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STRONTIUM-90 DETERMINATION IN FISH FROM THE BRAZILIAN COAST

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A radiochemical procedure for low level strontium-90 analysis in fish samples as well as the levels of this radionuclide in fish collected along the Brazilian coast are presented. The method developed was applied in reference samples from the IAEA in order to verify the precision and accuracy of the methodology established. Results obtained for strontium and yttrium yields were about 90%. Strontium-90 levels in fish bones varied from 3 to 12 $mBq.g^{-1}$ Ca and these data are reference values to our country.

INTRODUCTION

The presence of strontium-90 in environmental and biological materials in due mainly to atmospheric nuclear weapons testing, nuclear waste discharges and nuclear accidents. The estimates of input of strontium-90 by fallout into the oceans are of the order of $3.7x10^{2}$ PBq. The inputs to the oceans in the southern

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hemisphere have been half of those in the northern hemisphere. The artificial radionuclide could affect marine organisms and its total activity is only a very rough guide to risks[1,2].

Strontium-90 has a high ecological importance because it accumulates in bone tissues and has long physical and biological half-lives, 28.6 and 49.3 y, respectively. For this reason strontium-90 has been of great interest for environmental and radioecological research.

Determination of radionuclides in environmental samples requires ashing and radiochemical separations. In this work, the method for strontium-90 analysis consisted of strontium leaching from sample ashes and elimination of the magnesium and calcium interference; preconcentration of strontium by using sulfuric acid, removal of the other interferences by ferric hydroxide scavenger, ingrowth of the daughter, separation of strontium-90 from yttrium-90 and β-counting of the yttrium-90 in a low background Geiger-Müller detector.

The strontium yield was determined with strontium-85 tracer, and the yttrium yield was determined gravimetrically. The yttrium-90 purity was verified by decay curves.

EXPERIMENTAL

Strontium-85 tracer

About 400 mg of strontium nitrate was irradiated in the IEA-R1 reactor of the Instituto de Pesquisas Energéticas e Nucleares (IPEN-CNEN/SP - Brazil), at a neutron flux of $10^{12} n.cm^{-2}.s^{-1}$, for 8 h. After the irradiation it was dissolved in water, acidified with concentrated hydrochloric acid and diluted in water to 25 ml.

Fish sampling

Fish were obtained by means of the Coordenadoria para Projetos Especiais - COPESP/SP in Brazilian coast regions. Muscles and bones of the most consumed fish species by local population were taken for the analysis of strontium-90, such as: tainha (Mugil liza) from Belém (00°26'S, 47°49'W) and Itacuruçá (22°57'S, 43°25'W), serra (Scomberomurus brasiliensis) from Recife (08°02'S, 34°51'W) and pescada (Cysnoscium sp.) from Paranaguá (25°37'S, 48°16'W).

Equipment

Gamma-ray spectrometer, high purity Ge detector, type POP-TOP of EG & ORTEC, 20190 model, connected to a IBM-PC microcomputer and associated electronics;

Low background (<0.3 cpm) anticoincidence Geiger-Müller multicounter system GM-25-5, gas flow (99% argon - 1% methane), and high counting efficiency (28% for yttrium-90), from Risoe, Denmark.

Strontium-90 analysis

About 1 to 2 kg of each fish was dried in a muffle at 110 °C for one week. Later on the temperature was gradually increased to 450 °C until ashing. The muscle was separated from bone by using sieves.

About 20 to 50 g of muscle and bone ashes were taken for the analysis. Further, 20 mg of strontium carrier (strontium nitrate) per gram of ash, strontium-85 tracer, 100 ml of 8M nitric acid and drops of hydrogen peroxide were added. The leaching was carried out for 16 h.

The residue was separated by filtration; the retention of strontium was lower than 0.05%. To the superna-

tant, concentrated sulfuric acid (10% of solution volume) was added in order to precipitate strontium and a small amount of calcium and magnesium sulfate.

