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ANAIS - PROCEEDINGS

## RADIOCHEMICAL DETERMINATION OF CESIUM-137 IN SEAWATER

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## ABSTRACT

Seawater samples were collected from the Atlantic Ocean, in the vicinity of Ubatuba (São Paulo State - Brazil), acidified to pH 1 and stored in polyethylene containers. Cesium was precipitated with ammonium phosphomolybdate (AMP), synthesized in our laboratory. The elements potassium and rubidium present in the seawater are also coprecipitated by AMP and adequate decontamination of the cesium is made by preparing a column by mixing Cs-137 AMP precipitate and asbestos. The interfering elements were eluted with 1.0 M ammonium nitrate solution whereas cesium was eluted with 1.0 M sodium hydroxide solution. Cesium was reprecipitated by acidifying the solution with concentrated hydrochloric acid. The overall chemical yield of cesium was of 75%.

## SUMÁRIO

Amostras de água do mar foram coletadas no Oceano Atlântico na região de Ubatuba (Estado de São Paulo-Brasil), acidificadas em pH 1 e armazenadas em frascos de polietileno.

O césio foi precipitado com o fosfomolibdato de amônio (AMP), sintetizado em nosso laboratório. Os elementos potássio e rubídio presentes na água do mar são também coprecipitados pelo AMP e a purificação do césio é feita preparando-se uma coluna com o precipitado de Cs-137-AMP e asbestos.

Os elementos interferentes foram eluídos com solução de nitrato de amônio 1,0 M enquanto o césio foi eluído com solução de hidróxido de sódio 1.0 M. O césio foi reprecipitado, acidificando-se a solução com ácido clorídrico concentrado. O rendimento químico global do processo para o césio foi de 75%.

## INTRODUCTION

Probably the most important from the radiologically view point and widely dispersed artificial radionuclide in the marine environment is cesium-137 which, together with  $^{90}\text{Sr}$ , has been the subject of the majority of worldwide surveillance programmes.

Considering that cesium-137 is of great significance from the point of view of environmental impact and the lack of information concerning the contamination levels in Brazilian coastal region, it would be relevant to establish a radiochemical procedure for the determination of cesium-137 in seawater.

The determination of this radionuclide presents serious difficulties because of its low concentration and the limit of detection established by counting equipment. It is necessary to preconcentrate cesium from large volumes of water before its determination. There is a wide variety of methods (1-5) for the analysis of the samples, but all follow a similar outline: preconcentration, separation of cesium from interfering elements and sample preparation for counting.

In this work, the steps for preconcentration of cesium from seawater samples with ammonium phosphomolybdate (AMP) and its separation from interfering elements have been systematically studied. Experiments were performed to determine the effects of various chemical variables, such as quantity of AMP, acidity of the solution, settling time on the coprecipitation of cesium as well as the nature and concentration of eluting agents on the adsorption of cesium.

Based on the obtained results, a procedure for determination of cesium 137 in water samples has been proposed.

## EXPERIMENTAL

### Seawater Samples

A series of seawater samples were collected by the Oceanography Institute of the University of São Paulo. Surface seawater samples were collected from the Atlantic Ocean, in the vicinity of Ubatuba, coastal region of the State of São Paulo (45° 6.2' longitude, 23° 30.6' latitude). The samples were collected with appropriate samplers, acidified to pH 1 and stored in polyethylene containers.

In order to facilitate the experiments to establish the best conditions of the analysis, the samples of seawater were purposely contaminated with radioactive tracers of the elements in study.

The chemical yield of cesium in the separation procedure was determined by counting the tracer cesium-134.

### Radioactive Tracers

Cesium-134 was obtained by irradiation of 10 mg of cesium chloride for 8 h at the IPEN-R1 swimming pool reactor.

The potassium tracer (K-40) was obtained by irradiation of 400 mg of potassium nitrate for 8 hours.

In order to obtain rubidium tracer, 10 mg of rubidium chloride was irradiated for 8 hours.

In all the cases, the samples were irradiated at a thermal neutron flux of about  $10^{12}$  n.cm<sup>-2</sup>.s<sup>-1</sup>. After irradiation, the samples were dissolved in water.

#### Preconcentration Experiments

To the seawater samples, known quantities of cesium tracer and cesium carrier (10 mg) were added. The AMP was prepared in our laboratory by the method of Smit et al(6). Variable quantities of concentrated hydrochloric acid and AMP were added to the seawater samples. The solution was stirred during an appropriate time. The precipitate was then decanted. The precipitate was filtered and counted.

