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DETERMINATION OF FALLOUT RADIONUCLIDES IN SEDIMENT AND BIOTA SAMPLES FROM ANTARCTICA

Ieda I.L. Cunha(1), Adir Janete G. Santos(1), Sandra R.Mattiolo Marchese(2) and Rosalina C. Montone(3)

(1) Instituto de Pesquisas Energéticas e Nucleares C.P.11049, Pinheiros, Sao Paulo

(2) Coordenadoria para Projetos Especiais - COPESP

(3) Instituto Oceanográfico da Universidade de São Paulo

ABSTRACT

In the present work a method has been proposed for determining ^{241}Am, ^{137}Cs and $^{239+240}Pu$ in environmental samples from Antarctic Region. Sediment and biological marine samples were analysed after have been dry ashed. This is a preliminary study and the method also allows to perform sequential determination of uranium and thorium, when necessary.

In order to determine ^{241}Am and ^{137}Cs contents, all samples were submitted to non destructive gamma-ray spectrometry. For the plutonium evaluation it is always necessary radiochemical separation, including steps of sample dissolution, ion-exchange chromatography, electroplating and alpha spectrometry.

1. INTRODUCTION

Radioactive material of technogenic origin, mainly fission products of uranium and plutonium were found in the atmosphere after 1945 due to radioactive waste discharges from nuclear power plants, nuclear tests, nuclear accidents and the disposal of package solid radioactive wastes.

The long lived fission products and the actinide elements including the transuranics play an important role in the environmental aspects of nuclear power production. Nowadays, there is a great concern about the environmental health impact of these elements specially alpha emitters of high potential biological hazards. Some of the most dangerous contaminating elements are ^{137}Cs, $^{239+240}Pu$ and ^{241}Am. Numerous procedures for the determination of these radionuclides have been reported (1-4) and many of them are reviewed in a recent literature (5-7).

The main problems in the artificial radionuclide analysis are related to their low concentration and separation from the matrix.

Depending on the radioactivity level and the matrix to be analysed, ^{137}Cs and ^{241}Am can be determined by gamma-ray counting.

Plutonium analysis requires preconcentratrion and purification procedures before the alpha activity measurement. This is necessary because some natural alpha emitter nuclides have energies close to the nuclides to be measured ($^{239+240}Pu$ and plutonium tracer). Other stable elements may also interfere with the plutonium detection. Lanthanides and iron can be plated as oxides during the electroplating process, forming a layer on the disc, that absorbs the alpha radiation.

In this paper, sediments and biota samples from the Antarctic region were analysed to determine ^{137}Cs, ^{241}Am and the plutonium analysis method was applied for reference samples in order to determine $^{239+240}Pu$. The sampling was carried out at different points of George King Island, Antarctic Region.

The setting up in 1974 of Brazilian station called *"Estação Antarctica Comandante Ferraz" on King George* Island in the region of Admiralty Bay ($62^{o}09'8''S$, $58^{o}28'6''W$) has created conditions for a multidisciplinary research in this area. Only this type of research allows the understanding of the functioning of the ecosystem as a whole

2 - REAGENTS AND EQUIPMENT

- All the reagents used were of analytical grade and the solutions were prepared in deionized water.
- High alpha purity ^{238}Pu was obtained from the Instituto de Radioproteção e Dosimetria, Rio de Janeiro, Brazil.
- An EG&G Ortec alpha spectrometer model 576-A with 450 mm^2 surface barrier detector and 100 um of minimum sensivite

thickness coupled to a CANBERRA 512K multichannel analyser was used for the $^{239+240}Pu$ determinations.
- The gamma spectrometry was performed by using a 15% or a 60% efficiency HPGe Ortec detector with 4K-ADCAM Ortec system plus an AT computer for data acquisition.

3 - ANALYTICAL PROCEDURE

Sample Collection and Site Description

King George is the largest island of South Shetlands with an area of 1338 km^2. Highest elevation of the island is 675 m above sea level. The island is almost totally covered by an average thickness of 100 m of ice with a maximum of 326 m.

Admiralty Bay was the area chosen for our ecological investigations. It is largest bay of the South Shetlands Archipelago. It has a character of a fiord with a branching system of bays. The southern limit of Admiralty Bay is a line between Demay Point and Syrezol Rocks in Bransfield Strait (8). In the northern part of Admiralty Bay there are three branches: Ezcurra Inlet, SW, MacKeller, N and Martel Inlet, NE. The Brazilian Station is located at MacKeller Inlet, as shown in figure 1.

Samples were collected during the period from december 1992 to january 1993, at different points of Admiralty Bay, named Hernnequim, Ullman, Plaza, Ferraz, Refúgio 2, Furmanczyk and Tomas, showed in figure 1.