The strontium sulfate was filtered and converted to carbonate by additon of 1 g of sodium carbonate per gram of ash. The strontium carbonate was dissolved with concentrated nitric acid. Iron carrier (10 mg of Fe) was added and the pH was increased up to 8 in order to precipitate ferric hydroxide. The retention of strontium in the hydroxide was lower than 15%.

To the supernatant, 1 g of sodium carbonate per gram of ash was added, the strontium carbonate was stored for 14 d in order to attain radioactive equilibrium. The separation of strontium-90 from yttrium-90 was carried out in several steps.

Strontium carbonate was dissolved with concentrated nitric acid and yttrium carrier (10 mg of Y) was added. The solution was heated for fifteen minutes. The yttrium was precipitated as hydroxide by addition of concentrated ammonium hydroxide (pH 8). After filtering, the precipitate was dissolved with concentrated hydrochloric acid in the presence of 10 mg of strontium as holdback carrier. The yttrium was again precipitated as hydroxide three times as described here.

Finally, the yttrium hydroxide was dissolved with concentrated hydrochloric acid and 3 ml 1M oxalic acid solution (pH 1.5) was added. The yttrium oxalate was assayed by β-counting. The β-counting obtained for the yttrium-90 precipitate was corrected for build-up and decay of yttrium-90, counter-background, detector efficiency, strontium and yttrium yields and blank value in order to obtain the strontium-90 activity. Analyses of the blank were performed simultaneously with every sample.

Calcium analysis

The determination of calcium in fish bones was done by instrumental neutron activation analysis (INAA). Samples and standards (magnesium nitrate and calcium oxide) were irradiated for 5 min, using a pneumatic station of the IEA-R1 reactor, under a neutron flux of 10^{12} $n.cm^{-2}s^{-1}$. The average of the results obtained for calcium percentage in the fish samples was 30%.

RESULTS AND DISCUSSION

Figure 1 shows the scheme for strontium-90 radiochemical analysis in environmental samples.

Results obtained for the strontium-90 levels in fish bones and muscles are presented in Tables 1 and 2. The strontium yield was higher than 85% and the yttrium yield was above 90%.

Strontium-90 analysis in reference material

The method developed in this work was applied to reference materials from the International Atomic Energy Agency (IAEA), viz. air filter (IAEA-083), marine sediment (IAEA-367) and soil (Soil-6). Results obtained are presented in Tables 3, 4 and 5.

Lower Detection Limit (LDL)

The lower detection limit was calculated for each analysis carried from the following equation[3]:

$$LDL = \frac{4.66 \cdot S_b}{60 \cdot E_Y \cdot R_q \cdot e^{-\lambda t} \cdot m}$$

