

# Isobars Separation ( $^{137}\text{Cs}$ - $^{137\text{m}}\text{Ba}$ - $^{137}\text{Ba}$ ) from Marine Sediments, in Order to Evaluate Directly Their Radioactive Contamination by Mass Spectrometry

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## Abstract

Marine sediments contamination by fission product  $^{137}\text{Cs}$ - $^{137\text{m}}\text{Ba}$  is a fact since the period 1945-65, when plus than two thousand atomic explosion tests were performed mainly in the southern seas, earth region with minor population density. However, marine flows have produced dissemination of this radioactive pair through the sea bottom all over the world, at different levels, because the sea movement and natural decaying of radioactive pair: parent  $^{137}\text{Cs}$  ( $t_{1/2} = 30.17$  years) and daughter  $^{137\text{m}}\text{Ba}$  ( $t_{1/2} = 2.55$  minutes). Radioactive detection of these contaminants, compared as percentage with that of natural  $^{40}\text{K}$  ( $t_{1/2} = 1.28 \times 10^9$  years, 0.0118% of elementary K) leads to radiation contamination factor (RCF), as one possible unit to measure the radioactive contamination intensity in different regions, as well to determine if there is some other possible source of this contaminant, for example water cooling from power nuclear reactors when it is discharged at sea. However, radioactive detection always implies an unavoidable statistical variation, which makes more difficult to appreciate the changes as function of time and region. But at beginning of this century, mass spectrometry has got impressive advances, which makes it much more precise and sensible than radioactive detection [1]. This paper attempts to measure with other units the radioactive contamination:  $^{137}\text{Cs}$  atoms number per gram of sample, instead radioactivity, which could be more direct and with minor standard deviation than radioactive detection, solving at same time the isobars separation:  $^{137}\text{Cs}$  versus  $^{137\text{m}}\text{Ba}$  plus elementary  $^{137}\text{Ba}$  (11.23% of Ba element).

## Keywords

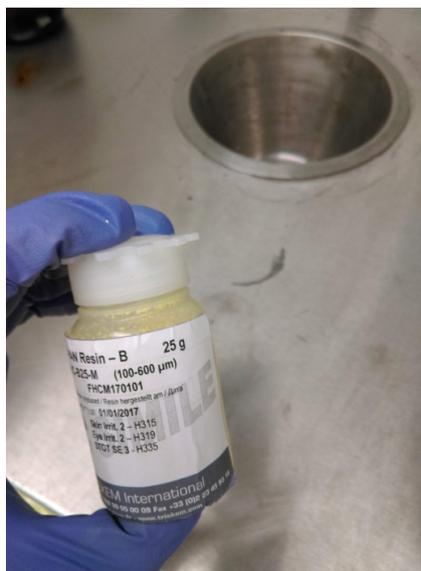
Isobars, Separation,  $^{137}\text{Cs}$ - $^{137\text{m}}\text{Ba}$ - $^{137}\text{Ba}$

## 1. Introduction

Till now, Radioactive Contamination Factor (RCF) has been established by radioactive detection of contaminant product  $^{137}\text{Cs}$ - $^{137\text{m}}\text{Ba}$ , present in marine sediments, in order to compare it with  $^{40}\text{K}$  natural radioactivity as a percentage [2] [3]. This procedure requires to set up about half kilogram of conditioned dry sample in a Marinelli container to be detected either by a NaI(Tl) low background detector during 8 - 12 hours, or to be detected longer time by a HPGe detector. Efficiencies of these procedures have been about 5.6% for  $^{137}\text{Cs}$  and 2.9% for  $^{40}\text{K}$  in NaI(Tl) scintillation detector, and 0.47% for  $^{137}\text{Cs}$  and 0.25% for  $^{40}\text{K}$ , in HPGe detector, basic figures to obtain the RCF, in spite of some high statistical variation, even when detection times were as large as possible. So, this paper describes how one cation exchanger resin allows separating isobars from IA and IIA columns of Periodic Table, corresponding to alkaline and earthy-alkaline metals, to establish only atoms number of radioactive contaminant  $^{137}\text{Cs}$ - $^{137\text{m}}\text{Ba}$ . In order to obtain this result by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), it becomes necessary the previous separation of natural isotope  $^{137}\text{Ba}$  (11.23% of natural Ba), to count only  $^{137}\text{Cs}$ - $^{137\text{m}}\text{Ba}$  atoms with much lower statistical variation than that of radioactive detection.

