Evaluation of radiochemical methods for thorium-isotopes determination in environmental and industrial samples by alpha-spectrometry

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Abstract

Thorium is a very sensitive element to matrix effects that appear at different stages of its preparation to be measured by alpha-particle spectrometry. These effects are particularly important for inorganic solid samples from environmental and industrial origin. To deal with this problem and to define the most suitable method, not only from a technical point of view but also considering cost, time and chemical reagents used, a research project was started. In this work, the main results of this project are shown.

Introduction

Alpha spectrometry is the most widely used methodology to obtain the contents of Thorium isotopes (^{232}Th, ^{230}Th, ^{228}Th) in environmental and industrial samples. This technique involves a set of steps: sample pre-treatment to obtain a solution containing the thorium contents in the sample; radiochemical separation to isolate the thorium contents in the sample solution from other interfering chemicals, electrodeposition to obtain a test sample ready to be measured by alpha spectrometry, and finally, alpha measurement.

For each one of the first three steps there are different methods that could be applied, so, the most suitable methodology should be a proper and coherent selection of a method for each step. To define this most suitable methodology, and with the financial support of the Spanish Nuclear Safety Council (CSN), a research project was developed and a resume of its results is presented here.
To improve the quality of results, four working groups (WG) belonging to four different universities had participated in this project.

Materials and Methods

Materials

The 4 WG used the same material: alpha-spectrometer, from Canberra, equipped with passivated implanted silicon (PIPS) type, with an active area of 450 mm^2 and a nominal background of 0.1389 s^{-1}m^{-2}. Thorium tracers, ^{229}Th and ^{230}Th, provided by NIST and class PA chemicals reagents.

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Methodology

Calculus:

Formulae for activity concentration, uncertainties and characteristics limits have been developed, following GUM (ISO, 1995) and ISO 11929 (ISO, 2010), respectively, to make results comparable.
The total yield of the process is the product of its chemical yield (sample pre-treatment plus radiochemical separation) and electrodeposition yield. It is calculated as:

$$R = \frac{(r_{gt} - r_{0t})}{A.\ \varepsilon}$$

Where A is tracer activity added; r_{gt} and r_{0t} are the tracer gross counts rate in the sample test spectrum and background spectrum, respectively, and ε is the detector efficiency.

Developed experiments:

Experiment 1: Selection of radiochemical separation method.

The objective of the first experiment is the choice, among those methods implemented in the laboratories, of the most suitable and robust one to be used, for all the WG, when the capability of the sample pre-treatment methods will be compared.
To achieve this goal, four different radiochemical methods, TBP+II-anionic, II-anionic, and specific chromatographic resins type UTEVA and TEVA were analyzed, starting from a HNO_3 sample solution obtained by different pre-treatment methods.
These four methods have been applied to the following samples: phosphate rock (FR), ilmenite (ILM), sediments (SED), sludge coming from water plant treatment (SLG), ground water with high saline contents, blank water and reference samples of ^{232}Th (MR232) and ^{230}Th (MR230). Solid samples were previously dissolved (pre-treated) and each one of the 4 WG applied one of the methods described to 5 aliquots of these dissolved samples. At the beginning of the radiochemical process ^{229}Th tracer were added to the sample.
The solutions, containing Thorium, obtained from the radiochemical separation processes, were electrodeposited in 1 in diameter stainless steel disk, all the WG followed the method provided by Hallstadius (Hallstadius, 1984), to obtain the test samples to be measured by alpha spectrometry. The selected measurement times were always 300000 sec and the source-detector distance 5mm. Then, the total (separation+ electrodeposition) yield of the process was obtained.

Experiment 2: Performance of pre-treatment methods.

