Determination of uranium and polonium in *Sparus aurata* by alpha spectrometry

M. Luna Porres[1], G. Manjón Collado[2], I. Díaz[2], M. Rentería[1], M.E. Montero Cabrera[1*]
[1]*Centro de Investigación en Materiales Avanzados, S.C.,*
Miguel de Cervantes 120, Complejo Ind. Chihuahua, Chihuahua, Chih., México
[2]*Departamento de Física Aplicada II de la Escuela Técnica Superior de Arquitectura,*
Universidad de Sevilla, España.
[*]*Corresponding author: elena.montero@cimav.edu.mx*

Recibido el 3 de junio de 2011; aceptado el 4 de febrero de 2012

The aim of this study was optimizing conditions for the specific activities determination of some uranium-series radionuclides present in *Sparus aurata* by alpha spectrometry. Determinations of specific activities were conducted varying the type of digestion: acid attack on hot plate, controlled microwave digestion and acid attack after calcination of the sample. The latter procedure was applied only to the case of uranium isotopes determination. The variation in the isotope extraction method consisted of applying the techniques of liquid-liquid extraction using Tributyl phosphate (TBP) or chromatographic UTEVA resin. Results depending on the type of treatment given to the samples were compared based on obtained chemical yields. The results reveal a higher bioaccumulation of polonium in the liver sample, with activities of 0.809, 2.495 and 2.439 Bq kg^{-1} fresh wt compared with the fillet. The best chemical yields for polonium were close to 60% for samples that were digested by microwave. In the case of uranium the best chemical yields, close to 80% for fillet, were obtained with a previous calcination of the sample and using the UTEVA resin.

Keywords: Uranium; polonium; alpha spectrometry; fish.

El objetivo de este estudio fue la optimización de las condiciones para la determinación de las actividades específicas de algunos radionúclidos de la serie del uranio presente en *Sparus aurata* por espectrometría alfa.Las determinaciones de las actividades específicas se realizaron variando el tipo de digestión: ataque ácido en parrilla, en microondas y ataque ácido después de la calcinación de la muestra. Este último procedimiento fue aplicado solamente en el caso de la determinación de los isótopos de uranio. La variación en el método de extracción del isótopo, consistió en la aplicación de las técnicas de extracción líquido-líquido utilizando el fosfato de tributilo (TBP) o separación cromatográfica empleando la resina UTEVA. Los resultados obtenidos en los diferentes tipos de tratamientos que se les dio a las muestras, fueron comparados con los rendimientos químicos obtenidos. Los resultados revelan una mayor bioacumulación de polonio en la muestra de hígado, con actividades de 0.809, 2.495 y 2.439 Bq kg^{-1} de peso fresco en comparación con el filete.Los mejores rendimientos químicos para el polonio fueron cercanos al 60% para las muestras que se sometieron a digestión por microondas. En el caso del uranio los mejores rendimientos químicos, cercanos al 80% en filete, se obtuvieron con una calcinación previa de la muestra y el uso de la resina UTEVA.

Descriptores: Uranio; polonio; espectrómetro alfa; peces.

PACS: 91.62.+g; 89.60.-k.

1. Introduction

The importance of studying contamination levels by heavy metals and metalloids (HMM) in the aquatic environment is due to the fact that HMM are bioaccumulative, not biodegradable, and may be easily incorporated into the food chain. This contamination may have serious effects on human health [1,2].

Organisms with metals in their tissues are often used to indicate and quantify the levels of contaminants or their bioavailability in the environment. A bioindicator is an organism that contains information about the quality of the environment; a biomonitor contains information about the quantitative aspects of the quality of the environment [3,4]. In the marine environment different organisms such as oysters, shrimp and fish [5] have been used for contamination monitoring.

Fish are ideal indicators of pollution because they occupy different trophic levels; furthermore, fish samples are of different sizes and ages [1].

The uptake of radionuclides by fish depends on variables such as dietary habits, location, fish physiology and physical-chemical variables such as pH, temperature and water (including the concentration of radionuclides) [6].

The Po-210 enters the human body via inhalation of radon gas Rn-222 and ingestion of food and water, ingestion of food being the major route [7]. Marine biota have been found to contain high concentrations of Po-210, which is considered to be the major contributor to radiation dose received by man (about 0.11 mSv $year^{-1}$) [8, 9]. Therefore, many countries and several international organizations have determined the concentrations of this radionuclide in seafood [7].

