ at a flow rate of 2 mL min⁻¹, then 10 mL of sample are passed through the column at a flow rate of 0.8 mL min⁻¹. After that, and in order to eliminate possible interferences, 1 mL of 3 mol L⁻¹ HNO₃ was passed. Then 2 mL of 9 mol L⁻¹ HCl are dispensed in order to change the resin to chloride system at a flow rate of 2 mL min⁻¹. After that the sequential separation of thorium and uranium

isotopes was performed by using first 10 mL of a 5 mol L⁻¹ HCl – 0.05 mol L⁻¹ oxalic acid solution to elute thorium isotopes, and then 10 mL of 0.1 mol L⁻¹ HCl to elute uranium isotopes. Both isotopes were collected in different vials situated in the autosampler which turn in each elution from column. The flow rate used in this last step was 2 mL min⁻¹. In order to reuse the resin for the analysis of more samples, the last step was a clean-up using 20 mL of oxalic acid 0.1 mol L⁻¹. After the separation process, uranium and thorium fractions were evaporated in the bath sand. When almost dry, the residues, which contain uranium or thorium, were reconstituted by adding 1 mL of 0.3 mol L⁻¹ Na₂SO₄. This solution was then

dried, the residue treated with 0.3 mL of concentrated H_2SO_4 and then 5 mL of distilled water were added. The solution was then transferred to an electrodeposition cell and submitted to electrolysis for 2 hours, under current density of 1.5 A cm^{-2} . The electrodeposition apparatus was used to obtain a uniform film in stainless-steel disks of 20 mm in diameter containing the uranium and thorium isotopes. After electrodeposition, the disc was counted for 72 hours to determine the activity of uranium and thorium isotopes using an alpha-spectrometer (ORTEC Plus).

3. Results and discussion

The present study is conducted to determine uranium and thorium isotopes in NORM samples from two different origins. It is important to have information, from a radiological point of view, of the individual contributors to the activity levels of these samples. For that purpose, we have developed a semi-automated method based on a SIA system to separate both isotopes using an extraction chromatographic resin, and then the measurement is performed by alpha spectrometry. In the following sections the optimization of the separation process is detailed. Moreover, the main results obtained when intercomparison samples have been analyzed are presented and compared with the obtained for the same samples obtained using a classical method for the determination of uranium and thorium (Mola

et al., 2013).

3.1. Optimization of MSFIA experimental conditions

In this study, SIA technique has been combined with a selective extraction resin to separate uranium and thorium isotopes. In particular we have selected an UTEVA column, which is a commercially available material specific for uranium and tetravalent actinides. This kind of chromatographic resin for extraction has given the opportunity to develop fast and simple separation methods for many radionuclides as U as well as Th isotopes (Casacuberta et al., 2012; Mola et al., 2013).

In order to find the best operational conditions for separation with the SIA system used (see Figure 1), we performed a series of studies. In particular we focused in the study of the elution conditions for uranium and thorium, namely the elution solvents and their volumes and also the flow rate. Our purpose was to achieve the highest recoveries for two tracers, ^{232}U for uranium and ^{229}Th for thorium, which are calculated by the measurement of the final fractions obtained after the SIA procedure by alpha spectrometry. Based on previous studies and also on the method described by Eichrom industries we prepare the sample in an acidic media, in particular in a 3M HNO_3 solution (Avivar et al., 2010, 2012; Casacuberta et al., 2012; Mola et al., 2013) since the extractant in the resin shows affinity for nitrate complexes of actinide elements and

the formation of these complexes is driven by the concentration of nitrate in the sample solution. Moreover, we added to the sample $\text{Al}(\text{NO}_3)_3$ to be able to work with samples that have a high phosphate content (Avivar et al., 2010; Mola et al., 2013). The sample volume was 10 mL and the flow rate in the loading step was 1 ml min^{-1} . Under these conditions, the analytes were quantitatively retained in the resin.

For the study of the elution solvent volumes we selected a solution 5 mol L^{-1} HCl – 0.05 mol L^{-1} oxalic acid for thorium, and in the case of uranium the elution was done using 0.1 mol L^{-1} HCl since these solvents have been demonstrated to be a good alternative for the elution of the studied radionuclides (Casacuberta et al., 2012; Mola et al., 2013). For each eluent we tried different volumes ranging from 1 to 15 mL at a 0.5 mL min^{-1} flow rate. From the obtained results, it was observed that with volumes lower than 10 mL the retained radionuclides were not completely eluted and the best results were obtained using 10 mL, so this was selected as the optimal volume in both cases.

In the optimization of the flow rates used for the elution step in the uranium and thorium radiochemical separation process, we evaluate the range between 0.5 and 3 mL min^{-1} . Through the obtained recovery values for the tracers, 0.8 mL min^{-1} was found to be the best with values of $96 \pm 3 \%$ for ^{232}U and $89 \pm 5 \%$ for ^{229}Th . For higher flow rates values the recoveries

were lower, probably due to the less contact between the eluents with the resin. So, under the optimum conditions found in this part of the study, it is possible to achieve the quantitative extraction of uranium and thorium radionuclides.

The resin lifetime was also studied. In that sense, it was evaluated the number of experiments that could be done with the same resin without any effect on the obtained response. Comparing the recovery values obtained in repetitive analysis it was possible to conclude that after 20 analyses with the same resin is recommended a replacement of that resin. At this point it is important to highlight that the periodicity in changing the resin is also dependant on the sample matrix, but under our conditions, the recovery values were not affected after 20 analyses.

3.2. Determination of uranium and thorium from intercomparison exercise

Once the separation process using the SIA system was optimized, an intercomparison sample (IAEA 2008) was analyzed. Moreover, the obtained results were compared with the obtained with another existing method in our laboratory, in particular with a method based on the classical extraction using the UTEVA resin in an off-line way. The results obtained when both methods were applied to the intercomparison sample ($n=4$) are summarized in Table 1. The average recoveries of the tracers obtained for the automated method

were slightly higher than the obtained for the classical method with average values of 93 ± 5 % for ^{232}U and 70 ± 3 % for ^{229}Th . On the other hand, in the table we also have included the reference activity values reported by the IAEA and also the Z-score results obtained for both methods. In general, from the obtained results, it can be concluded that both methods trueness, precision, relative standard deviation (% RSD) and minimum detectable activities (MDA) similar results were obtained when both methods were applied, even that recovery results were better for the semi-automated method. Also, it is worth to mention that the SIA based method is a faster method and also improves the analyst safety since there is a minimization of sample handling and the consumption of toxic solvents is greatly reduced. So it appeared that this method is an excellent alternative to the classical method for the determination of uranium and thorium activities.

3.3. Determination of uranium and thorium in NORM samples

Different NORM samples such as sludge from a drinking water treatment plant and waste sludge accumulated in the river located in front of a dicalcium phosphate (DCP) industry have been analysed by using, as in the case of the intercomparison samples, the two methods.

The samples from the DWTP were selected since from previous studies reported by our group (Palomo et al., 2010b, 2010c) it has been demon-

strated that the sludge produced by water treatment plants can concentrate radioactive constituents from source waters and among them we could quantify uranium and thorium emitting isotopes. Moreover, if this kind of samples are reused for different applications such as building materials (Husillos Rodríguez et al., 2010; Ravisankar et al., 2012), it is extremely important to have an exhaustive information about its radiological content and in this sense the possibility of having methodologies that allow a rapid characterization are very useful. For this study we collected three different samples which were numbered as DWTP1, DWTP2 and DWTP3 and the obtained results for four replicates when uranium and thorium radionuclides have been determined for these samples are shown in Table 2. Average recoveries for both tracers were in general higher when the semi-automated method was used and they were similar than the obtained for the intercomparison sample. On the other hand MDA values were slightly lower when the SIA system is used. The quantified activity values for these sludge samples using the automated approach were between 164 Bq Kg^{-1} and 217 Bq Kg^{-1} for ^{238}U , and between 207 Bq Kg^{-1} and 225 Bq Kg^{-1} for ^{234}U isotopes. These values for uranium isotopes are comparable with other studies previously reported in the literature focused in the study of the activity levels in solid waste material of different DWTP (Gäfvvert et al., 2002; Kleinschmidt and Akber, 2008;

Table 2. Uranium and thorium results obtained for sewage sludge samples in different times. Uncertainties are expressed at K=1, n=4.

