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**NEW TECHNIQUE FOR SYNTHESIZING AMP: PRECIPITATION INSIDE AN
ION-EXCHANGE RESIN AND ITS APPLICATION TO SEPARATION
OF CESIUM FROM FISSION-PRODUCTS AND TO
A ^{137m}Ba GENERATOR**

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ABSTRACT

This work deals with a new technique for synthesizing ammonium molybdophosphate, an inorganic ion exchanger which retains selectively cesium-137 from a mixture of fission products.

Normally the use of this exchanger in column operation requires the use of asbestos, silica-gel or organic polymers as binder, due to its microcrystalline form. The new process employs a strong anionic resin, saturated with molybdate anions. This method enables the precipitation of ammonium molybdophosphate directly into the resinous structure by adding dihydrogen ammonium phosphate in 7,5M HNO_3 . The reactants maintained at 60°C for a period of four hours has been found to be the optimum condition for a maximum yield of this compound (anionic resin-ammonium molybdophosphate = R-AMP).

The tests performed for characterizing this compound are: molybdenum-phosphorus ratio determination, electronic absorption spectra, infra-red absorption spectra, reflection microscopy observations, electron probe micro-analysis and X-ray powder patterns. The mentioned analysis confirmed the presence of the ammonium molybdophosphate in the resinous structure, permitting, thereby, its use as a cation exchanger. R-AMP showed a capacity of 0,48 mE/g of dry material.

The cesium retention studies were made using columns charged with R-AMP compound. The behavior of some polyvalent fission products was also studied. The R-AMP columns was finally applied to separate cesium from irradiated uranium solutions.

A method for the isolation of ^{137m}Ba by successive elutions from R-AMP (^{137}Cs) exchanger (generator) is described.

Several methods for cesium recovery have been proposed based mainly on precipitation, solvent extraction and ion-exchange.

Ion-exchange on organic resins^(5,10) received a great deal of attention, but these exchangers are very susceptible to radiation damage and therefore are unsuitable for processing highly radioactive solutions. So, more recently, the emphasis has been given to mineral exchangers^(6,9,16) and particularly to the development of synthetic inorganic ion-exchangers. Among these compounds a number of insoluble hydroxides and metal salts^(7,8) have been investigated to separate alkali ions. But the most selective exchange properties for cesium was observed with ammonium molybdophosphate^(1,11,12,14). It has been known that ammonium ions in AMP are reversibly exchangeable with alkali ions, specially cesium, and its saturation capacity is comparable to that of organic resins⁽¹³⁾. The main disadvantage is its microcrystalline form, making difficult its use for chromatographic ions separation on columns.

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Column beds of this material would be impervious to fluids. Normally, the application of this exchanger in column operation requires the use of asbestos^(4,14), silica-gel^(2,3) or organic polymers⁽¹⁶⁾ as binders.

This paper describes a new technique for synthesizing AMP to separate cesium-137 selectively from a mixture of fission-products. The process employs a strong anionic resin in molybdate form. This method enables the precipitation of AMP directly into the resinous structure by adding dihydrogen ammonium phosphate. This exchanger was also applied to prepare a ^{137m}Ba generator.

Experimental Procedures

Synthesis of AMP. Precipitation into Strong Anionic Resin as Binder (R-AMP)

The exchanger hereafter marked out as R-AMP was prepared using macroreticular anionic resin, amberlite IRA-900, saturated with molybdate anions. To ascertain the suitable conditions for AMP precipitation inside the resin structure, contact time between resin and $\text{NH}_4\text{H}_2\text{PO}_4$ solution and the temperature of precipitation were studied. The precipitation efficiency was verified by determining the retention percentage of cesium-137 on R-AMP. ^{137}Cs was analysed by gamma counting of 0.662 MeV photopeak of its ^{137}Ba daughter. To a 15 ml of resin, 6 g of dihydrogen ammonium phosphate dissolved in 30 ml of 7.5 M HNO_3 is added. The reactants maintained at 60°C for a period of four hours has been found to be the optimum conditions for a maximum yield.

Cesium Retention on R-AMP

In these experiments, 230 ml of tracer solution of cesium-137 (13300 cpm/ml specific activity total counting) in 2M HNO_3 was passed at a flow-rate of $0.5\text{ ml}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$ through a glass chromatographic column (0.6 cm I.D. and 25 cm long) containing 4 ml R-AMP compound. Cesium sorption on the R-AMP column is illustrated by a typical breakthrough curve shown in Figure 1.

To recover the retained cesium from the column, several eluents containing different concentrations of HNO_3 and NH_4NO_3 were tested (Figure 2). The best elution (95%) was achieved with 10M NH_4NO_3 – 0.2M HNO_3 .