The objective of this experiment was to analyze the performance of four different pre-treatment methods: acid attack in a closed container (DAHC), acid attack in an open container (DAPA), microwave oven ((DAMO) and alkaline fusion (PIRO).
To deal with this objective, these four methods have been applied by the four WG to the following samples: uranium ore (MU), ilmenite (ILM), tionite (TIO), soil (SU), sludge from a water plant treatment (SLG), and ashes from vegetal origin (CE). Each WG's have been applied the aforementioned pre-treatment methods in 3 aliquots of each sample type, and after dissolution, all the WG applied the radiochemical isolation method selected in Part 1 as the most robust and suitable for all types of samples, II-anionic.
After that, test samples were prepared and measured in the same way than in Experiment 1, obtaining the activity concentration, uncertainties and detection limits of the samples.
The differences among the activities concentrations obtained for the same sample, when different methods are used, allow the comparison of the ability of the different sample pre-treatment methods

to provide a representative dissolution from the original sample. In addition, samples will be characterized for ^{232}Th, ^{230}Th and ^{228}Th activity concentration contents.

Experiment 3: Factors that affect the variability of the total yield.

From the results obtained in Exp. 1 and also in Exp. 2 it can be seen that total yields show a high variability; not only among the different type of samples, but also among the different analyses carried out in the same sample. So, the objective of this third experiment is to analyze if this variability is due to the separation methods or to the electrodeposition one. Also, if needed, which factors affect electrodeposition yields are analyzed.
To carry out this experiment the same samples than those used in the Exp.2, now characterized for ^{230}Th, ^{232}Th and ^{228}Th, were dissolved and divided in aliquots. In one of these aliquots conventional chemical analyses were carried out. The other aliquots were used to apply the four radiochemical separation methods, without using ^{229}Th tracer. After separation, the obtained solutions were divided in two aliquots; in one of them the conventional chemical analyses were carried out once again; so, the ability of each one of the radiochemical methods to clean up chemicals from the original sample was stated. The other aliquot was traced with ^{229}Th before to be electrodeposited and measured by alpha spectrometry; so, the electrodeposition yield is obtained using Eq. 1 and therefore, radiochemical separation yield.
A flow chart of this Experiment is show in Fig. 1.

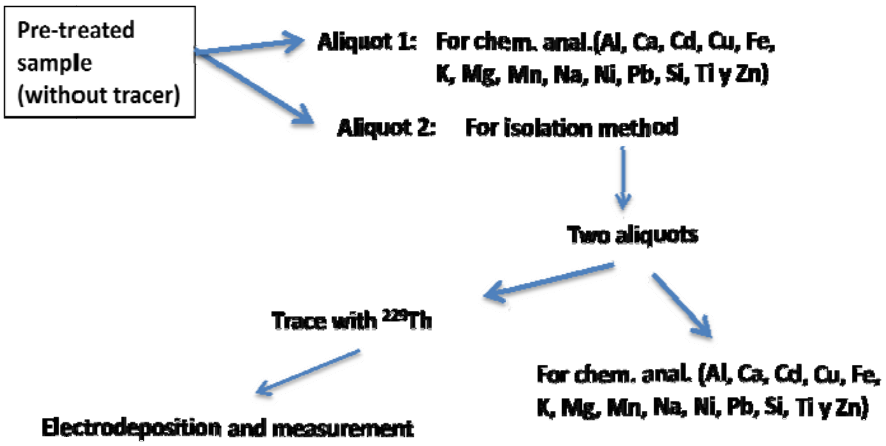

Figure 1. *Flow-chart of Experiment 3*

Results and Discussion

Experiment 1:

Results obtained for the Th isotopes activity concentration are shown in Figure 2 for the samples with highest activity contents.
In this Figure it can be seen that results obtained are very similar for all samples regardless of the separation method used. Also, there is a good coincidence on isotopic relations. So, it can be concluded that, all the analyzed methods work properly and in a similar way.