The objective of this study was optimizing the procedure for the determination of specific activities of some uranium-series radionuclides present in *Sparus aurata* by alpha spectrometry.

This species was selected for the present study because it is farmed in almost all Mediterranean countries and its size can vary from 20 to 57 cm. These are important factors for

considering it as a possible biomonitor of contamination by radionuclides.

2. Materials and methods

Fish samples were obtained from a local supermarket at the city of Seville in Spain .The target species was *Sparus aurata* (commonly known as "Golden"). Seven fish samples were used for the radiochemical analysis. Fish sizes varied from 26 to 28 cm of length, for not introducing size or age as a variable in our analysis.

2.1. Sample preparation

Before dissection, the samples were washed thoroughly with distilled water and then they were measured and weighed. Subsequently the fish were separated for analysis into three parts: liver, edible fillet and bone; the weights of these three parts were recorded for further calculations. Biological samples were lyophilized for five days to extract the water. Weights were recorded to get the moisture loss and finally, seven samples of each part of the fish were combined and homogenized before the analysis.

2.2. Radiochemical methods and measurement techniques

Samples were subjected to radiochemical analysis of Po-210, U-234 and U-238. The procedures employed were previously described [10, 11]. The standards yield tracers used (from Isotope Products) were Po-209 (Activity=172.7$\pm$5.2 mBq/g) and U-232 (Activity=117.8$\pm$0.6 mBq/g).

Alpha spectrometry with surface barrier silicon PIPS detectors (from CANBERRA) was the method applied to determine the specific activities in fish samples.

General procedure for the digestion of samples is presented in Figure 1.

2.2.1. Polonium determination

A standard yield tracer Po-209 was added in different quantities to fish samples which were digested by microwave or hot plate.

Autodeposition of polonium was done by using ascorbic acid in HCl solution, then solution was heated to 80^{o}C and Powas spontaneously plated onto a rotating copper disc. Po-210 activity was corrected for recovery by comparison with the measured activity of the Po-209 yield tracer.

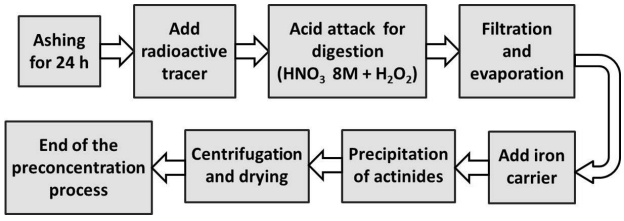

FIGURE 1. General procedure for sample digestion.

2.2.2. Uranium determination

A standard yield tracer U-232 was added in different quantities to fish samples which were digested by calcination or in solution with a hot plate.

The isotope extraction methods applied were liquid-liquid extraction with tributyl phosphate (TBP) and chromatographic UTEVA resin. The isotope extraction methods are based on the method initially developed [12-14].

The mentioned extraction methods are presented in Figures 2 and 3.

Figure 3 shows the flow diagram of uranium and thorium chromatographic separation with UTEVA resin. The digested sample is poured on the resin and then 5 mL HNO_3 3M is added. The extraction method for thorium and uranium is performed sequentially by adding acids solution in concentrations shown by the arrows in step 3 and 4.

Uranium was electrodeposited from the solution on a polished stainless-steel disc, using Hallstadius methods [15]. The cell used for this electrodeposition is made of teflon which prevents the radionuclides from adsorbing on the wall of the cell [10, 15-17].

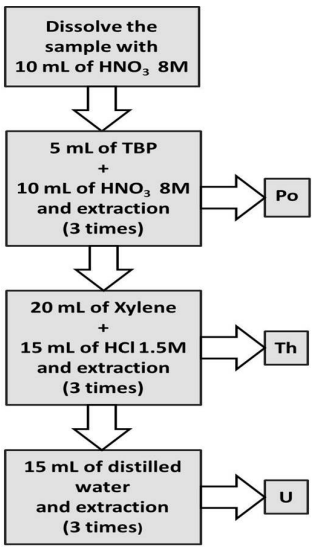

FIGURE 2. Liquid - liquid extraction technique.

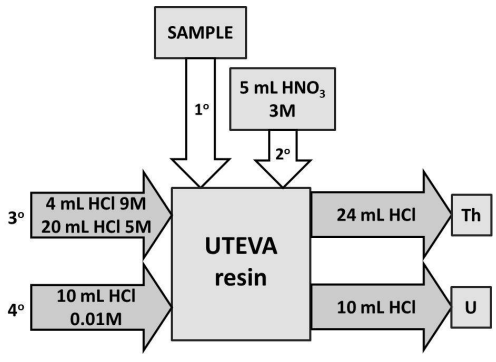

FIGURE 3. Chromatographic separation technique using UTEVA resin.