Sample	Technique	²³² U	²³⁸ U			²³⁴ U		
		Recovery (%)	A (Bq/kg dry weight) ± u	MDA*	RSD (%)	A (Bq/kg dry weight) ± u	MDA*	RSD (%)
DWTP1	MANUAL	67 ± 5	198 ± 9	2,7	4	217 ± 9	4,0	2
	AUTOMATED	80 ± 4	217 ± 4	1,5	2	225 ± 9	1,3	4
DWTP2	MANUAL	76 ± 4	156 ± 5	2,7	4	180 ± 6	4,0	2
	AUTOMATED	87 ± 1	164 ± 3	1,1	2	207 ± 3	1,4	1
DWTP3	MANUAL	71 ± 3	191 ± 7	2,7	5	214 ± 1	4,0	3
	AUTOMATED	90 ± 4	205 ± 4	1,2	2	222 ± 3	1,5	1
Sample	Technique	²²⁹ Th	²³⁰ Th			²³² Th		
		Recovery (%)	A (Bq/kg dry weight) ± u	MDA*	RSD (%)	A (Bq/kg dry weight) ± u	MDA*	RSD (%)
DWTP1	MANUAL	54 ± 5	<AMD	2,5	-	27,1 ± 1,5	2,9	13
	AUTOMATED	68 ± 7	4,0 ± 0,2	0,5	4	32,6 ± 0,7	0,8	6
DWTP2	MANUAL	58 ± 2	7,3 ± 1,0	0,7	6	37,0 ± 1,5	2,8	6
	AUTOMATED	64 ± 4	9,7 ± 0,3	0,2	5	37,3 ± 1,6	0,6	3
DWTP3	MANUAL	65 ± 7	4,7 ± 0,9	3,2	10	29,7 ± 1,6	2,9	5
	AUTOMATED	80 ± 8	5,9 ± 0,2	0,5	4	26,0 ± 1,7	0,6	6

* MDA (minimum detectable activity)

Palomo et al., 2010b), from which it is clearly demonstrated that the sludge from a water treatment plant can contain enhanced levels of different radionuclides which are present in the raw treated water at lower levels.

In the case of thorium, the measured activities were lower than in the case of uranium as expected, being between 4.0 Bq Kg⁻¹ and 9.7 Bq Kg⁻¹ for ²³⁰Th and between 26.0 Bq Kg⁻¹ and 37.3 Bq Kg⁻¹ for ²³²Th. These values are also in agreement with previous studies that reported similar values (Palomo et al., 2010b). Thorium has less affinity with water than uranium and most of the thorium which can be in the raw water will be present in suspended matter or in sediment in the river course. For this reason, the concentration of soluble thorium in the water will be very low. Moreover, we can highlight that the activity values found in the present study for ²³²Th are similar to the values reported as the natural radionuclide content in soil ("natural background"), which is 30 Bq Kg⁻¹ for this radionuclide

(UNSCEAR, 2000).

We also analyzed NORM samples from the DCP plant of Flix. We selected three different samples (DCP1, DCP2 and DCP3) from the area located in front of this industry, which has been demonstrated by previous studies that is radiologically contaminated (Casacuberta et al., 2009). The corresponding values obtained for these samples are shown in Table 3. The different activity values obtained for these samples can be attributed to the different sampling point, since for example DCP3 was taken just in front of the DCP plant in the first meter of depth, whereas DCP2 was exactly from the same area but it was from the third meter of depth and this has an influence over the measured values, since higher activity was found at the superficial level, whereas at three meters of depth, the measured activities were lower and this behaviour can be attributed to a decrease of the influence of the DCP plant as depth increased. In the case of DCP1, this

Table 3. Uranium and thorium results obtained for sediment sludge accumulated in one side of the river samples from DCP. Uncertainties are expressed at $K=1$, $n=4$.

Sample	Technique	^{232}U	^{238}U			^{234}U		
		Recovery (%)	A (Bq/kg dry weight) \pm u	MDA*	RSD (%)	A (Bq/kg dry weight) \pm u	MDA*	RSD (%)
DCP1	MANUAL	89 \pm 3	1310 \pm 205	1,5	2	1399 \pm 217	1,5	8
	AUTOMATED	81 \pm 4	1322 \pm 148	1	1	1336 \pm 156	1,1	2
DCP2	MANUAL	90 \pm 5	956 \pm 153	1,0	4	1040 \pm 166	1,4	5
	AUTOMATED	92 \pm 4	946 \pm 111	1,0	2	1045 \pm 141	1,0	1
DCP3	MANUAL	68 \pm 4	2478 \pm 384	0,9	5	2599 \pm 401	1,2	4
	AUTOMATED	77 \pm 1	2637 \pm 285	1	3	2678 \pm 368	0,6	3
Sample	Technique	^{229}Th	^{230}Th			^{232}Th		
		Recovery (%)	A (Bq/kg dry weight) \pm u	MDA*	RSD (%)	A (Bq/kg dry weight) \pm u	MDA*	RSD (%)
DCP1	MANUAL	72 \pm 7	2217 \pm 377	0,9	6	51 \pm 13	0,8	10
	AUTOMATED	79 \pm 3	2265 \pm 321	0,2	1	53 \pm 5	0,4	8
DCP2	MANUAL	80 \pm 5	1668 \pm 235	0,8	3	37 \pm 8	0,6	10
	AUTOMATED	90 \pm 7	1739 \pm 248	0,3	1	41 \pm 4	0,4	5
DCP3	MANUAL	89 \pm 6	3520 \pm 586	0,8	5	48 \pm 13	0,5	12
	AUTOMATED	94 \pm 6	3604 \pm 371	0,3	3	47 \pm 5	0,3	6

* MDA (minimum detectable activity)

sampling point was located in the area of influence of the DCP of Flix, but in front of a wastewater treatment plant, so for this sample the measured activities were lower. Recoveries for the tracers (^{232}U and ^{229}Th) and MDA values were similar than the obtained for the DWTP sludge sample. Regarding the measured activities for uranium and thorium of these samples, they were in agreement with previous studies (Casacuberta et al., 2012; Mola et al., 2013), showing that the high activity levels correspond to those isotopes that belong to the ^{238}U decay series and this can be attributed to the DCP industrial activity which contributes to the enhancement of the activities of those isotopes (^{238}U , ^{234}U and ^{230}Th). On the other hand, the measured activities of ^{232}Th are in the range of the usual values from uncontaminated soils (30 Bq Kg⁻¹) (UNSCEAR, 2000).

4. Conclusions

In this work, a semi-automated method based on the use of a SIA

system for the sequential separation of uranium and thorium radionuclides was developed. With this method, activity concentrations of uranium and thorium radionuclides in an IAEA intercomparison material were close to the reference values. Moreover, a comparison between the analytical performance of the developed method with a classical method has been carried out and the results showed that the SIA method is a good alternative to the classical method with some advantages as high precision, reduction of the time and also minimization of the sample and reagents required in the analysis with an improvement in the safety. The proposed semi-automated methodology was successfully applied to the determination of U and Th nuclides in different NORM samples,

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**3.2.2. Determination of ^{90}Sr and ^{210}Pb in sludge samples
using a LOV-MSFIA system and liquid
scintillation counting**

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DETERMINATION OF ^{90}Sr AND ^{210}Pb IN SLUDGE SAMPLES USING A LOV-MSFIA SYSTEM AND LIQUID SCINTILLATION COUNTING

M. Mola^{a,b}, J. Avivar^c, A. Nieto^{a,b}, A. Peñalver^{a,b}, C. Aguilar^{a,b}, L. Ferrer^c, V. Cerdà^d, F. Borrull^{a,b,*}

^a Universitat Rovira i Virgili Marcel·lí Domingo s/n, 43007 Tarragona (Spain)

^b Unitat de Radioquímica Ambiental i Sanitària (URAI) Consorci d'Aigües de Tarragona (CAT), Ctra Nacional 340, km 1094, 43895 L'Ampolla (Spain)

^c Environmental Radioactivity Laboratory, University of the Balearic Islands, Ctra. Valldemossa km 7.5, 07122 Palma de Mallorca (Spain)

^d Chemistry Department, University of the Balearic Islands, Ctra. Valldemossa km 7.5, 07122 Palma de Mallorca (Spain)

Abstract

There has been increasing interest recently in the capacity of water treatment plants to concentrate and eliminate radionuclides from raw water. As the normal operation in these plants generates high quantities of sludge, which can be considered a naturally occurring radioactive material, it is important to gather information about its radiological content. Therefore, in order to determine the activity values of two radioactive beta emitters with minimal sample manipulation, an automated lab-on-valve and multisyringe flow injection system has been developed to achieve the sequential preconcentration and separation of ^{90}Sr and ^{210}Pb using an extraction chromatographic resin (Sr-spec). Activities of both isotopes were measured by liquid scintillation counting (LSC). The developed method was validated by analysing two samples from two different intercomparison exercises and good Z-score values (between 0.7 and 1) and trueness values (between 14% and 17%) were obtained. The method was then also satisfactorily applied to sludge samples taken from a Spanish drinking water treatment plant which treats water from the Ebro River. The proposed method offers advantages over existing methods as it allows the sequential separation of both isotopes, simply by changing the elution conditions and using a semi-automated approach. Therefore, the method is less time consuming and environmentally friendly.