Samples of bottom sediment, sand beach, moss (Drepanocladus uncinatus) and seaweeds (Desmarestia sp) were collected. Marine sediments were collected at the water-sediment, boundary at several characteristic depths. The sampling was carried out by the Instituto Oceanográfico of São Paulo University.

Sample Pretreatment

The samples were dried at 60°C. After homogenization, sieving and weighing, the samples were transfered to a polyethylene vial for stocking.

Gamma-ray Spectrometry

For the determination of ^{241}Am and ^{137}Cs activities, the samples were measured for 150 ks or more by conventional gamma-ray spcetrometry. The counting system efficiency was determined by means of standards prepared by using Amersham calibrated solutions.

^{241}Am and ^{137}Cs activities were calculated through the peak area divided, by the system efficiency, counting time, sample mass and absolute gamma intensity.

Plutonium Radiochemical Separation

The plutonium separation was carried out as described below.

After addition of plutonium tracer (25 mBq - ^{238}Pu) the samples were dissolved with 8 M nitric acid solution and the organic matter was oxidized by hydrogen peroxide. After centrifugation, the residue was redigested and then discarded. The combined filtrate was evaporated almost to dryness. Ferric hydroxide coprecipitation was carried out by adding ammonia in the presence of chloride ions, followed by dissolution in 8M nitric acid/sodium nitrite and plutonium was purified by an anion exchange chromatography (Dowex 1X8, 100-200 mesh, 8M nitric acid medium, column 10X0.8cm) at a flow rate flux (1 $mL.min^{-1}$).

After the washing steps with 8M nitric acid and 10M hydrochloric acid, the plutonium was eluted with 1.2 M hydrochloric acid and hydrogen peroxide mixture. The final purification was carried out by an anion exchange chromatography (Dowex 1X8, 100-200 mesh, 8 M nitric acid medium, column 5X0.8 cm) and plutonium was eluted with 10M hydrocloric acid-0.1 M ammonium iodide mixture.

Electroplating

The eluate was evaporated almost to dryness in a small beaker and the residue was dissolved with the mixture of 0.3 M natrium sulphate solution and concentrated nitric acid and was heat to neat dryness. After heating the residue was diluted in sulphuric medium. The solution was partially neutralized with ammonia to pH 2.0, using m-cresol purple as indicator, transfered to a disposable polyethylene vial as electrolysis cell by washing with 1% sulphuric acid solution.

Plutonium was electroplated on a polished stainless steel disc (20 mm diameter) at pH 1.9-2.2. The power supply furnished a constant current of 1.0 A for 1.0 hour. The disc was washed with 1 % ammonia and acetone.

Alpha Spectrometry

The electroplated plutonium samples were measured by alpha espetrometry. The average counting efficiency was found as 30% and the alpha resolution for the 5.49 MeV of the ^{241}Am peak wasfound to be approximately 35 MeV.

4 - RESULTS

This method for plutonium analysis was checked only for reference samples from the International Atomic Energy Agency. The results are preseted in table 1 compared with other authors.

TABLE 1: $^{239+240}$Pu analysis

SAMPLE	AMOUNT(g)	TRACER RECOVERY(%)	Bq.Kg^{-1} dry OUR WORK	OTHERS
IAEA-367	0.5	69.6	37.6±4.2	34.4-39.8
IAEA-308	5.29	88.7	0.54±0.06	0.46-0.52
IAEA-134	0.55	85.3	15.7±1.1	16.9+1.9
SAI-29	10.05	63.0	0.048±0.005	-
SAI-36	10.07	55.0	45.1±4.1	48.7

As we can see, our results are in good agreement with other literature values. Also our average recovery ranged from 55 to 90%.

The results obtained for ^{137}Cs in sediments, moss, sand beach and seaweed are summarized in the table 2. The standard deviations were assumed to be of the order 30%, considering the area errors.

By gamma spectrometry it was observed that the ^{241}Am values are very close to the equipament detection limit. Radiochemical separation and alpha spectrometry will be necessary for the americium analysis.

TABLE 2: ^{137}Cs levels in environmental samples from Antarctic Region, Bq.Kg^{-1}

Local	Beach sediment	Bottow sediment	Seaweed	Moss
Refugio 2	0.16	-	1.2	2.9
Plaza	LD	-	1.5	5.4
Thomas	0.24	-	-	4.7
Ullman	0.40	-	0.64	1.4
Furmanczki	0.28	0.68	1.8	3.9
Ferraz	0.49	0.55	LD	2.6
Hernnequim	-	0.94	0.79	-

5 - DISCUSSION

Hidrology and hydrodinamics in Admiralty Bay are influenced by an exchange of waters with Bransfiel Strait, by the inflow of fresh waters from the land and by local processes characteristic for fiord. At the bottom of Admiralty Bay there is an inflow of cold waters of high salinity from Bransfiel Strait (8,9).