TABLE I. Po-210 activity concentrations given on fresh weight basis, obtained for different types of sample treatment and different sample tissues. F means fillet and L means liver.

SAMPLES	Po-210 (Bq kg^{-1})	YIELDS (%)	TREATMENTS
S1-F	0.21±0.03	27	Hot plate
S2-F	0.16±0.03	28	Hot plate
S3-F	0.44±0.08	11	Hot plate
S4-F	0.15±0.02	61	Microwave
S5-F	0.12±0.02	62	Microwave
S6-F	0.14±0.02	56	Microwave
S1-L	2.50±0.13	66	Microwave
S2-L	2.44±0.13	60	Microwave
S3-L	0.81±0.11	61	Microwave

3. Results and discussion

The data obtained from the radiochemical analysis of Po-210, U-234 and U-238 in all fish samples are presented on the basis of fresh weight.

3.1. Polonium concentration in fish edible fillet and liver

Figure 4 presents an alpha spectrum of polonium isotopes extracted for a fish sample, showing both Po-210 and tracer Po-209 lines. The data obtained from the radiochemical analysis of Po-210 in fish samples are presented in Table I. It shows that the chemical yields attained for samples digested in hot plate are very low, varying between 11.25% and 28.04%. It was observed a yellowish suspension, suggesting that this procedure does not fully digest the lipids present in the samples, and then it hinder the precipitation process of actinide necessary after digestion. By contrast, microwave sample digestion produced chemical yields about 60%, because digestion of lipids present in the fish sample was almost complete.

Determination of polonium concentration in sea fish muscle in Syria shows concentrations about 0.12±0.01 and 0.13±0.042 Bq kg^{-1} wet weights for the species *Sparus aurata* [7]. Results obtained in the present work for the same species (see Table I are of the same order of magnitude as those reported in [7], particularly for those obtained by microwave digestion procedure. The differences between values reported in the present work and those reported in [7] may be justified according to feeding patterns and concentrations of polonium present in the aquatic environment where fish live.

Polonium in liver samples showed the highest specific activity values (see Table I). This is expected because this organ typically bioaccumulates more polonium [18].

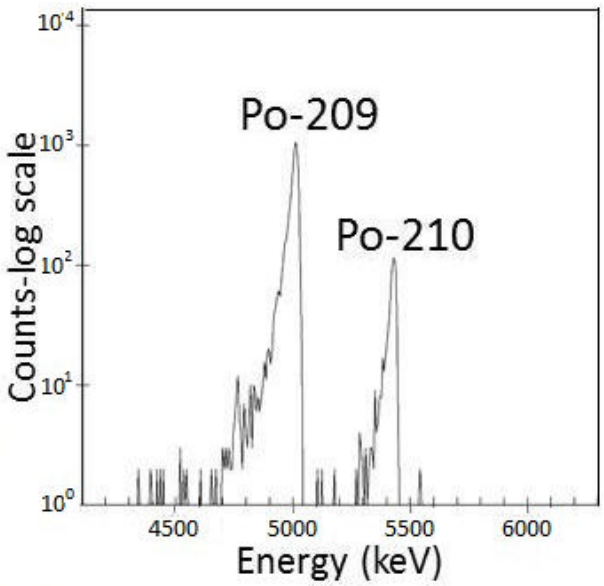

FIGURE 4. Alpha spectrum of polonium isotopes, in logarithmic scale, extracted from a fish liver sample.

TABLE II. U-238 and U-234 activities concentrations, given on fresh weight basis, obtained for different types of sample treatment. **Note:** LD denotes below detection limit = 0.004 Bq/kg.