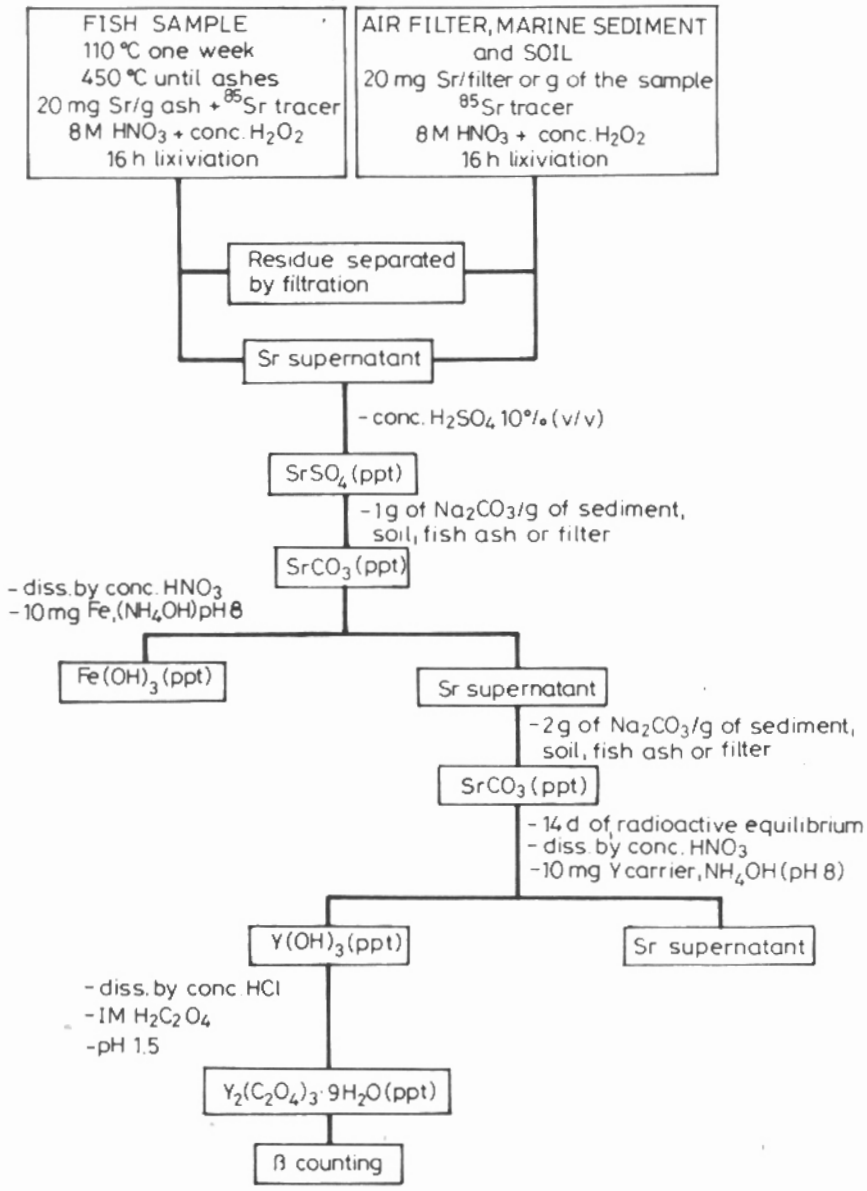

Fig. 1. Scheme for the radiochemical analysis of strontium-90 in fish, air filter, marine sediment and soil samples

TABLE 1

Data obtained in the analyses of Brazilian coast fish bone samples (date of sampling: August and September, 1991)

Fish (specie)	Region	Sr yield, %	Y yield, %	^{90}Sr activity $mBq.g^{-1}$ ash	$mBq.g^{-1}$ Ca
Mugil liza	Belém	90.1 ± 0.8	96 ± 6	8 ± 2	3 ± 1
Scomberomorus bras.	Recife	83.1 ± 0.3	86 ± 5	42 ± 9	12 ± 3
Mugil liza	Itacuruçá	86.4 ± 0.8	94 ± 5	18 ± 7	5 ± 2
Cysnoscium sp.	Paranaguá	90.1 ± 0.8	100 ± 6	42 ± 11	11 ± 3

TABLE 2

Data obtained in the analyses of Brazilian coast fish muscle samples (date of sampling: August and September, 1991)

Fish (specie)	Region	Sr yield, %	Y yield, %	^{90}Sr activity, $mBq.kg^{-1}$
Mugil liza	Belém	92.7 ± 0.7	68 ± 4	75 ± 21
Cysnoscium sp.	Paranaguá	92.7 ± 0.7	99 ± 6	19 ± 7

TABLE 3

Data obtained in analyses of the reference material air filter (IAEA-083)

Air filter (IAEA-083)	Sr yield, %	Y yield, %	^{90}Sr activity, $Bq.filter^{-1}$
(1)	90.0 ± 0.4	85 ± 5	247 ± 38
(2)	96.9 ± 0.6	99 ± 6	219 ± 34
(3)	96 ± 1	91 ± 5	213 ± 32
Mean value and standard deviation	94 ± 4	92 ± 7	226 ± 18
Certified value (Reference date: 01/01/86)			231 (222-241)