Wind is the main meteorological phenomenon in this region; its action is decisive about the course of a great number of processes going on in water and on land. Westerly winds are prevailing. When this occurs part of the water of Bransfield Strait enters Ezcurra Inlet. As a consequence, surface strata have a high nutrient content, higher salinity and lower temperatures (8,10).

It could be expected that the lowest radionuclide levels would be observed near the entrance of the Bay, where the water circulation and frequent strong winds blowing in this area cause intensive mixing of surface waters, which can be cause diversified processes of erosion and/or one difficult accumulation. The cesium can be dilluted and/or removed from seawater before they be incorporated into sediments and biota.

In evaluating the results obtained for cesium it was seen that the highest ^{137}Cs levels are presented in the moss and seaweed samples. This can be explained to the greater transfer factor of ^{137}Cs for these organism types. The same results were obtained for organoclhoride radical determinations (11).

The results here presented are one preliminary evalution. Geologycal transfer factors associated to the collecting sites, can not already satisfactorily explain the data obtained.

So that is important to continue the evaluation of this study in Antarctic region, as well as to carry out other sampling near the entrance of Admiralty bay.

The key to an accurate measurement of ^{238}Pu and $^{239+240}Pu$ by alpha particle spectrometry is to obtain plutonium fraction free from major matrix components such as silica, iron, aluminium, organic matter and other alpha-emitters . The method here decribed is adequate to obtain high decontamination factors for plutonium from all interferences. It requires a precise control over the plutonium oxidation states. Without stabilization, oxi-redction occurs and Pu^{4+} is converted to a mixture of several especies.

The precise and accurate determination of plutonium isotopes also demands the preparation of thin and homogeneous high-resolution sources.

Alpha-sources prepared from sample fractions not adequately separated from interferences will produce spectra with overlapping peaks and will cause degradation of the alpha spectra by self-absortion.

As a general rule, high-resolution alpha-spectrometry requires alpha sources that have absorbing surface density of less than 30 ug/cm^3 (2,12). The resolution of the sources decreases detectably as the amount of absorbing material increases above of 40 ug/cm^2. Electrodeposition losses will occur if the separated final fractions contain more than 100 ug of interferences (1).

The results here obtained for plutonium in the reference samples are in good agreement with the published values and the method is being applied to the same samples already analysed to ^{137}Cs and ^{241}Am.

Considering the lack of basic data on artificial radionuclides in Brazilian samples we consider very interesting in the future to extend this same study to Brazilian samples.