SAMPLES	U-234 (Bq kg^{-1})	U-238 (Bq kg^{-1})	YIELDS (%)	U-234/U238	TREATMENTS	
S1-F	LD	LD	38.15	-	Hot plate	UTEVA resin
S2-F	LD	LD	25.41	-	Hot plate	TPB
S3-F	LD	LD	10.05	-	Hot plate	TPB
S4-F	0.008±0.002	0.005±0.001	83.96	1.67	Calcination	UTEVA resin
S5-F	0.007±0.001	0.005±0.001	68.62	1.33	Calcination	TPB
S6-F	0.012±0.001	0.008±0.0005	59.73	1.37	Calcination	TPB
S7-F	LD	LD	79.50	-	Calcination	UTEVA resin
S1-B	0.28±0.05	0.74±0.17	10.89	0.38	Calcination	UTEVA resin
S2-B	0.27±0.03	0.57±0.18	3.73	0.47	Calcination	TPB

3.2. Uranium concentration in fish edible fillet and bone.

The data obtained from the radiochemical analysis of U-234 and U-238 in fish samples are presented in Table II. It shows that the chemical yields achieved for samples digested by acid attack on the hot plate are very low, varying between 10% and 38%. By contrast, the calcination of the samples before acid attack for digestion produced chemical yields about 60%, because it ensures the digestion of material that could interfere with uranium determination (see Table II).

In the case of bone samples, it was not possible to achieve good measurements because calcium (very abundant in bones) interfered with the precipitation of actinides. Therefore, developing procedures to avoid interference by calcium is needed for uranium determination in bone.

4. Conclusions

The best alternative for determining uranium in fillet and liver biopsies is the calcination of the samples before acid attack for digestion, followed by UTEVA resin extraction. This is a faster procedure, higher chemical yields are obtained and it ensures uranium measurement in the sample. The best procedure for polonium determination was obtained by microwave digestion. Developing procedures to avoid interference by calcium for uranium determination in bone is suggested.

Acknowledgements

This research has been partially supported by Becas Mixtas CONACYT and the University of Seville, Spain. Authors want to thank C. Solis for suggestions and fruitful discussions.

1. J. Burger, K. Gaines, C.S. Boring, W.L. Stephens, J.Snodgrass, C.Dixon, M. McMahon, *et al.*, *Environmental Research* **89** (2002) 85.
2. X. Wang, T. Sato, B. Xing, and S. Tao, *Science of The Total Environment* **350** (2005) 28.
3. B. Markert, *Journal of Trace Elements in Medicine and Biology* **21** (2007) 77.
4. M.Y. Luna Porres, M.T. Alarcon Herrera, M.E. Montero Cabrera, M.A. Rodriguez Villa, M.R. Villalobos, and E.H. Peraza, *Revista Mexicana de Física* **57** (2011) 40.
5. D. Gay and W. Mahr, *Water Research* **37** (2003) 2173.
6. F.V. Clulow, N.K. Davé, T.P. Lim, and R. Avadhanula, *Environmental Pollution* **99** (1998) 199.
7. M.S. Al-Masri, S. Mamish, Y. Budeir, and A. Nashwati, *Journal of Environmental Radioactivity* **49** (2000) 345.
8. M. Heyraud, R.D. Cherry, H.D. Oschadleus, C.J. Augustyn, M.I. Cherry, and J.C. Sealy, *Journal of Environmental Radioactivity* **24** (1994) 253.
9. R.D. Cherry, M. Heyraud, and A.G. James, *Journal of Environmental Radioactivity* **10** (1989) 47.
10. I. Díaz-Frances, Determinación de 210Po y 210Pb en diversas matrices naturales como base para estudios dosimétricos y atmosféricos, Thesis in: Departamento de Física Atómica, Molecular y Nuclear de la Facultad de Física, Universidad de Sevilla, (2010)
11. A. Aarkrog, M.S. Baxter, A.O. Bettencourt, R. Bojanowski, A.Bologa, S.Charmasson, I. Cunha, *et al.*, *Journal of Environmental Radioactivity* **34** (1997) 69.
12. E. Holm and R. Fukai, *Talanta* **24** (1977) 659.
13. G.J. Ham, *Science of the Total Environment* **173-174** (1995) 19.
14. J.E. Roane, T.A. DeVol, J.D. Leyba, and R.A. Fjeld, *Journal of Environmental Radioactivity* **66** (2003) 227.
15. L. Hallstadius, *Nuclear Instruments and Methods in Physics Research* **223** (1984) 266.
16. R. García-Tenorio, Estudios sobre el método de fechado por 210 Pb y su aplicación en sedimentos, Thesis in: Facultad de Física, Universidad de Sevilla, 1986.
17. A.E. Lally and K.M. Glover, *Nuclear Instruments and Methods in Physics Research* **223** (1984) 259.
18. P. Bustamante, P. Germain, G. Leclerc, and P. Miramand, *Marine Pollution Bulletin* **44** (2002) 997.