The cesium activities were measured using a single channel analyser coupled to a NaI(Tl) detector. The overall amount of the coprecipitated cesium was calculated by comparing its activity with a standard.

#### Interferences

Most radioactive constituents of seawater are separated from the cesium due to the fact that they are not coprecipitated by AMP. However, the potassium and rubidium present in the seawater are partially coprecipitated, and as both these elements contain natural beta emitters (K-40 and Rb-87) adequate decontamination of the cesium must be ensured if the cesium-137 is to be assayed by beta counting. A column containing AMP-asbestos was prepared and used to separate cesium from the interferences.

#### Adsorption Experiments

The cesium-AMP precipitate was mixed with 1 g of asbestos. Columns were prepared by mixing the precipitate of Cs-AMP and asbestos in a beaker and slurring the mixture with 0.1 M ammonium nitrate solution. The mixture was transferred to a glass tube (1.0 cm diameter). The column was washed with 0.1 M ammonium nitrate solution. A number of eluents were tested in order to obtain one which would remove potassium and rubidium from the column without removing the cesium. The solutions were percolated with a flowrate of 60 ml.h<sup>-1</sup>.

During the adsorption and elution procedures, aliquots of the solutions were collected and the cesium activities measured using a single channel analyser coupled to a NaI(Tl) detector. The overall amount of the sorbed or eluted cesium was calculated by comparing its activity with a standard.

#### RESULTS

The coprecipitation of cesium with AMP is related to the volume of solution and amount of AMP. It is necessary, to add 400 mg of AMP per liter of solution, in order to obtain a complete coprecipitation of cesium. For 25 liters of seawater were used 10 g of AMP. In this case, more than 90% of cesium was coprecipitated.

Another important variable is the settling time. For small volumes, the solution was left standing for some hours, while for 25 liters of

samples, the precipitate was decanted overnight.

The possibility of separating cesium from potassium and rubidium has been studied. Experiments in which only one radioactive species was studied, showed that about 10% of potassium and rubidium were retained in the column. These elements were eluted with 1.0 M ammonium nitrate solution. In this condition; 10% of cesium was also eluted. The complete elution of cesium was carried out with 1.0 M sodium hydroxide solution, which too dissolves the AMP. The cesium and the AMP dissolved in basic medium, can be reprecipitated by acidifying the solution with concentrated hydrochloric acid.

Based on the results obtained, a procedure for determination of cesium 137 in seawater samples has been proposed.

#### Procedure for Analysis of Cesium

To 25 L of seawater were added 200 mL conc. HCl and the solution was stirred for 2 h. The carrier (10 mg) and tracer cesium were added to the sample. The AMP (10 g) was added and the solution was stirred for 3 h. The precipitate was decanted overnight.

The supernatant was siphoned to a polyethylene container to the lowest possible level so that the precipitate is not disturbed. It was reserved for strontium analysis.

The precipitate was dissolved with 20 mL of 10 M NaOH. The solution was evaporated on a hot plate until  $\text{NH}_3$  fumes are no longer detected with wet pH paper. Fifteen mL of conc. HCl were added to adjust the solution to pH2. After the addition of 1 g of AMP, the solution was stirred for 10 minutes. The solution was left standing for 4 h. Then, the supernate was discarded.

The cesium-AMP was mixed with 1 g of asbestos. Columns were prepared by mixing Cs-AMP precipitate asbestos, and 15 mL of 0.1 M ammonium nitrate solution. This mixture was transferred to a glass column (1.0 cm diameter). The column was washed with 15 mL of 0.1 M ammonium nitrate solution.

The potassium and rubidium were eluted with 100 mL of 1.0 M ammonium nitrate solution whereas the cesium was eluted with 25 mL of 1.0 M sodium hydroxide solution. The solutions were percolated with a flowrate of  $60 \text{ ml}\cdot\text{h}^{-1}$ .

The cesium and AMP were reprecipitated by acidifying the solution with conc. HCl. The cesium-AMP precipitate was filtered on chimney glass filter then dried for 2 h in the muffle, and counted.

The procedure described above was tested by adding known amounts of cesium-137 activity to water samples. The overall yield of cesium obtained for 6 experimental runs was of 75%, relative standard deviation 3.4%. This radiochemical procedure gives reproducible values of cesium recovery and good decontamination from potassium and rubidium. Due to the high radiochemical purity cesium-137 may be assayed by beta counting.

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