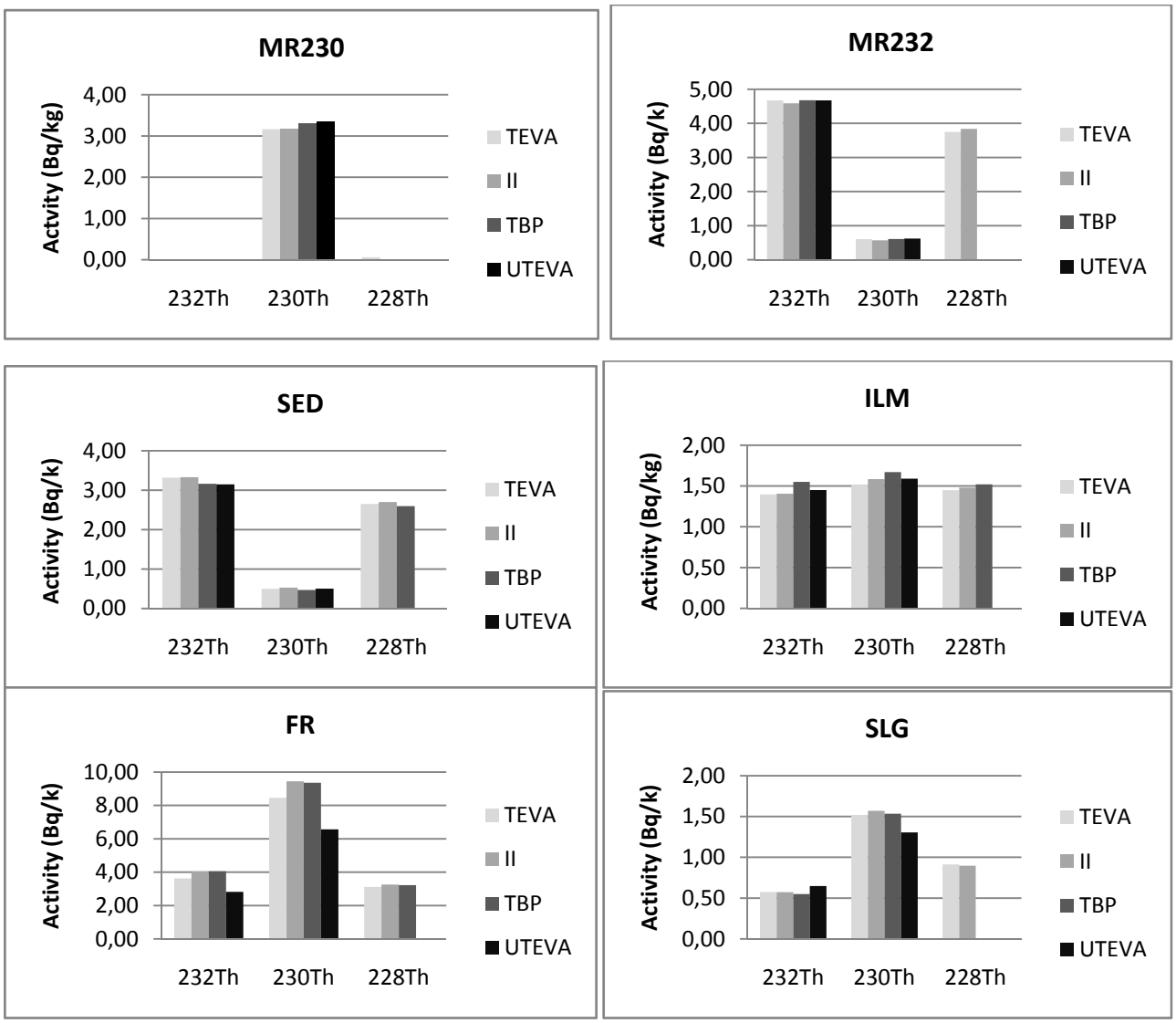

Figure 2. *Five aliquots mean values of Th radioisotopes activity concentration of samples, obtained by the four radiochemical separation methods.*

In Table 1, the mean values of the 5 aliquots obtained for the total yields are showed for all measured samples by the four separation methods. Values appear with its standard deviation (k =1).