## 2. Experimental

As cation exchanger was used AMP-PAN cesium resin, ammonium molybdo-phosphate (AMP), embedded in an organic matrix of polyacrylnitrile (PAN), produced by Triskem International Laboratory in Rennes, France (Figure 1). Also possible was to elaborate either zirconium antimonate or zirconium vanadate as cation exchangers [4] [5], but the efficiency proof performed with the first one to obtain 97% - 99% in the final basic solution from a  $^{137}\text{Cs}$ - $^{137\text{m}}\text{Ba}$  acid



**Figure 1.** Triskem International AMP-PAN (ammonium molybdo phosphate embedded in polyacrylnitrile) resin cation exchanger.

solution with known radioactivity was satisfactory enough, obtained by comparing counts per hour from the acid solution and resin after it trapped the radioactive  $^{137}\text{Cs}$  from the initial solution (**Figure 2**), with counts obtained in the final basic solution (97% of  $^{137}\text{Cs}$ - $^{137\text{m}}\text{Ba}$  in solution previously filtrated twice in the resin) (**Figure 3**). To do it, 1 gram of resin was conditioned in 10 ml of  $10^{-5}$  M HCl, and put in the filtration plastic tube as compacted as possible. Then it was filtered through it 20 ml of solution pH = 1.5 ( $^{137}\text{Cs}$ - $^{137\text{m}}\text{Ba}$ , 10 Becquerel). Then the final recovery was performed by 10 ml, 5M  $\text{NH}_4\text{Cl}$ , pH = 9.5 solution. When this basic solution was detected, it was found 97% of counts produced by  $^{137}\text{Cs}$ - $^{137\text{m}}\text{Ba}$  acid solution previously filtered. Nevertheless, it should be considered for this separation, that transient equilibrium established between  $^{137}\text{Cs}$ - $^{137\text{m}}\text{Ba}$  represents one extreme case of different half lives for radioactive parent and daughter, since  $t_{1/2}(^{137}\text{Cs}) = 30.07$  years, while  $t_{1/2}(^{137\text{m}}\text{Ba}) = 2.55$  minutes. As a consequence, the proportion between both decay constants is as great as:

$$\lambda_1(^{137}\text{Cs}) = 0.693/30.07 \times 365 \times 24 \times 60 = 4.385 \times 10^{-8} \text{ min}^{-1} \text{ and}$$


**Figure 2.** AMP-PAN filtration columns to trap  $^{137}\text{Cs}$  from acid solution and exchange it into a basic solution.



**Figure 3.** Activity detection of  $^{137}\text{Cs}$ - $^{137\text{m}}\text{Ba}$  standard acid solution before filtration, and after recovery of radioactive pair in basic solution.

$\lambda_2(^{137m}\text{Ba}) = 0.693/2.55 = 0.272 \text{ min}^{-1}$ . Therefore, the difference between the larger one  $\lambda_2(^{137m}\text{Ba})$  and the smaller one  $\lambda_1(^{137}\text{Cs})$  is negligible:  $0.272 - 4.385 \times 10^{-8} = 0.27199$ , while the quotient between the larger and the smaller one is very great:  $0.272/4.385 \times 10^{-8} = 6.203 \times 10^6$ . So, when this radioactive pair is separated, their radioactive equilibrium ( $A_1 = A_2$ ,  $\lambda_1 N_1 = \lambda_2 N_2$ , where  $\lambda_2 \gg \lambda_1$  and  $N_1 \gg N_2$ ), is recovered in only 3.68 minutes. In this way, if the equation proposed by G. R. Choppin [6], to evaluate either number of daughter or parent nucleus in radioactive equilibrium, as a function of  $\lambda_1$  and  $\lambda_2$ , when half lives of both are in a relation from days to hours (not so great as years to minutes), may be simplified, since the difference  $\lambda_2 - \lambda_1$  is negligible ( $0.272 - 4.385 \times 10^{-8} = 0.27199$ ), and we can consider that:

$$N_2 = \lambda_1 N_1 / (\lambda_2 - \lambda_1) \text{ is the same that } N_2 = \lambda_1 N_1 / \lambda_2 \text{ and } N_1 = N_2 \lambda_2 / \lambda_1$$