Keywords: ^{90}Sr ; ^{210}Pb ; lab-on-valve - multisyringe flow injection analysis; liquid scintillation counting; sludge

INTRODUCTION

Due to the processes carried out in drinking water treatment plants (DWTP), several radionuclides, which

are present in raw water, are concentrated in the sludge generated as waste as a result of their operation. This sludge is usually dried and accumulated near the plant and, in

some cases, it is reused for different purposes, such as a component of building materials. Due to the presence of several radionuclides in these sludge samples, and also taking into account the capacity of this kind of water treatment plant in terms of concentrating certain radioisotopes, these plants are considered to be naturally occurring radioactive material (NORM) industries [1-5]. In previous studies performed by our research group [1, 6], several sludge samples from the DWTP located in L'Ampolla (Tarragona, Spain) were analysed by gamma spectrometry to evaluate both natural (^{214}Pb , ^{40}K , ^{238}U , ^{232}Th , among others) and artificial (as ^{60}Co or $^{110\text{m}}\text{Ag}$) radionuclides. This plant treats water from the Ebro River and, according to the results obtained in the previous studies, it may be concluded that the radioactive content in the sludge is influenced by different industrial activities present along the course of the river. In particular, it is worth mentioning the presence of a nuclear power plant as well as the fact that there are more than 300,000 tons of sludge residues with high levels of radioactivity accumulated in the vicinity of a dicalcium phosphate plant (DCP) [7].

Apart from the previously quantified isotopes, there are other potential radionuclides which may be present in these samples and, in this respect, they may increase the radioactive levels of the sludges generated. In particular, two pure beta emitters, ^{90}Sr and ^{210}Pb , were considered in this study. These radionuclides have a

high biological toxicity as, once they have been incorporated into the human body, they remain in the skeleton for a long time due to their relatively long half-lives (^{90}Sr $T_{1/2} = 28.6$ years and ^{210}Pb $T_{1/2} = 22.3$ years) [8, 9]. Thus, it is necessary to develop accurate and reliable methods that allow the determination of these isotopes in order to ensure the health of workers and the public in general, as well as ascertaining their impact on the environment. Furthermore, the reuse of the sludge generated in the DWTP, for example, in the manufacturing of construction materials, highlights the extreme importance of their radiological characterization [2, 10].

To date, several analytical methods have been developed for the determination of ^{90}Sr and ^{210}Pb in different samples, such as human urine, bone and soils [11-14], but before their radiochemical measurement, it is important to ensure the separation of the two isotopes to achieve pure ^{90}Sr and ^{210}Pb spectra of the respective separated fractions by liquid scintillation counting (LSC). In general, the most commonly used procedures include different steps: sample pretreatment, chemical purification, separation and detection. The chemical purification and separation steps are the most critical since they involve multi-stage operations. Over the past few decades, enormous effort has been made to develop new methods which involve a certain degree of automation [15-18]. Ever since flow analysis techniques

emerged, different strategies have appeared in order to achieve lower reagent consumption, higher repeatability and reproducibility, higher sample throughput, complete automation of the analytical procedure with low manipulation by the analyst, and miniaturization. In this respect, the main flow methodologies employed in recent years are multicommutated flow techniques, such as multisyringe flow injection analysis (MSFIA) [19] and lab-on-valve (LOV) [20, 21] due to the ability to develop systems within a framework of green chemistry. In a recent study by Rodríguez *et al.* [16], a LOV-MSFIA system was developed for the determination of total strontium and ^{90}Sr in spiked water samples [22]. In that paper, the authors presented an interesting automated approach using a solid phase material (an Sr-resin) to separate strontium from potential interferences present in the water samples analysed, such as calcium or magnesium. In our study, an alternative method is proposed which allows the separation of two beta emitters (^{90}Sr and ^{210}Pb) by using a similar approach to the method proposed by Rodríguez *et al.* but with certain modifications to enable the use of a semi-automated method for the sequential separation of both isotopes for the first time. Finally, the developed method has been applied to the determination of both isotopes in sludge samples from a DWTP.

2. Experimental

2.1. Reagents and standard solutions

All solutions were prepared from analytical grade reagents with Millipore quality water. HCl (38%), HNO_3 (65%) and $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (99.5%) were supplied by J.T. Baker (Deventer, Holland), $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ a.r. was supplied by Chem-Lab (Zedelgem, Belgium), the liquid scintillation cocktail used was Optiphase Hifase 3, supplied by Perkin Elmer (Waltham, USA), polyethylene (PE) scintillation vials were supplied by Sarstedt (Nümbrecht, Germany). Sr-resin 50–100 μm was supplied by Triskem Industries (Bruz, France) and glass fibre pre-filters were purchased from Millipore (Madrid, Spain). Digested samples were filtered with 0.45 μm filters supplied by Whatman (Maidstone, England).

Standard solutions of $^{90}\text{Sr}/^{90}\text{Y}$ and ^{210}Pb used in the calibrations were provided by CIEMAT (*Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas*, Madrid, Spain). The certified nominal activity concentration of $^{90}\text{Sr}/^{90}\text{Y}$ (prepared in 1 mol L^{-1} HCl) was 246.7 ± 0.3 Bq g^{-1} , and the certified nominal activity concentration of $^{210}\text{Pb}/^{210}\text{Bi}/^{210}\text{Po}$ (prepared in 3 mol L^{-1} HNO_3) was 580 ± 10 Bq g^{-1} . Stock standard solutions for ICP were prepared from 1,000 mg L^{-1} of strontium and lead (at 2% HNO_3) supplied by Scharlab (Barcelona, Spain) by an appropriate dilution with

2 mol L⁻¹ HNO₃. Silver and bismuth (1,000 mg L⁻¹ in 1% HNO₃), used as internal standard solutions to allow correction for instrumental drift of the ICP-MS instrument, were supplied by Sigma-Aldrich (Madrid, Spain).

2.2. Instrumentation

A speedwave four microwave digestion system with built-in, non-contact temperature and pressure measurement supplied by Berghof (Eningen, Germany) was used for the digestion of samples. Twelve pressure vessels made of TFM fluoropolymer were located in a rotor with a gas collection system in which 1,450 W of microwave power can be obtained.

An ultra-low background Quantulus 1220™ liquid scintillation spectrometer (Perkin Elmer) was used for the measurements of ⁹⁰Sr and ²¹⁰Pb. It was equipped with three sample tray tables with 20 positions, EASY View Spectrum Analysis program and pulse shape analyser.

For the optimization of the separation process and the calculation of the recovery of the extraction process for both radionuclides, an ICP-MS Elan DRC-e (Perkin Elmer, Spain) was used. The system was fitted with a Scott spray chamber and a crossflow nebulizer (Perkin Elmer, Spain). ²⁰⁹Bi and ¹⁰⁷Ag (2 µg L⁻¹) were used as internal standards [13, 23] to compensate for the instrument drift between runs.

The LOV-MSFIA system, which is shown in Figure 1, was based on a design used in previous studies [16, 24] with certain modifications. In

Figure 1, the different integrated parts can be seen: a multisyringe burette (BU4S; Crison Instruments, Barcelona, Spain) equipped with a 10 mL syringe (S1) and two 5 mL syringes (S2, S3) (Hamilton, Switzerland) which were used as liquid drivers and reservoirs of internal standards, a LOV microconduit (Sciware Systems, Palma de Mallorca, Spain) encompassing eight peripheral integrated microchannels (1.5 mm i.d./16.0 mm length, enclosing the bead column channel) installed on top of an eight-port multiposition selection valve (Crison Instruments, Barcelona, Spain) and connected through the central port to S1 via a holding coil (HC). An external solenoid commutation valve (V) (MTV-3-N 1/4 UKG; Takasago, Japan) was connected to the peripheral port 2 of the LOV in order to direct the flow as desired (on: in-line flow towards the autosampler; off: to waste). A 4-way connector (Sciware Systems) was used to connect S2, S3, the autosampler and the outlet of the LOV through V (on). The system was automatically controlled by the software package AutoAnalysis 5.0 (Sciware Systems).

