

Simultaneous analysis of ^{137}Cs , ^{90}Sr , ^{238}Pu and $^{239+240}\text{Pu}$ in Brazilian seawater

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Methodologies for simultaneous analysis of ^{137}Cs , ^{90}Sr , ^{238}Pu and $^{239+240}\text{Pu}$ were developed and applied to seawater samples. ^{137}Cs levels in Brazilian coastal seawater ranged from 0.12 to 4.7 $\text{Bq}\cdot\text{m}^{-3}$, for ^{90}Sr from 2.0 to 8.6 $\text{Bq}\cdot\text{m}^{-3}$, for $^{239+240}\text{Pu}$ from 0.8 to 4.5 $\text{mBq}\cdot\text{m}^{-3}$ and for ^{238}Pu it was of 1.9 $\text{mBq}\cdot\text{m}^{-3}$. The artificial radioactivity levels in Brazilian seawater are typical values due to fallout deposition.

Introduction

The environmental contamination from radionuclides originating from nuclear weapon tests, dumping operation and nuclear accidents have introduced artificial radionuclides to the environment, in particular, into the marine environment. The radionuclides can be transported across long distances from their emission source.

Considering this problem and the lack of information in our country, methodologies for simultaneous analysis of ^{137}Cs , ^{90}Sr , ^{238}Pu and $^{239+240}\text{Pu}$ were developed and applied to seawater samples. Analysis was carried out in 60 liters of seawater. Radioactive tracers of ^{242}Pu , ^{85}Sr and ^{134}Cs were used to determine radionuclide recovery yields. After precipitation of iron(III) hydroxide, plutonium was separated from strontium and cesium. ^{137}Cs was precipitated using AMP and counted by gamma-spectrometry. ^{90}Sr present in the AMP supernatant was purified by several steps of precipitation (carbonate, sulphate). After the radioactive equilibrium, yttrium was precipitated as hydroxide, further as oxalate and assayed by beta counting. Plutonium-238 and $^{239+240}\text{Pu}$ radionuclides present in the iron hydroxide precipitate were purified by using an anionic exchange column (Biorad AG1X8 resin), electrodeposited and counted by alpha-spectrometry.

The analytical quality control for radionuclide analysis was verified by regular participations in international intercomparison as well as reference material analyses.

Experimental

Equipments

Gamma-ray spectrometer, low background Ge detector, Ortec (GEM60120P model); dual alpha-spectrometer, surface barrier Si detector (Ortec 576, 450RV model); low background anticoincidence Geiger-

Müller multiscaler (GM-25-5 Risøe National Laboratory, Denmark) gas flow, high counting efficiency equipments were used.

Seawater sampling

Seawater samples (600 l) were collected by the Oceanographic Institute (University of São Paulo) from the offshore of southern Brazilian coast (from 24°39'25"S latitude, 41°12'00"W longitude to 29°27'00"S latitude, 46°29'00"W longitude). Samples were stored in polyethylene containers and acidified to pH 1.0.

Radionuclide analysis in seawater

Radioactive tracers of ^{85}Sr , ^{242}Pu and ^{137}Cs were added to 60 liters of seawater as well as cesium (10 mg), strontium (3 g) and iron (200 mg) carriers. Ammonium hydroxide was added to precipitate iron hydroxide. Plutonium remains in the precipitate while cesium and strontium are found in the supernatant.

Plutonium analysis

The iron hydroxide precipitate was dissolved by using 8M HNO_3 , after addition of sodium nitrite, under heating. The solution was loaded onto the conditioned anion exchange column (AG1-X8). Americium was eluted by 8M HNO_3 (80 ml), while thorium, uranium and iron were desorbed from the column by passing through 10M HCl (80 ml). Plutonium was eluted by using 10M HCl (100 ml) in the presence of 0.4 g of NH_4I . Iodine was eliminated by heating of the solution and addition of conc. HNO_3 . The solution was evaporated almost to dryness and 0.3M sodium sulphate solution (1 ml) was added. After evaporation, 300 μl of conc. sulphuric acid was added and plutonium was electrodeposited (pH 1.5 to 2.2, constant current of 1.8 A for 75 minutes) and assayed by alpha-spectrometry. Blank analyses were performed simultaneously to the seawater analysis.