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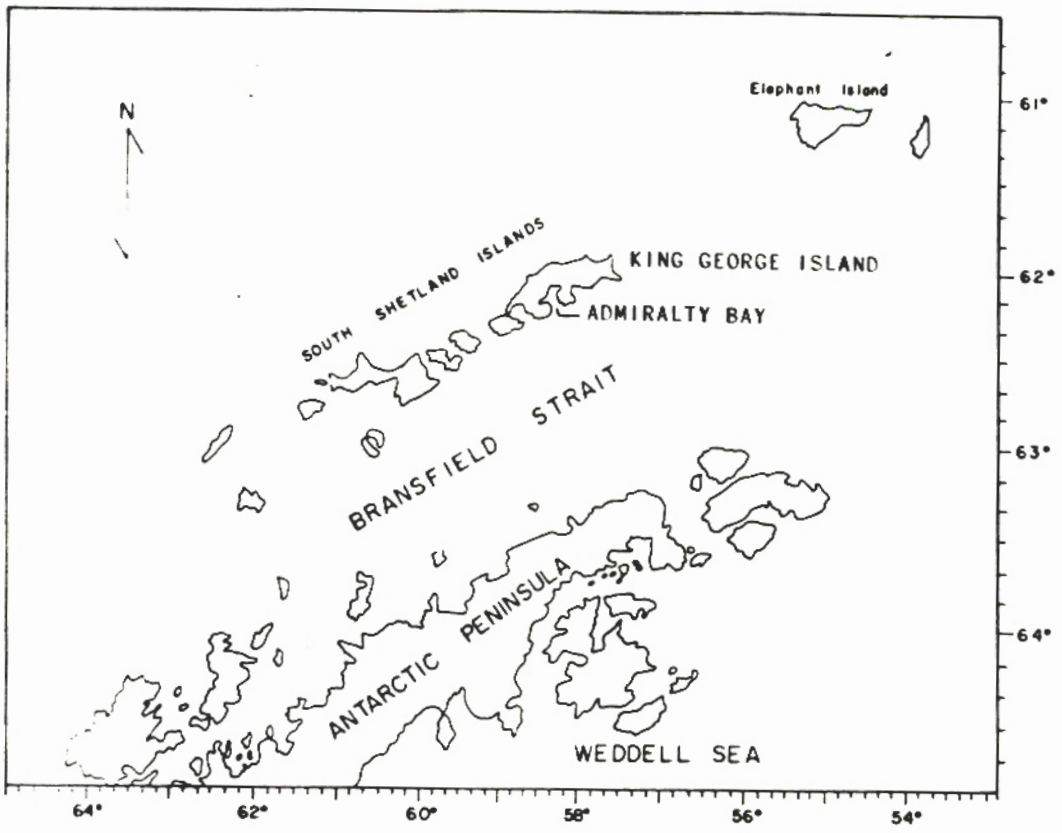
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Elephant Island
SOUTH SHETLAND ISLANDS
KING GEORGE ISLAND
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BRANSFIELD STRAIT
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61°
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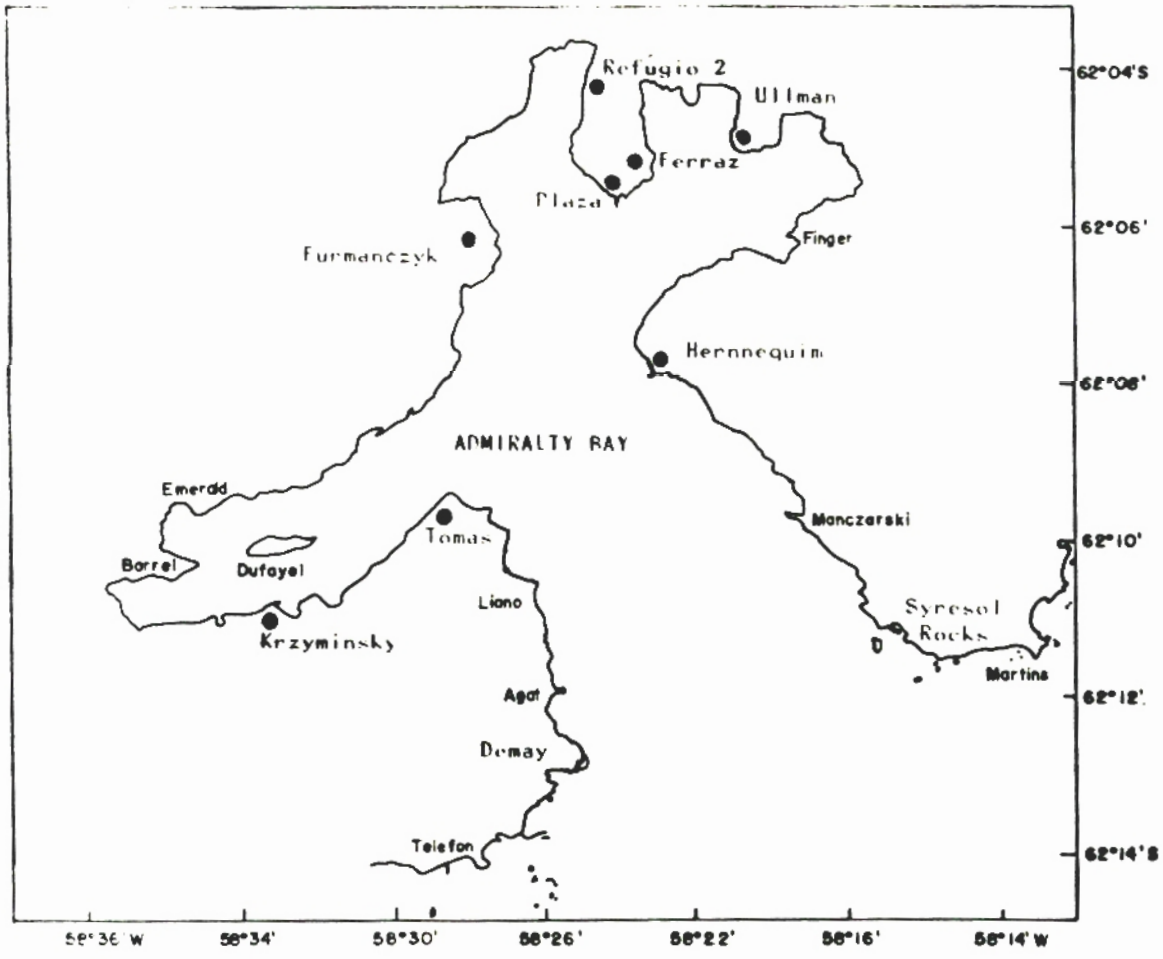
Refúgio 2
Ullman
Ferraz
Furmanczyk
Finger
Hennequin
ADMIRALTY BAY
Emerdd
Tomas
Barrel
Dufayel
Liono
Krzyminsky
Manczarski
Syresol Rocks
Martins
Agat
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62°06'
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62°10'
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