As a matter of fact, it is possible to use for this case the simpler equation of radioactive father and daughter in equilibrium:  $A_1 = A_2$ ,  $N_1 \lambda_1 = N_2 \lambda_2$ ,  $N_1 = N_2 \lambda_2 / \lambda_1$ , where  $\lambda_2 / \lambda_1 = K$  (constant value). It means that constant value  $K$  is equal to quotient  $t_{1/2(1)} / t_{1/2(2)} = 0.272 / 4.358 \times 10^{-8} = 6.241 \times 10^6$ .

So, if a number of nucleus are counted by mass number, for the isobaric pair  $^{137}\text{Cs}$ - $^{137m}\text{Ba}$ , will be obtained some number  $R$ , sum of  $N_1 + N_2 = R$ , where  $N_2$  may be replaced by its value  $N_2 = \lambda_1 N_1 / \lambda_2$ , and in such a case  $N_1 + \lambda_1 N_1 / \lambda_2 = R$ , and  $N_1 (1 + \lambda_1 / \lambda_2) = R$ . But if it is considered that  $1 + 6.241 \times 10^6$  is equal to  $6.241 \times 10^6$  for our purpose, then  $N_1 = R / 6.241 \times 10^6$ , which means number of  $^{137}\text{Cs}$  atoms, while  $R - N_1 = N_2$ ,  $^{137m}\text{Ba}$  number of daughter atoms in all cases. Therefore, if it is related the atoms number of radioactive contaminant  $^{137}\text{Cs}$ , with atoms number of natural radioactive  $^{40}\text{K}$ , in order to evaluate the intensity of radioactive contamination in marine sediments, we have to consider that in the extremely remote case the activity of contaminant  $^{137}\text{Cs}$  could reach up that of natural  $^{40}\text{K}$ , the meaning of that unlikely but possible event, should be 2.35 single atoms of  $^{137}\text{Cs}$  related to  $1 \times 10^8$  atoms of natural  $^{40}\text{K}$ , because:

$$\begin{aligned} t_{1/2}(^{137}\text{Cs}) \ll t_{1/2}(^{40}\text{K}) \text{ and } \lambda_1(^{137}\text{Cs}) \gg \lambda_2(^{40}\text{K}). \text{ Consequently, if} \\ A_1(^{137}\text{Cs}) = A_2(^{40}\text{K}), \text{ then } N_1 \lambda_1(^{137}\text{Cs}) = N_2 \lambda_2(^{40}\text{K}) \text{ and} \\ N_1(^{137}\text{Cs}) / N_2(^{40}\text{K}) = \lambda_2(^{40}\text{K}) / \lambda_1(^{137}\text{Cs}) = t_{1/2}(^{137}\text{Cs}) / t_{1/2}(^{40}\text{K}) \\ = 30.07 \text{ years} / 1.28 \times 10^9 \text{ years} = 2.35 \times 10^{-8} = 2.35 / 10^8 \end{aligned}$$

**Time calculation to get the radioactive equilibrium between parent  $^{137}\text{Cs}$  (valence 1), and daughter  $^{137m}\text{Ba}$  (valence 2), after their separation by using ion exchange resins.**

After recovery with a very basic solution (pH = 9.5) the  $^{137}\text{Cs}$  ( $t_{1/2} = 30.17$  years), from the exchange resin, it is estimated the necessary time to get up the radioactive equilibrium with her daughter  $^{137m}\text{Ba}$  ( $t_{1/2} = 2.55$  m). So, if it is named  $N_1$  the number of parent atoms and  $N_2$  the number of daughter atoms,  $\lambda_1$  and  $\lambda_2$  decay constants for parent and daughter respectively, at time zero the sample has only  $N_1$  and no  $N_2$ , but the time starts and  $N_2$  begins to grow up, according the next equation:

$$N_2 = (N_1 - N_1 e^{-\lambda_1 t}) e^{-\lambda_2 t} = N_1 e^{-\lambda_2 t} - N_1 e^{-(\lambda_1 + \lambda_2)t} = N_1 (e^{-\lambda_2 t} - e^{-(\lambda_1 + \lambda_2)t})$$

where the time function  $f(t) = e^{-\lambda_2 t} - e^{-(\lambda_1 + \lambda_2)t}$  determines the daughter  $^{137\text{m}}\text{Ba}$  growing up by the parent  $^{137}\text{Cs}$  decaying, and the first derivative  $f'(t)$  equal 0 means the time when  $N_2$  stops growing and gets the equilibrium with parent, that is to say  $N_1 \lambda_1 = N_2 \lambda_2$  and radioactive equilibrium  $A_1 = A_2$ :

$$f'(t) = -\lambda_2 e^{-\lambda_2 t} + (\lambda_1 + \lambda_2) e^{-(\lambda_1 + \lambda_2)t} = 0$$

$$\lambda_2 e^{-\lambda_2 t} = (\lambda_1 + \lambda_2) e^{-(\lambda_1 + \lambda_2)t}$$

$$\lambda_2 / (\lambda_1 + \lambda_2) = e^{-(\lambda_1 + \lambda_2)t} / e^{-\lambda_2 t} = e^{-\lambda_1 t} = 1/e^{\lambda_1 t}$$

$$e^{\lambda_1 t} = (\lambda_1 + \lambda_2) / \lambda_2 = \lambda_1 / \lambda_2 + 1$$

$$\lambda_1 t = \ln(\lambda_1 / \lambda_2 + 1)$$

$$t = \ln(\lambda_1 / \lambda_2 + 1) / \lambda_1$$

Therefore:

$$\lambda_1 = 0.693 / 30.17 \times 365 \times 24 \times 60 = 4.37 \times 10^{-8} \text{ min}^{-1}$$

$$\lambda_2 = 0.693 / 2.55 = 0.272 \text{ min}^{-1}$$

$$t = \ln(1 + 4.37 \times 10^{-8} / 0.272) / 4.37 \times 10^{-8} = 3.68 \text{ min}$$

### 3. Results

Due to great difference between both radioisotopes: contaminant ( $^{137}\text{Cs}$ ,  $t_{1/2} = 30.17$  years) and natural ( $^{40}\text{K}$ ,  $t_{1/2} = 1.28 \times 10^9$  years), their decay constants are much greater for the minor half life ( $^{137}\text{Cs}$ ,  $\lambda_1 = 0.693 / 30.17 = 2.297 \times 10^{-2} \text{ years}^{-1}$ ) than that of much greater half life ( $^{40}\text{K}$ ,  $\lambda_2 = 0.693 / 1.28 \times 10^9 = 5.414 \times 10^{-10} \text{ years}^{-1}$ ). Therefore, for a given number of nucleus, the radioactivity of contaminant  $^{137}\text{Cs}$  should be much greater than that of natural  $^{40}\text{K}$  for a factor equal to  $4.243 \times 10^7$  times. But fortunately, this has not been the case for any sample examined till now, where the RCF has not surpassed 11.4% [7]. But this light contamination also implies the continue production of  $^{137\text{m}}\text{Ba}$  ( $t_{1/2} = 2.55$  m),  $\gamma$  rays emitter, which decays by isomeric transition to  $^{237}\text{Ba}$ , in mass not appreciable to surpass the natural percentage (11.23%) of this isotope in natural elementary Ba found in marine sediment samples, which could happens with much more appreciable contamination by radioactive  $^{137}\text{Cs}$ . So, to get the contamination by  $^{137}\text{Cs}$  in terms of mass percentage related to one gram of marine sediments, once separated natural Ba and  $^{137\text{m}}\text{Ba}$  from contaminant  $^{137}\text{Cs}$  by capture the  $^{137}\text{Cs}$  from the cation exchanger, after 3.68 minutes radioactivity from parent  $^{137}\text{Cs}$  and daughter  $^{137\text{m}}\text{Ba}$  get the radioactive equilibrium in which  $A_1(^{137}\text{Cs}) = A_2(^{137\text{m}}\text{Ba})$ . But  $N_1 \lambda_1 = N_2 \lambda_2$  implies that  $N_1(^{137}\text{Cs}) = \lambda_2 N_2(^{137\text{m}}\text{Ba}) / \lambda_1$ , and ICP-MS gives us the counts per second obtained only from  $^{137\text{m}}\text{Ba}$  nucleus previously separated of natural  $^{137}\text{Ba}$ , and so  $^{137}\text{Cs} = ^{137\text{m}}\text{Ba} \times t_{1/2}(^{137}\text{Cs}) / t_{1/2}(^{137\text{m}}\text{Ba})$ , both half lives expressed in minutes. Therefore, when number of  $^{137}\text{Cs}$  atoms is compared with Avogadro's number ( $6.02 \times 10^{23}$  atoms) for the molecular weight of it (137 g), we