SAMPLE	Radiochemical separation method			
	TEVA	II	TBP	UTEVA
MR230	0.77 ± 0.05	0.69 ± 0.07	0.88 ± 0.03	0.52 ± 0.10
MR232	0.73 ± 0.10	0.93 ± 0.06	0.80 ± 0.04	0.60 ± 0.12
ILM	0.68 ± 0.08	0.60 ± 0.09	0.72 ± 0.06	0.30 ± 0.04
FR	0.78 ± 0.08	0.64 ± 0.12	0.55 ± 0.15	0.45 ± 0.14
SED	0.82 ± 0.06	0.83 ± 0.11	0.53 ± 0.08	0.77 ± 0.07
LDF	0.87 ± 0.01	0.97 ± 0.03	0.35 ± 0.15	0.38 ± 0.08
ZAPR	0.11 ± 0.01	0.61 ± 0.08	0.77 ± 0.12	0.73 ± 0.11
H2O	0.90 ± 0.02	0.91 ± 0.01	0.54 ± 0.13	0.78 ± 0.05

Table 1. *Five aliquots mean values of total yields. In %.*

Following the results showed in this Table 1, it can be concluded that all radiochemical isolation methods were comparable among them, providing comparable mean values of total yields. Anyway, taking into account not only yields obtained but also its standard deviation, it can be concluded that the II-anionic methods are those that supply the highest and most reproducible yield results for all type of samples. However, the standard deviations obtained imply that total yield is not stables, not even for the same sample when the same method is used.

Experiment 2:

Mean values of the experimental data for activities concentrations for ^{228}Th, ^{230}Th and ^{232}Th for each type of sample and for each pre-treatment method are shown in Table 2. Data are provided with its uncertainty obtained following GUM method (ISO, 1995). Detection limits are not given, but in most cases, they are close to E-04 Bq/kg.

		^{232}Th		^{230}Th		^{228}Th	
MUESTRAS		**A (Bq/kg)**	**U (Bq/kg)**	**A (Bq/kg)**	**U (Bq/kg)**	**A (Bq/kg)**	**U (Bq/kg)**
SUELO	**DAPA**	43.4	0.7	43.9	0.2	44.9	0.8
	DAHC	39.6	3.3	40.9	1.9	43.1	5.6
	DAMO	42.3	1.5	56.3	0.8	48.2	2.1
	PIRO	44.7	0.3	45.0	2.1		
FANGOS	**DAPA**	50,5	1.5	58,3	1.7	73,0	1.1
	DAHC	52.1	3.0	55.3	3.1	76.6	4.1
	DAMO	50.5	1.4	56.3	1.6	76.3	1.0
	PIRO	52.0	2.5	54.7	3.4		
MIN URANIO	**DAPA**	503.7	13.1	3055.0	35.1	517.2	14.4
	DAHC	513.2	11.6	3144.0	51.1	548.7	20.2
	DAMO	531.5	4.5	3174.0	56.5	561.2	4.7
	PIRO	508.0	16.2	3188.0	82.4	--	
CENIZAS	**DAPA**	5.24	0.08	8.17	1.64	9.53	0.43
	DAHC	5.09	0.17	13.8	8.56	6.05	4.39
	DAMO	--		--		--	
	PIRO	4.67	0.333	6.33	0.88	--	
TIONITE	**DAPA**	117.3	1.0	77.8	2.4	651.1	45.4
	DAHC	105.9	11.7	168.0	16.7	191.0	17.2
	DAMO	122.0	4.1	105.1	5.0	884.6	180
	PIRO	93.3	5.8	107.0	4.0		
ILMENITA	**DAPA**	330.9	4.6	105.1	3.4	318.0	6.9
	DAHC	310.4	47.0	112.6	6.1	376.3	14.3
	DAMO	334.6	4.7	125.7	1.9	373.3	7.0
	PIRO	342.3	8.4	124.7	2.0	--	

Table 2. *Mean activity concentration values for the 3 aliquots for each sample and each attack method, with its uncertainty (k=1)*

In this Table 2 it can be seen that the different data provided by the WG for the samples analyzed are very similar. Dispersions from the sample-mean values are in most cases lower than 10%. Tionite, which shows noticeable deviation in ^{232}Th and ^{230}Th and huge deviations in ^{228}Th, is an exception and also some data from ashes are. In the case of Tionite, it should be considered that ^{228}Th activity can be in continuously evolving over time depending on the relation ^{228}Ra/^{232}Th; this fact can be the cause of the huge deviation. In any case, there is not a tendency that allows us to decide which pre-treatment method provides better results. In the case of ashes samples it should be considered that the activities concentration were smaller than on the other samples; uncertainties

reported when DAHC method was used were much higher than 50%, and so these values should be discarded for statistical reasons.
So, considering that all the WG have been used the same radiochemical separation method and the same electrodeposition procedure, it can be concluded that all the pre-treatment methods work properly for the samples analyzed. Regarding total yields the mean value was higher than 65%, higher for the most conventional samples, soil and ashes, than for the most complexes ones, tionite and ilmenite.
At the same time, all the WG have been used their own methods to asses thorium values to these samples, results are not provided here, but together with those on Table 2 have been used to assess the activity concentration reference values to these samples.

