

## DETERMINATION OF CESIUM-137 IN WATER BY ION EXCHANGE

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The preparation of ammonium molybdophosphate (AMP) precipitated directly into the IRA-900 resinous structure and their application to the determination of cesium-137 in waters are described. The sample of water is passed through the resin, which retains the cesium. After the removal of strontium-90 and potassium-40 with 0.1M ammonium nitrate solution, the cesium is eluted with 1M sodium hydroxide solution. The AMP dissolved in the alkaline solution is used to precipitate the cesium by acidifying the solution.

### Introduction

Atmospheric testing of nuclear weapons and nuclear reactor accidents have resulted in widespread distribution in the environment of radioactive fission products. Since long-lived radionuclides are highly hazardous from the point of view of environmental contamination, methods were developed primarily for the determination of strontium-90 and cesium-137.

Determination of these radionuclides in environmental samples presents serious difficulties because of their low concentration and the limit of detection established by counting equipment. For this determination, it is generally necessary to preconcentrate cesium and strontium from large volumes of water and to make the subsequent radiochemical analysis of the concentrate.

In a previous paper<sup>1</sup> we have reported a procedure for determination of strontium-90 in water samples. In this paper we studied the development of a procedure for analysis of cesium-137 in water samples, in the presence of strontium-90 and potassium-40.

Many procedures for determining low concentrations of cesium in water have been studied.<sup>2–6</sup> Since SMITH et al.<sup>2</sup> revealed the ion exchange properties of AMP for cesium, this exchanger has been used for the determination of cesium in environmental samples. The AMP is only obtained as very fine crystals, making it difficult to use

for chromatographic ions separation in columns. Columns with favourable flow rates may be prepared by precipitating AMP into the resinous structure.<sup>4,7</sup>

This paper describes the preparation of a cesium-selective ion exchange resin, with the formation of AMP in the structure of macroreticular anionic resin (Amberlite-IRA-900). The experimental conditions were based on the work of MATSUDA and ABRÃO.<sup>7</sup>

The adsorption behaviour of cesium on the resin was systematically studied. Experiments to determine the effects of various chemical variables such as composition of influent solution, mass of exchanger, flow rate, nature and concentration of eluting agents on the adsorption of cesium were performed.

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

## Experimental

### *Preparation of AMP-IRA-900 exchanger*

The resin employed was macroreticular Amberlite IRA-900. About 15 ml of resin were put into a glass column ( $d = 1.5$  cm). Solution of ammonium molybdate (46 g Mo per liter) was percolated through the column. After washing the column with 50 ml of water, the resin was transferred into a beaker containing 6 g of ammonium monohydrogen phosphate in 30 ml of 7.5 M nitric acid solution. The resin was heated to 60 °C and digested at that temperature for 4 hours with occasional stirring). The AMP-IRA-900 exchanger was washed with distilled water to remove free AMP.

### *Radioactive tracers*

A 2.5 g pellet of  $U_3O_8$  was irradiated for 320 h under a thermal neutron flux of about  $10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$  at the IEA-R1 swimming pool reactor and allowed to decay for 4 months. Cesium-137 used as tracer was separated from irradiated uranium as described by CUNHA and ANDRADE E SILVA.<sup>8</sup>

Cesium-134 was obtained by irradiation of 10 mg of cesium chloride for 8 h. The irradiated sample was dissolved in water.

In order to obtain the strontium-85 tracer, 400 mg of strontium nitrate was irradiated for 16 hours. After irradiation, the salt was dissolved in water.

The potassium tracer ( $^{40}\text{K}$ ) was obtained by irradiating 400 mg of potassium nitrate for 8 hours. The sample was dissolved in water.

In all cases the samples were irradiated at a thermal neutron flux of about  $10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ .



*Adsorption experiments of cesium on AMP-IRA-900 exchanger*

The water samples were purposely contaminated with known quantities of cesium-134 tracer and with cesium carrier (10 mg per liter). The acidity of the sample varied from 1 M to  $10^{-7}$  M in nitric acid.

An appropriate volume of influent solution was poured through the glass column ( $d = 1.2$  cm), containing the exchanger. The mass of exchanger varied from 0.5 to 4.5 g, depending on the volume of influent solution. The solution was percolated with a flow rate of  $60 \text{ ml} \cdot \text{h}^{-1}$ . After sorption of cesium on the exchanger, the column was washed with water. A number of eluents were tested in order to obtain one which would remove the cesium from the exchanger.

During the adsorption and elution procedures, aliquots of the solutions were collected and the cesium activities measured using a single channel analyzer 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 and discussion**

The amount of AMP retained in the IRA-900 resin was determined from a gravimetric method by difference weighing as indicated by BUNZL and SANSONI.<sup>9</sup> It was found to be 1.09 g of AMP per g of IRA-900.