2.3. Samples

To validate the proposed method, two samples from two intercomparison exercises organized by the Nuclear Safety Council (CSN-2005) and the International Atomic Energy Agency (IAEA, 2011) were analysed. In particular, the first sample was a vegetable ash from the areas of Huesca and Girona (Spain) and the

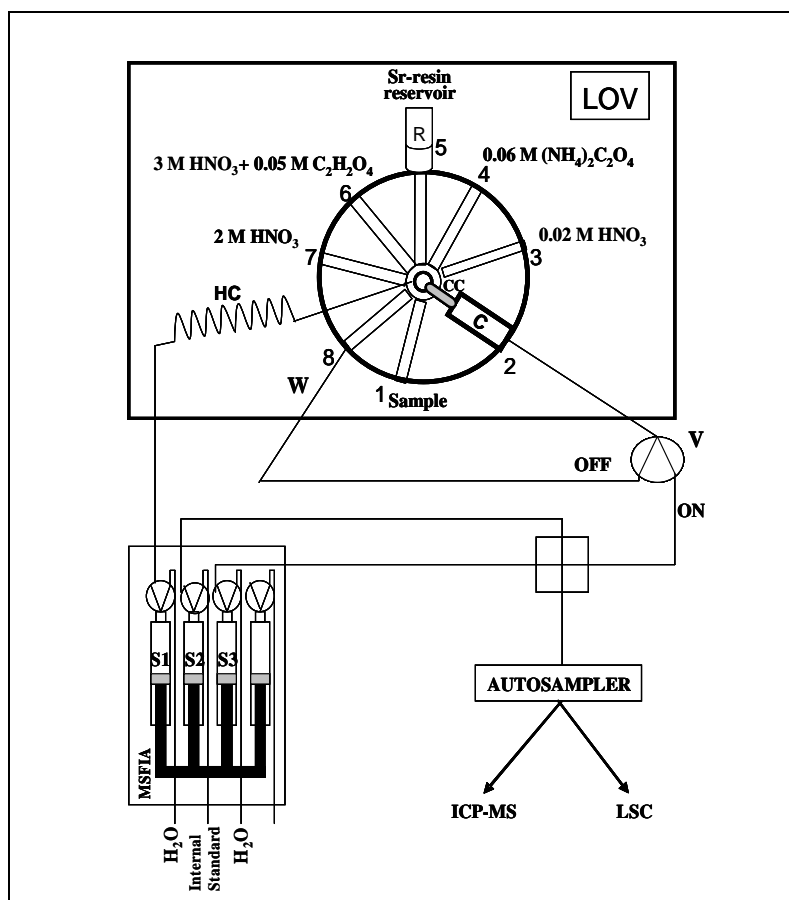


Figure 1: LOV-MSFIA system for Sr and Pb isolation and pre-concentration: S: syringe, HC: Holding Coil, V: Solenoid Valve, C: Column, CC: Central conduit.

second sample was milled, dried and sterilized soil from the Chernobyl area. These samples contained, among other isotopes, ^{90}Sr and ^{210}Pb in activity concentrations of $91.2 \pm 14.8 \text{ Bq kg}^{-1}$ and $87.0 \pm 16.5 \text{ Bq kg}^{-1}$, respectively, in the CSN-2005 sample, and $2.4 \pm 0.5 \text{ Bq kg}^{-1}$ and $42.6 \pm 2.2 \text{ Bq kg}^{-1}$, respectively, in the sample provided by IAEA.

Four sludge samples from the DWTP in L'Ampolla (Tarragona) were collected at regular intervals of one sample each three months (between March and November 2012). These

sludge samples were firstly centrifuged and the water was removed by decantation. Afterwards, they were transferred to a Pyrex glass tray and dried in a stove at a temperature of $110^\circ\text{C} \pm 5^\circ\text{C}$. The samples were then crushed in a ball mill and sifted in a $250 \mu\text{m}$ sieve before finally being stored in a plastic bag in the laboratory.

2.4. Analytical procedure

Initially, about 5 g of sample were placed in a muffle furnace at 550°C for 12 hours. After cooling, 0.5 g was

transferred into a vessel with 12 mL of a mixture of $\text{HNO}_3:\text{HCl}$ (3:1). Microwave digestion was then performed for 30 minutes at 13.33 Pa, reaching a temperature of 215°C [25]. After cooling, the sample was filtered through a $0.45\ \mu\text{m}$ pore-size syringe filter to remove any potential insoluble particles. The soluble part was then evaporated to dryness with a sand bath, before finally being re-dissolved to a final volume of 10 mL with $2\ \text{mol L}^{-1}\ \text{HNO}_3$, ready to be loaded into the automated separation system (port 1, Figure 1).

The complete operational sequence for the isolation and preconcentration of Sr and Pb was performed following the steps described in Table 1. Firstly, the reagents were located at the peripheral ports of the LOV as follows: port 1 (sample), port 2 (column packed with 0.030 g of Sr-resin), port 3 ($0.02\ \text{mol L}^{-1}\ \text{HNO}_3$), port 4 ($0.06\ \text{mol L}^{-1}\ (\text{NH}_4)_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$), port 5 (resin reservoir), port 6 ($3\ \text{mol L}^{-1}\ \text{HNO}_3 + 0.05\ \text{mol L}^{-1}\ \text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$), port 7 ($2\ \text{mol L}^{-1}\ \text{HNO}_3$) and port 8 (waste). To summarize, firstly the resin is conditioned with 1 mL of $2\ \text{mol L}^{-1}\ \text{HNO}_3$ and then 10 mL of the sample is passed through the column. After the removal of possible interferences with 0.2 mL of the preconditioning acid ($2\ \text{mol L}^{-1}\ \text{HNO}_3$) [23], the elution of the retained strontium is performed by passing 2 mL of HNO_3 at a concentration of $0.02\ \text{mol L}^{-1}$. At that point, the external solenoid valve (V) is in the 'on' position. Subsequently, deionized water is used to transfer the eluted

fraction of strontium to the autosampler. Lead is eluted with 4 mL of $0.06\ \text{mol L}^{-1}\ (\text{NH}_4)_2\text{C}_2\text{O}_4$, and, once again, the solenoid valve (V) is in the 'on' position and 0.9 mL of deionized water is used to transfer it to the autosampler. In order to clean the resin after the extraction of Sr and Pb and prepare it for the next extraction, 1 mL of $3\ \text{mol L}^{-1}\ \text{HNO}_3 - 0.05\ \text{mol L}^{-1}\ \text{C}_2\text{H}_2\text{O}_4$ was passed through the column. In addition, the resin was regularly and automatically changed every 10 analyses. Then, for measurement of the ^{90}Sr and ^{210}Pb , the remaining volumes (Sr fraction (2 mL) and Pb fraction (4 mL)) were collected directly in separate 20 mL PE liquid scintillation vials. In the case of strontium, the sample was mixed manually with 6 mL of MilliQ water and 12 mL of liquid scintillation cocktail. In the case of lead, the sample was mixed with 16 mL of liquid scintillation cocktail. Afterwards, the resulting mixtures were measured by using LSC during a single cycle of 500 minutes. The pulse shape analysis (PSA) measurement mode was used for ^{210}Pb [26] and, in this case, an optimal PSA level of 95 was selected in order to minimize τ_α , τ_β and total interference values [27]. In addition, ^{90}Sr was measured 15 days after its separation in order to achieve the secular equilibrium with ^{90}Y [28-30].

3. Results and discussion

The main aim of this study was to develop a method to determine ^{90}Sr and ^{210}Pb in sludge samples from a

Table 1. Automatic procedure for strontium and lead separation and preconcentration using the developed LOV-MSFIA system.

Sequential series	Flow rate (mL·min ⁻¹)	MSFIA-LOV				
		S1	S2	S3	V	LOV position
1. Column loading						
(a) Aspirate 1 mL Sr Resin	5	On	Off	Off	Off	5
(b) Filling the column (dispense)	2	On	Off	Off	Off	2
2. Conditioning of Sr Resin						
(a) Aspirate 1 mL HNO ₃ into HC	5	On	Off	Off	Off	7
(b) Dispense 1 mL on the column	2	On	Off	Off	Off	2
3. Sample loading						
(a) Aspirate up to 10 mL sample	5	On	Off	Off	Off	1
(b) Dispense up to 10 mL on the column	0.6	On	Off	Off	Off	2
4. Interferences elimination						
(a) Aspirate 0.2 mL HNO ₃	5	On	Off	Off	Off	7
(b) Dispense 0.2 mL on the column	2	On	Off	Off	Off	2
5. Elution of Sr						
(a) Aspirate 2 mL eluent	5	On	Off	Off	Off	3
(b) Dispense 2 mL on the column	1	On	Off	Off	On	2
6. Internal standard addition (0.1 mL Bi/Ag)	2	Off	On	Off	Off	Out
7. Sample loading into sampler collector	2	Off	Off	On	Off	Out
8. Elution of Pb						
(a) Aspirate 4 mL eluent	5	On	Off	Off	Off	4
(b) Dispense 4 mL on the column	1	On	Off	Off	On	2
9. Internal standard addition (0.1 mL Bi/Ag)	2	Off	On	Off	Off	Out
10. Sample loading into sampler collector	2	Off	Off	On	Off	Out
11. Column rinse						
(a) Aspirate 1 mL HNO ₃ + 0.05M C ₂ H ₂ O ₄	5	On	Off	Off	Off	6
(b) Dispense 1 mL on the column	2	On	Off	Off	Off	2
12. Change of sample						
(a) Aspirate new sample into HC	5	On	Off	Off	Off	1
(b) Discarding (dispense)	2	On	Off	Off	Off	8
13. Beads replacing						
(a) Aspirate old beads into HC	5	On	Off	Off	Off	2
(b) Discarding old beads	5	On	Off	Off	Off	8
(c) Aspirate new beads into HC	5	On	Off	Off	Off	5
(d) Filling the column	2	On	Off	Off	Off	2

S1: H₂O, S2: Bi/Ag solution, S3: H₂O; V: solenoid commutation valve.