TABLE 4

Data obtained in analyses of the reference material marine sediment (IAEA-367)

Marine sediment (IAEA-367)	Sr yield, %	Y yield, %	^{90}Sr activity, $Bq.kg^{-1}$
(1)	85.3 ± 0.5	100 ± 6	100 ± 24
(2)	92.9 ± 0.7	100 ± 6	135 ± 29
Mean value and standard deviation	89 ± 5	100	118 ± 25
Certified value (Reference date: 01/01/90)			102(62-129

TABLE 5

Data obtained in analyses of the reference material soil (Soil-6)

Soil (Soil-6)	Sr yield, %	Y yield, %	^{90}Sr activity, $Bq.kg^{-1}$
(1)	73.1 ± 0.4	97 ± 6	50 ± 11
(2)	81.1 ± 0.3	100 ± 6	41 ± 9
Mean value and standard deviation	77 ± 6	99 ± 2	46 ± 6
Certified value (Reference date: 01/30/83)			30.34(24.2-31.67)

where,

S_b - is the standard deviation of the blank sample;
E_y - is the counting efficiency for yttrium-90;
R_q - is the chemical yield of the process;
m - is sample mass in kilograms or grams of Ca;
λ - is the radioactive decay constant of yttrium-90;
t - is the time of cooling.

TABLE 6

Lower detection limits for strontium-90

Sample	LDL
Fish bone	11.5 $mBq.kg^{-1}$
Fish muscle	2.5 $mBq.g^{-1}$ of Ca
Air filter	0.4 $Bq.filter^{-1}$
Marine sediment	19.9 $Bq.kg^{-1}$
Soil	4.9 $Bq.kg^{-1}$

The results obtained for the lower detection limit (LDL) are presented in Table 6.

The chemical yields obtained for strontium and yttrium were about 85% and 90%, respectively. The elimination of calcium and magnesium was made by using sulfuric acid, based on the difference of solubilities of their sulfates. The strontium is precipitated, while most of the calcium and magnesium remains in solution. The volume of sulfuric acid added is critical in order to minimize strontium sulfate losses by solubility. This method does not require fuming nitric acid, which is an expensive reagent for a monitoring program. It is hazardous for the health and can only be applied where large quantities of samples are required.

The procedure of analysis developed here was applied in reference materials from the IAEA. The results showed good precision and accuracy for the method established. Table 6 gives some data for the lower detection limits of strontium-90, indicating the high sensitivity of the method. The yttrium-90 purity was verified by decay curves. The half-life of this radionuclide in the different analyses performed varied from (67±8) to (75±7) h.

This methodology for strontium-90 determination can be applied in routine analysis and information about levels of this radionuclide for the southern hemisphere are not available.

Strontium-90 levels in Brazilian coast fish varied from 3 to 12 $mBq.g^{-1}$ of Ca for bone and 19 to 75 $mBq.kg^{-1}$ for muscle. These concentrations are typical due to fallout for the southern hemisphere, and are lower when compared to other regions of the world such as Sellafield[4] (230 to 320 $mBq.kg^{-1}$), Baltic Sea[5] (20 to 410 $mBq.kg^{-1}$), Cap la Hague[6] (130 $mBq.kg^{-1}$) and Yellow Sea[7] (370 $mBq.kg^{-1}$), for fish muscles, and Baltic Sea[5] (8.3 to 27 $mBq.g^{-1}$ of Ca), and Japan Sea[8] (2 to 100 $mBq.g^{-1}$ of Ca) for fish bones, these areas being influenced by input from discharges of nuclear reprocessing plants or the Chernobyl accident.

Data obtained in this work are used as strontium-90 reference levels in Brazilian coast fish and in the future any alteration in this value can be attributed to a specific cause. This work is part of a research program that aims at providing technology for reliable assessment of radionuclide contamination, at ensuring the capability of our laboratory to perform strontium-90 analyse in environmental samples and at maintaining a data base of radionuclide levels.

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