**Table 1.** Mass of contaminant  $^{137}\text{Cs}$  in Cuban marine sediments, obtained by mass spectrometry.

Sample From	Sample Weight (grams).	$^{137\text{m}}\text{Ba}$ count/sec. (mass. spect.)	$^{137}\text{Cs}$ Atoms number	$^{39}\text{K}$ c/sec. (mas.spect.)	$^{40}\text{K}$ Atoms number	$\text{pg}^{137}\text{Cs/g. sample}$
Nautico	1.0644	$5.98 \times 10^4$	$3.7 \times 10^{11}$	$7.03 \times 10^7$	$8.92 \times 10^3$	79.
Guanabo	1.0103	$2.90 \times 10^4$	$1.8 \times 10^{11}$	$7.63 \times 10^7$	$9.68 \times 10^3$	41
Bibijagua	1.0227	$4.17 \times 10^4$	$2.6 \times 10^{11}$	$1.36 \times 10^8$	$1.72 \times 10^4$	58
Batabano	1.0168	$3.10 \times 10^4$	$1.92 \times 10^{11}$	$5.75 \times 10^7$	$7.30 \times 10^3$	43

obtain the weight of contaminant  $^{137}\text{Cs}$  present in determined mass of sediment sample, per gram when divided by the weight sample. Even when elementary K is separated in the exchanger resin together with  $^{137}\text{Cs}$ - $^{137\text{m}}\text{Ba}$ , and also present in the basic final solution with radioisotope  $^{40}\text{K}$ , it is not possible to obtain the number of  $^{40}\text{K}$  atoms by ICP-MS, because gaseous  $^{40}\text{Ar}$  mass is used to form the necessary plasma where bivalent cations  $^{137\text{m}}\text{Ba}$  are counted by second. Nevertheless, it is quite possible to count  $^{39}\text{K}$  atoms, which have one constant proportion in elementary K equal to 93.22%, and comparing this figure with that of  $^{40}\text{K}$  (0.0118%), it is obtained the number of  $^{40}\text{K}$  atoms present in the weight of marine sediments treated, and responsible of the natural radioactivity in the marine sediment sample. So, **Table 1** shows the results obtained in four samples of Cuban marine sediments, previously detected for  $^{137}\text{Cs}$  radioactive contamination, in order to compare it with natural  $^{40}\text{K}$  radioactivity [7], and at present using mass spectrometry instead disintegrations by time units.

#### 4. Conclusion

Even when cation exchanger AMP-PAN results highly efficient to separate  $^{137}\text{Cs}$  from the marine sediments, and it shows to separate also elementary K, since the characteristic 1.46 Mev peak of  $^{40}\text{K}$  appears in the final basic solution filtered by the resin, the number of  $^{39}\text{K}$  detected by mass spectrometry as counts per second appears to be lower than that obtained by  $^{40}\text{K}$  radioactive detection at known efficiency, comparing 0.0118% as isotope abundance of  $^{40}\text{K}$  with 93% of  $^{39}\text{K}$ . It seems to demonstrate that only a fraction of K much more abundant than contaminant Cs present in the sediment, appears in the final basic solution filtered in the resin. On the other hand,  $^{137}\text{Cs}$ - $^{137\text{m}}\text{Ba}$  mass separation results 97% - 99% efficient, and it allows to calculate directly the mass of contaminant  $^{137}\text{Cs}$  in atoms number as well as  $^{137}\text{Cs}$  ( $10^{-12}$  g) (picograms) per gram of sample.

#### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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