DWTP. The developed method is based on the use of an automated system for the separation of both isotopes and subsequent activity measurement using LSC equipment. The proposed methodology is a development of the work of Rodríguez *et al.* [16]. Based on the good results obtained for the measurement of total strontium in

spiked water samples content in that work, a modified approach was proposed in order to be able to separate ⁹⁰Sr and ²¹⁰Pb sequentially in solid sludge samples after pretreatment using microwave digestion. In the following sections, there is firstly a discussion of the main results obtained in the optimization process, followed by an analysis of different

samples, with two different intercomparison samples in particular, as well as sludge samples taken from a DWTP.

3.1. Optimization of the LOV-MSFIA experimental conditions

The optimization of the different variables which affect the proposed system was carried out, including the volumes and concentrations of different reagents. This was performed with an ICP-MS system using stable isotopes of Sr and Pb to save time and also to avoid working with radionuclides in this initial stage of the procedure optimization.

To perform the preconcentration and separation of Sr and Pb, a Sr-spec resin was selected. This resin provided good results for both elements [12, 16, 31-34]. In our case, a resin amount of 0.03 g was selected and the different parameters that may have an effect on the retention and elution of both isotopes were evaluated.

A good retention of Sr and Pb is achieved when 1 mL of nitric acid is used as the sample medium. As has been demonstrated previously by other authors, under these conditions, the corresponding nitrate complexes are formed with Sr and Pb present in the sample and these nitrates display good retention in the Sr-spec resin [12, 16, 31-33]. With this in mind, the effect of the nitric acid concentration in the sample to be loaded into the resin was studied. The corresponding experiments were carried out with a sample containing both isotopes at a concentration of 2 $\mu\text{g L}^{-1}$ and different

nitric acid concentrations were evaluated in the range between 2 and 8 mol L^{-1} . A concentration of 2 mol L^{-1} HNO_3 was selected as the sample medium as, under these conditions, good retention was obtained in both cases (98% for Sr and 90% for Pb). Moreover, this low HNO_3 concentration prevented corrosion on the materials used in the procedure over time.

After the retention of the analytes of interest was achieved, the elution step was optimized using a multivariate approach. Multivariate designs provide relevant knowledge on the effect of variables within the entire experimental domain selected, and the variance of the estimate of the response in every point of the domain is better than that obtained by univariate methods [35]. For this reason, and taking into account the optimal elution conditions reported in the literature, the range of conditions to be evaluated were selected. Specifically, Sr is normally eluted using HNO_3 at a concentration lower than 0.05 mol L^{-1} and in the case of Pb, the elution is normally achieved using HCl at a concentration ranging from 6 to 8 mol L^{-1} [32-34]. However, considering the materials used in this study, the relatively high acid concentrations for Pb elution have to be avoided, since they can produce interference in the LSC detection [27]. Moreover, additional intermediate steps may be required, such as the evaporation of the Pb elution fraction. Therefore, an alternative elution solvent was selected, namely $(\text{NH}_4)_2$

C_2O_4 , as it had previously been used by Sooksamiti *et al.* [34].

After selecting the eluents, four potentially critical variables related to the elution process were taken into consideration in the multivariate design optimization, namely the concentration and volume of $(NH_4)_2C_2O_4$, and the volume of HNO_3 . The computer statistical package Statistica 6 was used to build a multivariate two-level full factorial design in order to screen the variables and second-order interactions between them that have a significant influence upon the determination of trace elements (analytical response) and to discard them with negligible effects on the response.

The experimental design was built in a dimensionless coordinate system using factor coding, in which the highest and lowest levels are given as +1 and -1, respectively. A randomized complete block amounting to a total number of 16 experiments was performed, aimed at ensuring that the variability found in the response is attributable to the variables rather than random error. Three centre points were included to identify any irregularities, such as the loss of linearity in the center of the interval. Results showed that the curvature and the four variables studied were significant.

Finally, a Box-Behnken design [36, 37] was developed with a total number of 33 experiments with readjusted ranges for the variables following the screening results, in order to find the critical value of the variables. The

experiment ranges and levels of independent variables selected for the optimization were HNO_3 0.02 - 0.045 - 0.07 mol L^{-1} and 2 - 3 - 4 mL for Sr elution and $(NH_4)_2C_2O_4$ 0.05 - 0.075 - 0.1 mol L^{-1} and 2 - 3.25 - 4.5 mL for Pb elution. Critical values for both analytes were obtained from a desirability function commonly used for multi-response analysis. The best results were obtained when 2 mL of HNO_3 0.02 mol L^{-1} was used to elute the retained Sr and 4 mL of $(NH_4)_2C_2O_4$ 0.06 mol L^{-1} to elute the Pb. The mathematic model selected showed a 0.996 correlation coefficient for each radionuclide and low pure error values of 0.0002 for Sr and 0.00004 for Pb. Under the optimal conditions, recoveries of 90% and 98% for Sr and Pb were obtained, respectively.

3.2. LSC measurements

In order to ascertain the activities of ^{90}Sr and ^{210}Pb , a low background Quantulus 1220TM liquid scintillation spectrometer was used after the separation procedure. In the case of ^{210}Pb , the alpha/beta measurement mode with pulse shape analysis (PSA) was used. This measurement mode enables the separation of alpha and beta isotopes in two different windows, once the PSA parameter has been optimized, to obtain minimal interference [38]. The PSA was fixed at a value of 95, as this had been optimized in a previous study by our group [27]. For ^{90}Sr , the high-energy beta measurement mode was selected. In order to select the best conditions

(high efficiency and less quenching) for the measurement of ^{210}Pb and ^{90}Sr by liquid scintillation, five different combinations of the ratio between the sample volume and the liquid scintillation cocktail volume were tested. In the case of strontium, 2 mL of a standard sample of ^{90}Sr (74 Bq L⁻¹ in HNO₃ 0.02 mol L⁻¹) was introduced into 20 mL LSC PE vials with varying amounts of deionized water (0-8 mL) and LSC cocktail (Optiphase Hifase III, 8-18 mL) in order to obtain a final volume between 10 and 20 mL. Blanks for each combination were also measured using only deionized water with acid medium and liquid scintillation cocktail. To perform the measurement of the strontium content, 2 mL of sample, 6 mL of deionized water and 12 mL of liquid scintillation cocktail was chosen as the optimal combination, achieving the highest efficiency (63%) under the studied conditions. The selected window is shown in Figure 2a (channels 620-865).

With respect to the lead fraction, the same experiments were performed, in this case, using 4 mL of a standard sample of ^{210}Pb (42 Bq L⁻¹ in 0.06 mol L⁻¹ (NH₄)₂C₂O₄) with varying amounts of deionized water (0-6 mL) and LSC cocktail (Optiphase Hifase III, 6-16 mL). The efficiencies obtained ranged between 80% and 99%. Higher efficiency values were obtained with a volume of 4 mL of sample mixed with 16 mL of scintillation liquid, so these conditions were selected for further experiments. Figure 2b shows the spectrum for ^{210}Pb (channels 100-380)

and its daughter, ^{210}Bi . The backgrounds obtained were 0.55 and 0.94 for Sr and Pb, respectively.

3.3 Application to real samples

Once the method was optimized, its applicability to different real samples was tested. Specifically, the method was first evaluated by analysing two samples from two different inter-comparison exercises. Sludge samples taken from the DWTP located in L'Ampolla were then analysed.

3.3.1. Determination of ^{90}Sr and ^{210}Pb in reference materials

In order to evaluate the precision, accuracy and recoveries of each radionuclide with the developed method, samples from two different intercomparison exercises organized by the CSN in 2005 (a sample of vegetable ashes) and the IAEA in 2010 (a soil sample) were analysed with the proposed method. These samples contained different alpha and beta isotopes, and ^{90}Sr and ^{210}Pb were included among them.