The experimental results obtained for  $\text{HMoO}_4^-$  and AMP amounts retained in IRA-900 resin agree with the theoretical values, which were calculated assuming the composition of AMP to be  $(\text{NH}_4)_3 \text{P Mo}_{12} \text{O}_{40} \cdot 2\text{H}_2\text{O}$  and assuming the molybdenum species retained in the resin to be  $\text{HMoO}_4^-$ .

The exchange capacity of AMP for cesium was determined from the breakthrough curve. The procedure included passing through the column an excess of cesium solution of known concentration containing cesium-134 tracer and determining the activity of the fractions emerging from the column. Assuming the composition of AMP to be  $(\text{NH}_4)_3 \text{P Mo}_{12} \text{O}_{40} \cdot 2\text{H}_2\text{O}$  and all the ammonium ions on AMP should be exchangeable for cesium ions, its ion exchange capacity may then be calculated to be 1.57 m eq/g. The experimental results show that the ion exchange capacity of AMP for cesium was of 0.91 m eq/g of AMP, therefore, only 58% of the ammonium ions have been exchanged for cesium, which indicated the formation of  $\text{Cs}_2 \text{NH}_4 \text{PMo}_{12} \text{O}_{40} \cdot 2\text{H}_2\text{O}$ . This is in agreement with the results obtained by SMITH et al.<sup>2</sup>

The percent adsorption of cesium on the exchanger increases with decreasing pH of the influent solution, and attains 99% at pH 1.0. For solutions of pH higher than 1, the retention is lowered.

The retention capacity of the exchanger is related to the column flow rate. Adsorption of cesium is greater than 95%, with a flow rate of up to  $60 \text{ ml} \cdot \text{h}^{-1}$ .

Another important point is the proportion between the mass of exchanger and the volume of influent solution. It was verified that for influent solution volumes up to 250 ml, 1.5 g of exchanger retains more than 99% of cesium. For 1 liter of charge solution 4.5 g of exchanger is necessary.

Elution of cesium from the resin may be carried out using ammonium nitrate solutions or nitric acid-ammonium nitrate mixtures of various concentrations. Cesium is eluted up to 95% by 5M ammonium nitrate solution or with 3M ammonium nitrate - 1M nitric acid mixture.

The AMP is a precipitate in acid medium and can be dissolved in dilute alkaline solution. This behaviour of AMP was employed to desorb cesium from the resin structure. The most effective eluent for cesium was found to be 1.0M sodium hydroxide solution.

The possibility of separating cesium from strontium-90 and potassium-40 has been studied. The presence of strontium-90 as fallout contaminant, and of potassium-40, the naturally occurring radioactive isotope, will cause interference without appropriate purification. Experiments in which only one species was retained on the exchanger showed that 10% of strontium and 7% of potassium were retained on the resin. These elements can be removed from the exchanger with 0.1M ammonium nitrate solution, whereas cesium is only eluted at more concentrated ammonium salts solutions.

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

#### *Procedure for the determination of cesium-137 in water samples*

Fill a 1.2 cm diameter glass column with 4.5 g of AMP-IRA-900 exchanger.

Add cesium (10 mg) to a 1 liter water sample. Adjust the acidity of the influent solution to 0.1M in nitric acid. Pour the sample through the resin column at a flow rate of  $60 \text{ ml} \cdot \text{h}^{-1}$ .

Wash the column with 200 ml of 0.1M ammonium nitrate solution in order to remove strontium-90 and potassium-40.

Elute cesium from the column with 200 ml of 0.1M sodium hydroxide solution.

Add 200 ml of concentrated nitric acid to the cesium fraction eluted from the column. Heat to  $60^\circ\text{C}$ , digest the precipitate at this temperature for 1 hour, then filter the solution.

Dry the precipitate at  $110^\circ\text{C}$  for 30 minutes. Transfer the cesium ammonium phosphomolybdate precipitate to a glass counting tube. Count the cesium and compare the activity obtained with a standard source of cesium with known absolute activity.



The procedure described above was tested by adding known amounts of cesium-137 activity to water samples.

The exchanger retained 90% of cesium from 1 liter of water. During the removal of the interfering elements 3% of cesium were also eluted. Elution of cesium from the resin was more than 95% with 1M sodium hydroxide solution. After acidifying the eluted cesium fraction in order to obtain cesium precipitate with AMP, the average recovery of cesium obtained for 8 experimental runs was 88%.

The results show that this procedure gives reproducible values of cesium recovery and complete decontamination from strontium-90 and potassium-40.

The analysis of cesium using AMP on chromatographic columns gives better recovery of cesium in comparison with coprecipitation of cesium with AMP.

The AMP-IRA 900 exchanger is easily prepared and has been found suitable for the determination of cesium in water samples.

### References

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