Experiment 3:

Comparisons between the conventional chemicals present in the samples before and after radiochemical separation processes allow us to obtain the ability of these methods to remove chemical interferences for each type of sample. Results are shown in Figure 3, where mean values, for the samples analyzed, are shown for each separation method used and each chemical analyzed.

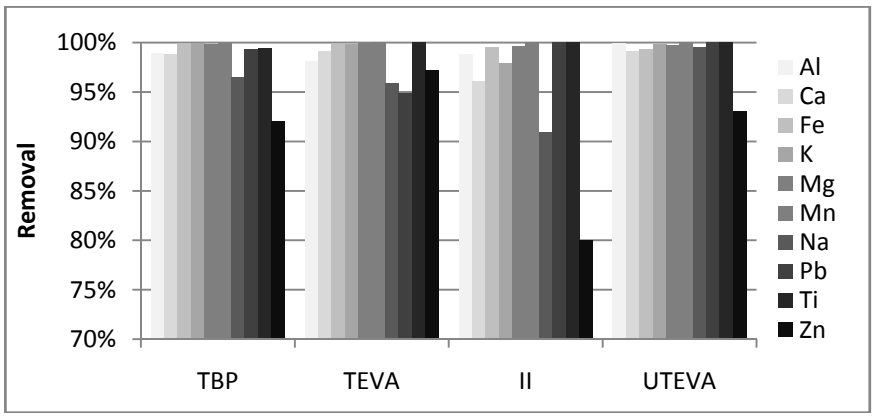

Figure 3. *Mean values of the removal percentage of chemical interferences when the four radiochemical separation methods are used in the different samples.*

Following the information contained in this Figure 3 it can conclude that all the separation methods are able to remove more than 90% of chemicals from the solution containing the dissolve sample, regardless of the sample type, being UTEVA resins those that provide the highest values.
It can be also seen that Zn shows values always higher than 80% but lower than the other chemicals, this behavior is due to Zn is quite an interchangeable element that appears in most of plastic made laboratory equipments.
Radiochemical separation yields were obtained for all samples and methods and data are shown in Figure 4
Regarding this Figure 4, it can be seen that the II-method is that which provide the more stable separation yields for the samples analyzed, with values higher than 70 %; biological ashes samples are the only exception, with separation yields close to 50%. The other separation methods provide yields that in some cases are higher than those from II-method but more variables depending on sample types. Regarding type of sample, it can be conclude that, being all of them very complexes, uranium ores is that in which thorium is separated with the highest and most stable yields regardless the separation method used.

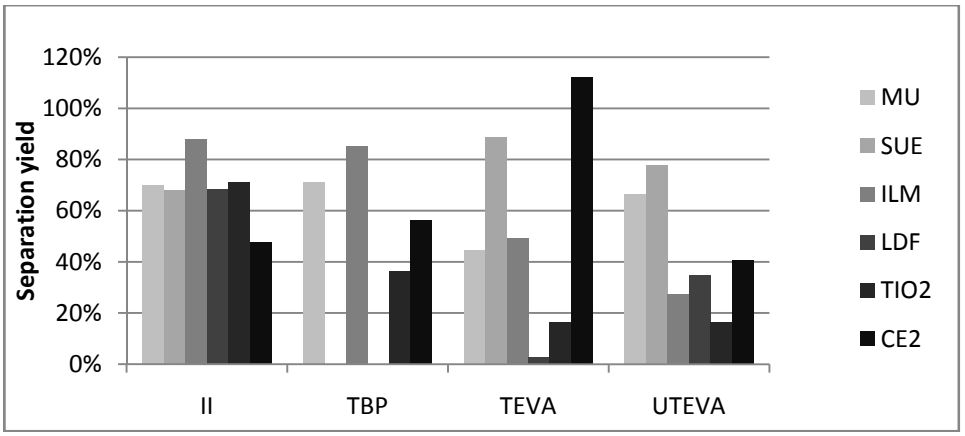

Figure 4. *Mean values of the radiochemical separation yield when the four methods are used in the different type of samples. In %.*

Finally, electrodeposition yields were obtained for all samples and methods; data are shown in Figure 5.