Table 2 shows the average results obtained for ^{90}Sr and ^{210}Pb and the reference activity values reported by the organizer of the intercomparison exercises (included as A_{ref}). The activity values obtained for Sr and Pb in the intercomparison samples were generally close to the activities established by the Nuclear Safety Council (CSN) and IAEA as the reference values, with the exception of the IAEA sample, in which strontium was not detected since the reported value given by the organization was

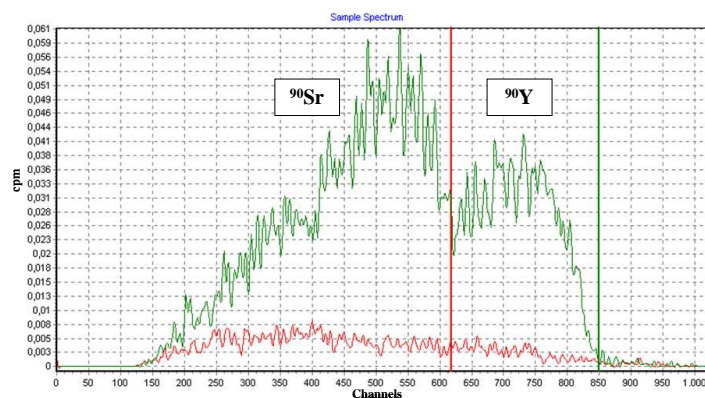


Fig. 2a.

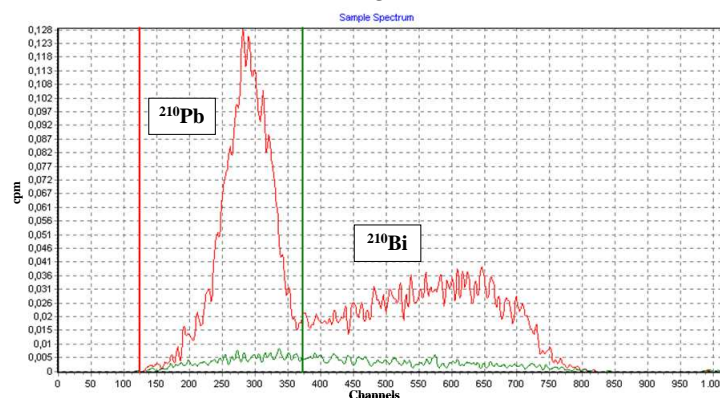


Fig. 2b

Figure 2: Figure 2a. Maximum efficiency of signal (cpm) activity spectrums of ^{90}Y (^{90}Sr) Figure 2b. Maximum efficiency of signal (cpm) activity spectrums of ^{210}Pb in standards.

lower than the minimum detection activity of our method ($\text{MDA} = 17.8 \text{ Bq Kg}^{-1}$). The MDA was calculated according to the recommendations of ISO 11929 [39] for a confidence level of 95%. As can be seen in Table 2, Z-score values between 0.7 and 1.0 and trueness between 14% and 17%, were obtained for ^{90}Sr and ^{210}Pb , respectively.

The reproducibility of the method, expressed as relative standard deviation (RSD), was obtained by analysing the intercomparison samples on seven consecutive days, and

the values obtained were 9% for ^{90}Sr and 11% for ^{210}Pb in the sample from the CSN 2005 and 6% for ^{210}Pb in the sample from the IAEA 2011.

To the best of our knowledge, this is the first system proposed for the determination of ^{90}Sr and ^{210}Pb developed in a flow-based approach exploiting the use of an extraction chromatography resin. Even though, in the literature, there are some approaches based on the use of automated systems for the determination of the mentioned radionuclides, those approaches are based

Table 2. Results obtained for two reference materials (CSN 2005 and IAEA 2011). Uncertainties (u) are expressed at $K=1$, $n=7$.

Sample	Radionuclide	$A \pm u^*$ (Bq/Kg)	MDA** (Bq/Kg)	$A_{ref} \pm u$ (Bq/Kg)	Z-score	Trueness (%)	Precision (%)
CSN 2005 (vegetal ashes)	^{90}Sr	76.5 ± 2.9	16.1	91.2 ± 14.8	1.0	16	17
	^{210}Pb	74.9 ± 2.4	13.5	87.0 ± 16.5	0.7	14	19
IAEA 2011 (soil)	^{90}Sr	<MDA	17.8	2.4 ± 0.5	-	-	-
	^{210}Pb	35.4 ± 2.2	11.2	42.6 ± 2.2	0.85	17	8

*u is the expanded uncertainty ($K=2$)

**MDA (Minimum detectable activity)

on the individual determination of one of them, in contrast to the sequential determination that is proposed in this case [16, 17, 40, 41].

3.3.2. Determination of ^{90}Sr and ^{210}Pb in sludge samples from a DWTP

^{90}Sr and ^{210}Pb activities (dry weight) were quantified with the proposed system in four sludge samples from the DWTP in L'Ampolla (Tarragona, Spain). Table 3 shows the average results obtained ($n=4$) for both isotopes with their respective uncertainties. Regarding the quantified activity values, in the case of ^{90}Sr (artificial radionuclide), the values ranged between 34 ± 3 Bq Kg^{-1} and 76 ± 3 Bq Kg^{-1} . Meanwhile, for ^{210}Pb , the values ranged between 38 ± 3 Bq Kg^{-1} and 63 ± 3 Bq Kg^{-1} . The minimum detectable activities obtained for ^{90}Sr and ^{210}Pb were 14.5 Bq Kg^{-1} and 12.0 Bq Kg^{-1} , respectively. Moreover, reproducibility was also calculated from the analysis of a sludge sample on seven consecutive days, expressed in % RSD, and it ranged between 1% and 14% for ^{90}Sr , and between 4% and 15% for ^{210}Pb .

In general, in the literature, ^{90}Sr data for environmental samples are relatively scarce and there are few studies involving the determination of ^{90}Sr concentrations (between 3 and 87 Bq Kg^{-1}) in sludge generated by 310 PWTP [42], but if our results are compared to those reported in other studies which focus on the determination of that isotope in soil samples, such as the studies of Lee *et al.* [43, 44] in which ^{90}Sr was quantified in different soil samples, it can be concluded that although our results show slightly higher activities, they are quite close to the values reported in the literature for uncontaminated soils.

In the case of ^{210}Pb , there is more literature as more studies focusing on the determination of radionuclides of natural origin have been reported [5, 42, 45]. Jiménez *et al.* [45] analysed sludge samples from a urban sewage treatment plant located in Valladolid (Spain), where there are only local pollution influences. This work reported ^{210}Pb concentrations in 21 sludge samples ranging between 25 Bq kg^{-1} and 69 Bq kg^{-1} and these ^{210}Pb

Table 3. Results obtained for sewage sludge samples in different times. Uncertainties (u) are expressed at K=1, n=4.

Radionuclide		Sludge samples			
		March	June	September	December
⁹⁰ Sr	A ± u* (Bq/Kg)	46 ± 3	63 ± 3	76 ± 3	34 ± 3
	MDA** (Bq/Kg)	14	15	14	15
	RSD (%)***	11	7	1	14
²¹⁰ Pb	A ± u* (Bq/Kg)	63 ± 3	55 ± 2	38 ± 3	54 ± 2
	MDA** (Bq/Kg)	12	12	13	12
	RSD (%)***	4	7	12	15

*u is the expanded uncertainty (K=2)

**MDA (Minimum detectable activity)

***Reproducibility was calculated as n=4

activities levels are similar to the values obtained in our study. It can therefore be concluded that the industrial activities developed in the Ebro River upstream of the PWTP do not have a significant effect on the activities of ²¹⁰Pb and ⁹⁰Sr found in the sludge samples.

4. Conclusions

The proposed automated LOV-MSFIA hyphenated system was successfully applied for the first time for the determination of ⁹⁰Sr and ²¹⁰Pb activities by liquid scintillation spectrometry. The methodology has shown to be a good alternative to manual radiochemical separations, determining both radionuclides with simple equipment, reduced consumption reagents, minimal production of effluents and minimal resin used. The proposed method has successfully been applied to two intercomparison materials and four sludge samples from a Spanish water treatment plant

obtaining good precision and reproducibility values and low minimum detection activities. Thus, the method has proven to be an interesting tool and a more complete and affordable alternative than other available options for the routine analysis of waste sludge samples.

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Montserrat Mola Arques
Dipòsit Legal: T.1294-2013

3.2.3. Discussió de resultats

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En els articles d'aquest bloc s'han desenvolupat i optimitzat sistemes de flux automatitzats per tal d'aconseguir l'extracció i separació de radionúclids individuals i després s'ha dut a terme la seva mesura amb els equips d'espectrometria alfa. A continuació destacarem els aspectes resultants més importants de cada article.

Tal i com s'ha comentat anteriorment, en aquests estudis es treballa amb un sistema de flux basat amb la tècnica SIA per tal d'aconseguir una separació seqüencial d'U i Th amb la resina Uteva i una altra tècnica basada amb la combinació LOV-MSFIA per aconseguir una separació seqüencial d'Sr i Pb amb la resina Sr-Spec.