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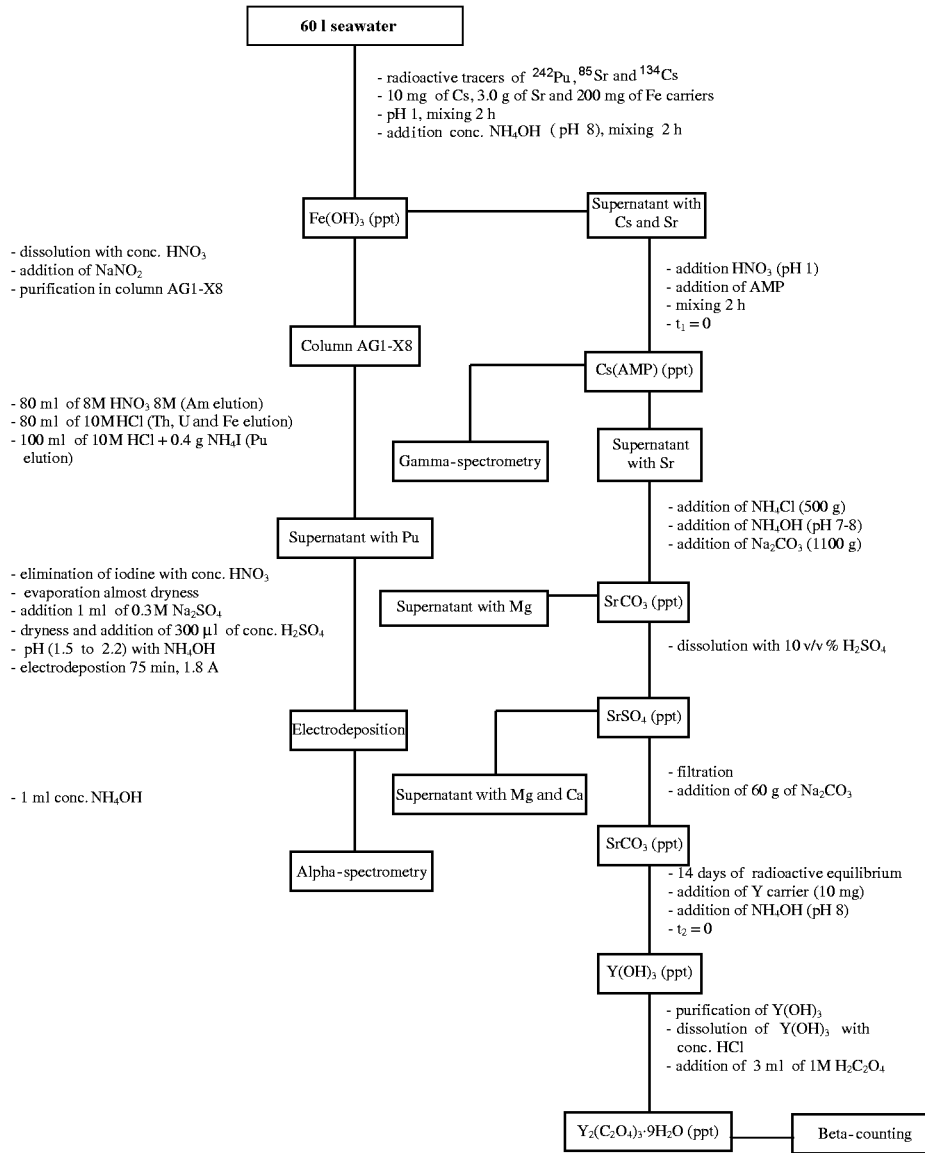


Fig. 1. Simultaneous determination of ^{137}Cs , ^{90}Sr , ^{238}Pu and $^{239+240}\text{Pu}$ in seawater samples

Table 1. Levels of ^{137}Cs , $^{239+240}\text{Pu}$, ^{238}Pu and ^{90}Sr in seawater samples from southern coast of Brazil

Sample	Latitude	Longitude	^{137}Cs , $\text{Bq}\cdot\text{m}^{-3}$	$^{239+240}\text{Pu}$, $\text{mBq}\cdot\text{m}^{-3}$	^{238}Pu , $\text{mBq}\cdot\text{m}^{-3}$	^{90}Sr , $\text{Bq}\cdot\text{m}^{-3}$
1	24°39'25"S	41°12'00"W	<MDC ¹	<MDC ²	<MDC ³	4.7 ± 1.7
2	24°45'05"S	43°29'08"W	<MDC ¹	1.3 ± 7.5	<MDC	<MDC ⁴
3	25°05'04"S	44°50'18"W	1.4 ± 0.8	13 ± 8	1.9 ± 0.8	2.0 ± 0.9
4	27°19'20"S	47°09'00"W	4.7 ± 0.9	3.4 ± 0.2	<MDC	2.0 ± 0.5
5	29°27'00"S	46°29'00"W	4.7 ± 0.5	4.5 ± 0.5	<MDC	8.6 ± 0.2

¹ MDC = 0.12 $\text{Bq}\cdot\text{m}^{-3}$.

² MDC = 0.8 $\text{mBq}\cdot\text{m}^{-3}$.

³ MDC = 0.8 $\text{mBq}\cdot\text{m}^{-3}$.

⁴ MDC = 2.0 $\text{Bq}\cdot\text{m}^{-3}$.

Cesium-137 analysis

The supernatant resulting of iron hydroxide precipitate contains ^{137}Cs , which was preconcentrated using ammonium phosphomolybdate (AMP). The precipitate was decanted overnight, filtered, dried and assayed by gamma-spectrometry.