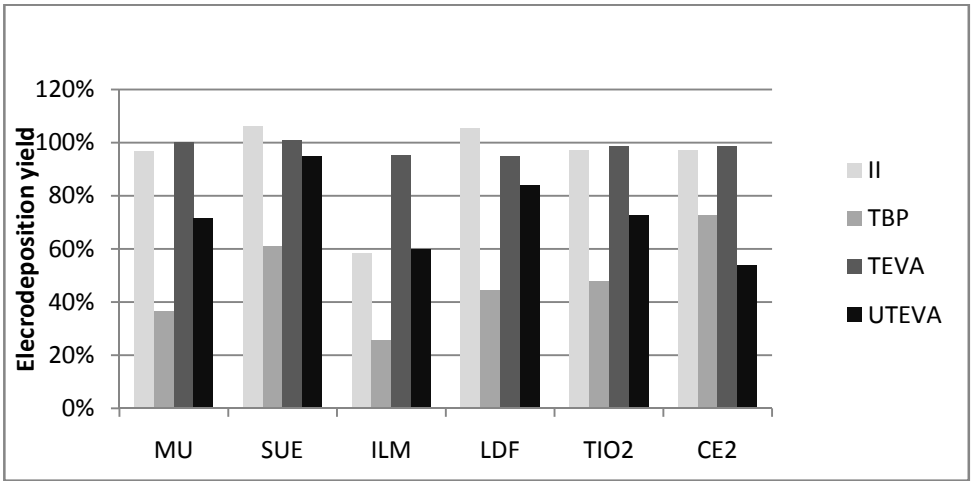

Figure5. *Mean values of the electrodeposition yield when the four radiochemical separation methods are used in the different type of samples. In %.*

Regarding this Figure 5, it can be seen how variables are the results obtained for every type of samples. A multivariate analysis has been carried out looking for a statistical relationship among the traces of chemicals remaining in the solution to be electrodeposited and the electrodeposition yield obtained. This analysis was no significant. So, it can be conclude that this huge variability is related to the physical parameters that can be varied during the electrodeposition process.

Conclusions

The four radiochemical separation methods analyzed: TBP+II-anionic, II-anionic, and specific chromatographic resins type UTEVA and TEVA, work properly and are able to preserve the isotopic equilibrium in the samples. However, the method II-anionic shows more stable results regarding total yield and also standard deviation of the activity concentration values obtained for different aliquots.

It can be also conclude that all the radiochemical separation methods are able to remove more than 90% of chemicals from the solution containing the dissolve sample, regardless of the sample type.

UTEVA resins are those that provide the highest values and II-method, the lowest one, being in any case, higher than 80%.
According to the results obtained it should be stated that all the pre-treatment methods studied: acid attack in on open container, acid attack in a close container, micro wave system and fusion method, are able to dissolve all the thorium contained in the sample.
The II-anionic radiochemical separation method is that which provide the more stables separation yields for the samples analyzed. The other separation methods provide yields that in some cases are higher than II method but more variables depending on samples types. Regarding type of sample, it can be conclude that, being all of them very complexes, uranium ores is that in which thorium is separated with the highest and most stable yields regardless the separation method used.
And finally, results obtained for electrodeposition yields are very variable for all type of samples. There is not a significant statistical relation between this variability and the traces of chemicals remaining in the solution to be electrodeposited. So, it can be conclude that this huge variability is related to the physical parameters that can be varied during the electrodeposition process.

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Acknowledgments

This work was supported by the Spanish Nuclear Safety Council (CSN). Special thanks to research teams from the different Universities involved in this project.