L'optimització de les variables experimentals va ser realitzada de forma diferent en cada treball degut al diferent nombre de variables a optimitzar. En el primer treball es va realitzar una optimització univariant, és a dir, amb la variació d'una única variable experimental de forma individual, mantenint de forma constant la resta. En aquest cas i ajudant-nos de l'experiència adquirida anteriorment amb l'extracció d'uranis i toris mitjançant la resina Uteva, les variables necessàries a optimitzar van ser: el flux de càrrega de la mostra (mL min^{-1}) i el volum dels eluents (mL). En primer lloc, es va comprovar mitjançant l'experimentació que el flux òptim en la càrrega de la mostra (testat entre tres) va ser de 0.8 ml min^{-1} . Després amb l'altra variable a optimitzar, tal i com podem veure en la Figura 3.2., es van provar sis volums diferents de cada eluent utilitzat en el sistema ($5 \text{ mol L}^{-1} \text{ HCl} - 0.05 \text{ mol L}^{-1}$ àcid oxàlic per a eluir el Th i $0.1 \text{ mol L}^{-1} \text{ HCl}$ per a eluir l'U). En els resultats globals de l'aplicació d'aquests diferents volums es van obtenir increments de les recuperacions químiques, fins obtenir uns màxims de recuperació del $89 \pm 5 \%$ per al traçador de tori i del $96 \pm 3 \%$ per al d'urani amb l'ús de 10 mL d'eluent en ambdós casos i per això, aquest va ser el volum escollit com a òptim.

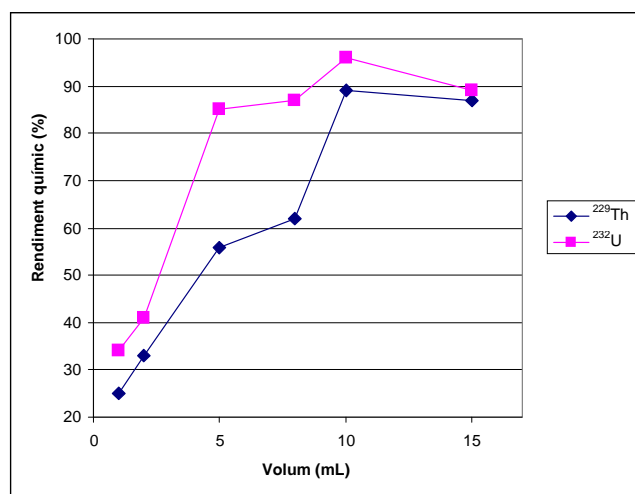


Figura 3.2. Evolució del rendiment químic segons el volum d'eluent utilitzat.

En el cas de l'estudi de l'extracció d'Sr i Pb mitjançant la resina Sr-spec no hi ha gaire informació bibliogràfica en el cas del Pb, i encara menys de la separació seqüencial d'ambdós radionúclids. En primer lloc, algun paràmetre es va fixar de forma univariant, com ara el flux de càrrega a 0.6 mL min^{-1} . Després, quatre variables crítiques es van considerar per a realitzar una optimització multivariable de la separació seqüencial entre l'Sr i el Pb sense interferents. Les variables van ser: concentració de $(\text{NH}_4)_2\text{C}_2\text{O}_4$ (rang d'estudi: $0.025 - 0.075 \text{ mol L}^{-1}$) i el volum (1 - 4 mL), la concentració de HNO_3 ($0 - 0.02 \text{ mol L}^{-1}$) i el volum (1 - 4 mL).

Amb el programa *statistics package Statistica 6* es va realitzar el disseny multivariant *two-level full factorial* per a realitzar un *Screening* i poder descartar les concentracions, etc., elevades o mínimes amb efectes negligibles. Aquest disseny experimental es va dissenyar amb una dimensió coordinada entre nivells alts i baixos anomenats +1 i -1, respectivament, i tres punts centrals per poder identificar algunes irregularitats, sobretot en casos de poca reproductibilitat i de pèrdua de linealitat al centre dels intervals. Finalment, a partir de les dades obtingudes del *Screening*, on totes les variables van mostrar tindre influència significativa entre elles, es va realitzar un segon disseny experimental de tres nivells i quatre factors mitjançant *Box-Behnken* [1,2] amb un total de 33 experiments amb tres punts centrals inclosos. Entre els resultats, cal destacar que el model matemàtic escollit ens va mostrar un correcte coeficient de correlació lineal per a cada isòtop amb mínims errors purs. Després, mitjançant la funció de la *desirability* es van decidir els punts crítics de la separació entre els dos radionúclids. Finalment, aquests van ser: 2 mL de HNO_3 0.02 mol l^{-1} per la elució de l'Sr i 4 mL d' $(\text{NH}_4)_2\text{C}_2\text{O}_4$ 0.06 mol L^{-1} per a l'elució del Pb, amb unes recuperacions químiques del 90% i del 98% per a l' ^{88}Sr i el ^{208}Pb , respectivament.

Un altre punt important a comentar d'aquest últim treball, va ser la fracció de còctel d'escintil·lació, aigua i volum de mostra (ja fixat després de la separació) utilitzat en cada cas, per a una mesura òptima en el LSC. Després de fer diferents proves amb patrons es van trobar les millors eficiències utilitzant 2 mL fracció Sr + 6 mL aigua desionitzada + 12 mL de còctel i 4 mL fracció Pb + 16 mL de còctel, sempre tenint en compte que el màxim de volum a treballar eren 20 mL per qüestions del recipient utilitzat en la mesura.

En l'anàlisi de dues mostres d'exercicis d'intercomparació (CSN i IAEA), que van servir com a mostres de referència per a validar els mètodes optimitzats d'ambdós sistemes estudiats, es van obtenir valors de reproductibilitat elevada i de Z-score inferiors a dos. A més, tots els valors obtinguts en precisió, exactitud, desviació i desviació relativa estàndard, ens indiquen valors experimentals propers al valor de referència en les dues tècniques automàtiques aplicades.

Finalment, concloure que els resultats de les mostres de fangs de l'ETAP i de la DCP ens mostren activitats d'U i Th més elevades que les fixades segons la UNSCEAR per a mostres de sòls espanyols [3], per tant es poden considerar material NORM. Tot i així, veiem que en el cas dels fangs de l'ETAP les concentracions baixes de tori (^{230}Th)

rebel·len que aquest es troba en el material en suspensió o sedimentat en el riu i per tant, no es concentra en forma de fangs durant el tractament de l'aigua en la planta potabilitzadora [4]. En aquests mateixos fangs de l'ETAP es van obtenir concentracions de entre $34 \pm 3 \text{ Bq Kg}^{-1}$ i $76 \pm 3 \text{ Bq Kg}^{-1}$ d' ^{90}Sr i de entre $38 \pm 3 \text{ Bq Kg}^{-1}$ i $63 \pm 3 \text{ Bq Kg}^{-1}$ de ^{210}Pb . Aquestes concentracions ens permeten corroborar la teoria de que hi ha presència de radionúclids artificials (^{90}Sr) provinents de la central nuclear uns kilòmetres aigües amunt, i que les concentracions trobades de ^{210}Pb són similars a les trobades en altres plantes de tractament d'aigües degut a la geologia del terreny.

A continuació es realitza una comparativa dels diferents aspectes dels dos mètodes utilitzats en els treballs d'aquest bloc. Tal i com es mostra en la taula següent, hem comparat els dos mètodes destacant diferents característiques i resultats obtinguts durant l'anàlisi de les mostres de fangs provinents de l'ETAP. En primer lloc veiem que el pretractament de la mostra, realitzat de forma *off-line*, ha estat en ambos casos el mateix amb la digestió per microones de 0.3 gr de mostra. Ara bé, amb la disminució del volum de la resina amb el sistema combinat LOV-MSFIA, s'ha obtingut més rapidesa en l'extracció amb la necessitat de menys volum de reactius i a més, amb recuperacions químiques dels traçadors més precises i elevades. Però d'altra banda, amb aquest sistema LOV-MSFIA també han augmentat considerablement els límits de detecció del mètode. A més, tal i com podem observar, en la separació d'U i Th s'han obtingut els interval més petits de la RSD deixant veure que el SIA ha resultat ser el mètode més sensible i reproduïble dels dos.