The gamma-counting consisted of several steps: determination of detector counting efficiency, accumulative countings of both background and seawater samples in regular intervals of counting time and photopeak smoothing.

Detector calibration was performed by means of several gamma-ray emitting radionuclides. IAEA reference materials were employed to determine the detector counting efficiency.

A study of background radiation variation in the region of ^{137}Cs photopeak in function of time was performed by means MAESTRO II software. Background counting was carried out until 250,000 seconds, in intervals of 10,000 seconds, statistical errors are very high for total counting times less than 70,000 seconds.

The same process was repeated for seawater sample. Comparison between the linear regression curves of background and seawater samples allowed the determination of seawater sample activity. For each registered time, the seawater sample countings were discounted from the background countings. Gamma-spectrum was smoothed according to a binomial algorithm, which replaced original data by smoothed data, channel by channel.

Strontium-90 analysis

To the supernatant of AMP precipitate, ammonium chloride (500 g) was added. The pH was increased up to 7–8 (by adding NH_4OH) and sodium carbonate (1100 g) was added to precipitate strontium carbonate. Further, it was converted to sulphate by addition of sulphuric acid (10% v/v). This precipitate was converted to carbonate using sodium carbonate (60 g). The strontium carbonate precipitate was stored by 14 days in order to obtain the radioactive equilibrium. The separation of ^{90}Sr and ^{90}Y was carried out in several steps. The strontium precipitate was dissolved with conc. nitric acid and yttrium carrier (10 mg) was added. Yttrium was precipitate as hydroxide (pH 8.0, NH_4OH), purified by dissolution with conc. hydrochloric acid, and yttrium was again precipitated as hydroxide. This process was repeated for 4 times.

Finally, the yttrium hydroxide was dissolved with concentrated hydrochloric acid and precipitated as oxalate (3 ml of the solution 1M oxalic acid).

The yttrium oxalate was assayed by beta counting. Corrections for building up and ^{90}Y decay, background countings, detector efficiency, strontium and yttrium yields and blank value were employed in order to obtain the ^{90}Sr activity. Blank analyses were performed simultaneously to the seawater analysis.

Results and discussion

Results obtained for radionuclide analyses in intercomparison water samples from USEPA and in solutions spiked with radioactive tracers of radionuclides in study presented good agreement with both certified and information values.

Figure 1 shows the steps employed to the simultaneous analysis of artificial radionuclides in seawater. Table 1 presents the radionuclide levels in seawater samples collected at the southern coast of Brazil. Cesium-137 levels in Brazilian coastal seawater ranged from 0.12 to 4.7 $\text{Bq}\cdot\text{m}^{-3}$, for ^{90}Sr , from 2 to 8.6 $\text{Bq}\cdot\text{m}^{-3}$, for $^{239+240}\text{Pu}$ from 0.8 to 4.5 $\text{mBq}\cdot\text{m}^{-3}$ and for ^{238}Pu it was of 1.9 $\text{mBq}\cdot\text{m}^{-3}$. The minimum detectable concentration values (MDC) for these radionuclides were of 0.12, 2.0, $7.8\cdot 10^{-4}$ and $7.8\cdot 10^{-4}$ $\text{Bq}\cdot\text{m}^{-3}$, respectively.

The concentrations of the radionuclides studied are very low and are typical values due to fallout deposition. The values are lower compared to areas influenced by inputs from discharge of nuclear reprocessing plants or Chernobyl accident. In the literature the reported radionuclide levels are as: ^{137}Cs in Arctic (10 to 15 $\text{Bq}\cdot\text{m}^{-3}$),¹ Baltic Sea (61 to 174 $\text{Bq}\cdot\text{m}^{-3}$),² Northeast of Atlantic (2.8 to 125 $\text{Bq}\cdot\text{m}^{-3}$)³ and Aegean Sea (10 to 118 $\text{Bq}\cdot\text{m}^{-3}$);⁴ ^{90}Sr in Baltic Sea (27 to 64 $\text{Bq}\cdot\text{m}^{-3}$)² and in Black Sea (19 to 22 $\text{Bq}\cdot\text{m}^{-3}$);⁵ $^{239+240}\text{Pu}$ in Arctic (14 to 23 $\text{Bq}\cdot\text{m}^{-3}$)¹ and United Kingdom (0.032 to 8.6 $\text{Bq}\cdot\text{m}^{-3}$);⁶ ^{238}Pu in Arctic (1.5 to 3.0 $\text{Bq}\cdot\text{m}^{-3}$)¹ and Ireland Sea (0.006 to 0.058 to 0.058 $\text{Bq}\cdot\text{m}^{-3}$).⁶

Conclusions

The methodologies described here provide effective methods for radionuclide analysis present in low concentration. Data represent reference values for our country and they will be used to estimate the radionuclide inventory in seawater. These estimations are necessary as a baseline for detection of any future contamination.

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