Taula 3.1. Taula resum de diverses característiques i resultats de dos mètodes automatitzats

	U/Th	Sr/Pb
Pretractament <i>off-line</i>	Digestió MW	Digestió MW
Mètode automatitzat	SIA	LOV-MSFIA
Resina/volum (mg)	Uteva/400	Sr-Spec/30
Volum d'eluent (mL)/Flux (mL/min)	10-10/0.8	2-4/0.6
η^* (%)	77-90/54-80	90/98
MDA**	1.1-1.8/0.2-0.5	14-15/12-13
RSD*** (%)	2/4-5	1-14/4-15
Detecció	Espectrometria alfa	LSC

* η és la recuperació química

**MDA és la activitat mínima que es pot detectar

***RSD és la desviació estàndard relativa

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4. CONCLUSIONS

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Les conclusions més importants derivades dels estudis realitzats en la present Tesi Doctoral són les que presentem a continuació:

1. En aquesta tesi una temàtica central ha estat l'estudi i la caracterització dels fangs acumulats enfront el complex industrial situat en Flix, més concretament, dels residus generats per una planta de producció de fosfat dicàlcic que va treballar a partir de la roca fosfòrica durant més de dos dècades.
2. Amb relació a les concentracions d'índex alfa total i beta total i els radionúclids individuals trobats a diferents profunditats dels fangs acumulats i establint un factor temporal amb les concentracions trobades de ^{137}Cs , podem concloure que els tres primers metres de profunditat es veuen molt influenciats per una gran producció de la DCP (voltants de l'any 1990). En majors profunditats s'ha vist una aportació residual menor d'aquesta planta, amb increments d'activitats puntuals que es poden relacionar amb èpoques més properes al 1973 (inici de la producció).
3. Una altre indicador que ens proporciona informació sobre la presència de material NORM és la relació entre el ^{40}K i l'índex beta total. S'ha comprovat en els primers metres de profunditat que aquesta relació no segueix el comportament normal (amb més activitat de ^{40}K més activitat d'índex beta total).
4. Les concentracions trobades de radionúclids descendents de la cadena de l' ^{238}U , en aquests primers metres de profunditat, com ara el ^{230}Th amb 3520 Bq kg^{-1} en el primer metre i després amb activitats de menys de 50 Bq kg^{-1} a partir del cinquè metre de profunditat, ens permet considerar aquest estudi com una referència per a l'actual retirada i posterior tractament dels residus.
5. En altres mostres minerals com són el fosfat i el carbó també s'han determinat diferents radionúclids de l'U i el Th, mostrant una composició elevada d'aquests radionúclids. Per això, tant la seva manipulació, com el transport i emmagatzematge s'hauria de dur a terme tenint en compte aquestes activitats radiològiques trobades.
6. En general, s'ha comprovat la influència de la industrialització als voltants de l'Ebre i l'embassament de Flix, a partir de les concentracions de radioactivitat trobades en matrius diferents. Les mostres d'algues, musclo zebra i silur

recollides i analitzades prop l'embassament, presenten activitats més elevades en alguns radionúclids que en les mostres recollides al punt de control situat en Riba-Roja, mostrant la influència dels residus acumulats. Més concretament, s'ha vist a partir dels resultats obtinguts una diferent absorció i acumulació per part de cada radionúclid estudiat amb la biota. També s'ha vist que la localització de les mostres de biota, ja sigui en aigües superficials o bé en zones on hi ha més terbolesa i presència de substrat, influeix amb les activitats trobades.

7. S'han desenvolupat i optimitzat diferents mètodes per a la preparació de la mostra, la preconcentració i extracció dels uranis i els toris. La digestió de totes les mostres es va realitzar mitjançant un digestor amb microones. L'etapa de la preconcentració òptima va ser mitjançant la formació d'un precipitat de $\text{Ca}_3(\text{PO}_4)_2$ ja que amb altres agents precipitants degut a la presència de Fe les recuperacions disminueixen. Per a la separació i detecció de l'urani i el tori es va utilitzar la resina d'extracció cromatogràfica Uteva i l'espectrometria alfa.
8. Amb l'ajuda dels mètodes automatitzats de flux, s'han desenvolupat i optimitzat mètodes d'extracció i separació seqüencial de dos radionúclids de manera més ràpida, reproducible i segura. En l'estudi de l'aplicació del mètode SIA per a l'extracció de l'U i el Th es van comparar els resultats obtinguts amb els de l'extracció manual en l'anàlisi de mostres similars. Finalment, amb el mètode de flux es van obtenir avantatges com ara una menor manipulació de mostra i volums utilitzats i un augment considerable de reproductibilitat.
9. Una extracció seqüencial del Sr i el Pb automatitzada, mitjançant la tècnica LOV-MSFIA, s'ha desenvolupat i optimitzat per primera vegada amb la resina Sr-Spec amb l'obtenció d'alts rendiments químics per ambdues espècies. Per a la mesura dels radionúclids d' ^{90}Sr i ^{210}Pb , es va emprar el detector d'escintil·lació líquida obtenint bones eficiències.
10. La planta de tractament d'aigua potable mostra la capacitat d'eliminar de l'aigua procedent del riu i de preconcentrar en els fangs produïts durant el procés de tractament de l'aigua, diversos radionúclids a diferents nivells. Degut a les concentracions de radionúclids naturals detectades en aquests fangs i comparades amb altres de la bibliografia són considerats material NORM. A més també hi trobem la presència de radionúclids d'origen artificial, com ara l' ^{90}Sr , mostrant la gran diversitat industrial d'aquesta conca del riu Ebre amb la presència de dues centrals nuclears.

11. Dintre del marc normatiu a seguir en el cas de la reutilització dels fangs com a material de construcció o bé per a la rehabilitació de sòls (d'exploració minera, agrònoms, etc.), no es tenen en compte els valors de radioactivitat. Amb els resultats obtinguts en aquest treball i en d'altres anteriors, del nostre grup d'investigació, cal considerar la necessitat d'aplicar una normativa per controlar els emissors radioactius en aquest tipus de mostres.

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ANNEXOS



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Annex I. Abreviacions utilitzades en aquesta Tesi Doctoral.

BBD: Disseny Box–Behnken

CSN: Consell de Seguretat Nuclear

DAAP: *Diamyl amyolphosphate*

DCP: Indústria de fosfat dicàlcic

EDAR: Estació depuradora d'aigües residuals

ETAP: Estació de tractament d'aigua potable

FIA: *Flow injection analysis*

IAEA: *International Atomic Energy Agency*

ICP-AES: *Inductively coupled plasma atomic emission spectroscopy*

ICP-MS: *Inductively coupled plasma mass spectrometry*

ICP-OES: *Inductively coupled plasma optical emission spectrometry*

LSC: Comptador d'escintil·lació líquida

LOD: Límit de detecció

LOV: *Lab-on-valve*

MDA: Activitat mínima detectable

MCFIA: *Multicommutated flow injection analysis*

MPFS: *Multipumping flow system*

MSFIA: *Multisyringe flow injection analysis*

NORM: *Naturally occurring radioactive materials*

PMMA: Poli-metilmetacrilat

PSA: *Pulse shape analysis*

PTFE: Poli-tetrafluoroetilè

RSD: Desviació estàndard relativa

SIA: *Sequential injection analysis*

TBP: Tri-n-butílic fosfat

UNSCEAR: *United Nations Scientific Committee on the Effects of Atomic Radiation*

USEPA/EPA: *United States Environmental Protection Agency*

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Annex II. Llistat de publicacions obtingudes en aquesta tesi doctoral, incloses en la part experimental, els quals estan publicats o enviats a revistes per la seva pròpia publicació en revistes científiques.

- M. Mola, A. Peñalver, C. Aguilar, F. Borrull, *Distribution of naturally occurring radioactive materials in sediments from the Ebro River reservoir in Flix (Southern Catalonia, Spain)*, Journal Hazardous Materials 198 (2011) 57-64 (apartat 3.1.1.).
- M. Mola, A. Peñalver, C. Aguilar, F. Borrull, *Comparative study of different analytical methods for the determination of ^{238}U , ^{234}U , ^{235}U , ^{230}Th and ^{232}Th in NORM samples (Southern of Catalonia)*, Journal of Environmental Radioactivity 115 (2013) 207-213 (apartat 3.1.2.).
- M. Mola, M. Palomo, A. Peñalver, C. Aguilar, F. Borrull, *Radionuclides in biota collected near a dicalcium phosphate plant, Southern Catalonia, Spain*, Journal of Radioanalytical and Nuclear Chemistry (acceptat i pendent de publicació).
- M. Mola, J. Avivar, A. Nieto, A. Peñalver, C. Aguilar, L. Ferrer, V. Cerdà, F. Borrull, *Determination of ^{90}Sr and ^{210}Pb in sludge samples using a LOV-MSFIA system and liquid scintillation counting*, Journal Hazardous Materials (enviat).
- M. Mola, A. Nieto, A. Peñalver, C. Aguilar, F. Borrull, *Uranium and thorium automatic sequential separation from NORM samples by using a SIA system*, Journal of Environmental Radioactivity (enviat).

A part de les publicacions incloses en la part experimental de la tesi, està publicat un capítol d'un llibre introduït en la introducció i pendent de publicació la participació en un article d'un grup de recerca extern.

- M. Mola, A. Nieto, A. Peñalver, C. Aguilar, F. Borrull, *Introduction and impact of radioisotopes in the environment due to NORM industries*, Radionuclides: source, properties and hazards, 2013, New York: Nova Science Publishers (apartat 1.2.2.).
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