The exchange capacity of R-AMP was also determined using the same procedure and passing 100 ml of 0.2M potassium nitrate. It has been found to be 0.4 mE/g of dry material.

Characterization of the R-AMP Compound

Various analysis to characterize the AMP precipitated into resinous structure were performed:

- molybdenum-phosphorous ratio determination

This analysis was made after destroying the organic materials and determining Mo and P by spectrophotometric methods. The medium value obtained for Mo:P ratio was near to 12:1, characteristic for the $(\text{NH}_4)_3\text{PO}_4\cdot 12\text{MoO}_3$ compound.

- electronic absorption in the ultra-violet region was obtained using a dual beam spectrophotometer. The sample was prepared spreading directly a mixture formed by powdered R-AMP and Canadian balsam diluted into xylene over a cellofane paper sheet. Figure 3 shows the absorption peak at 310 nm which is characteristic of the phosphomolybdate yellow compound.

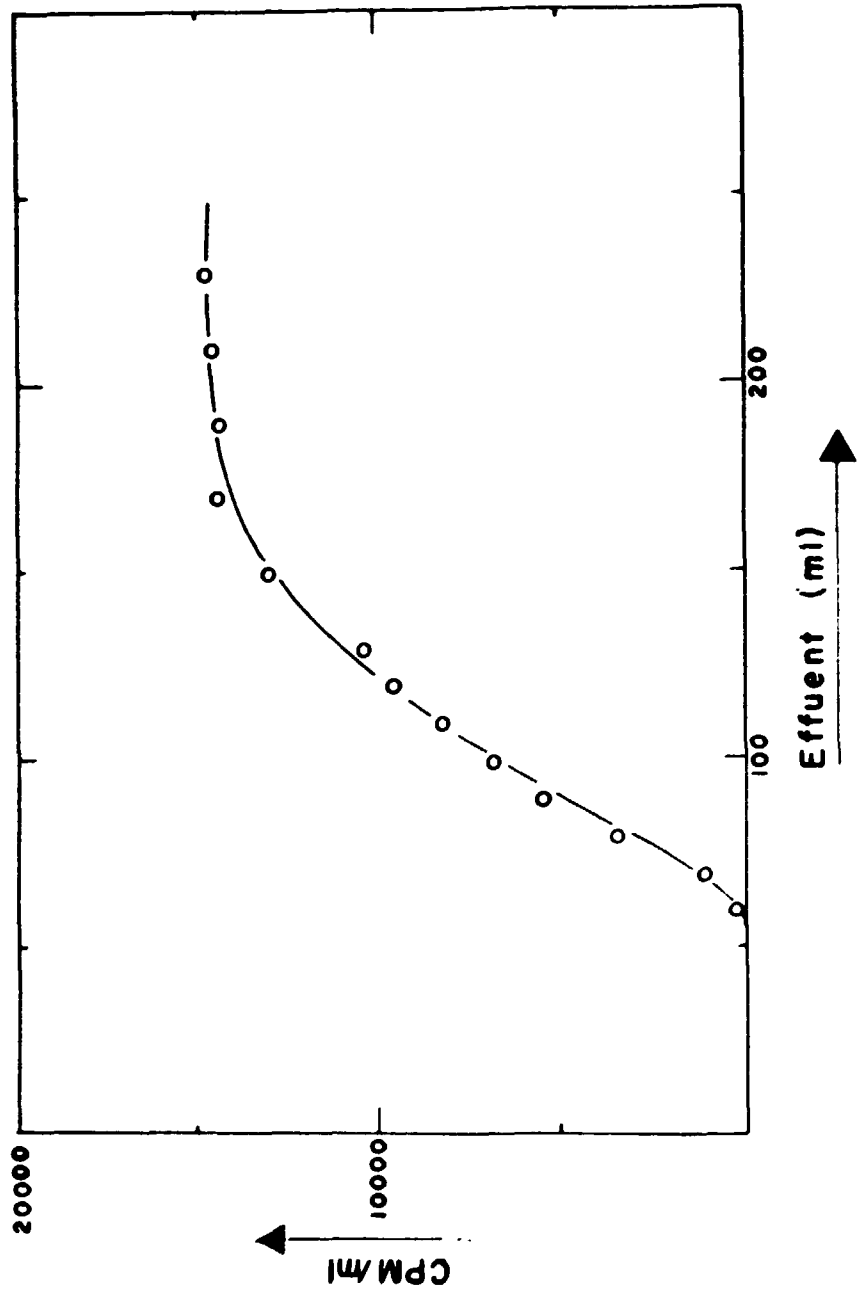


Figure 1 - Break-through curve for cesium-137 tracer in 2M HNO₃; volume of R-AMP: 4 ml

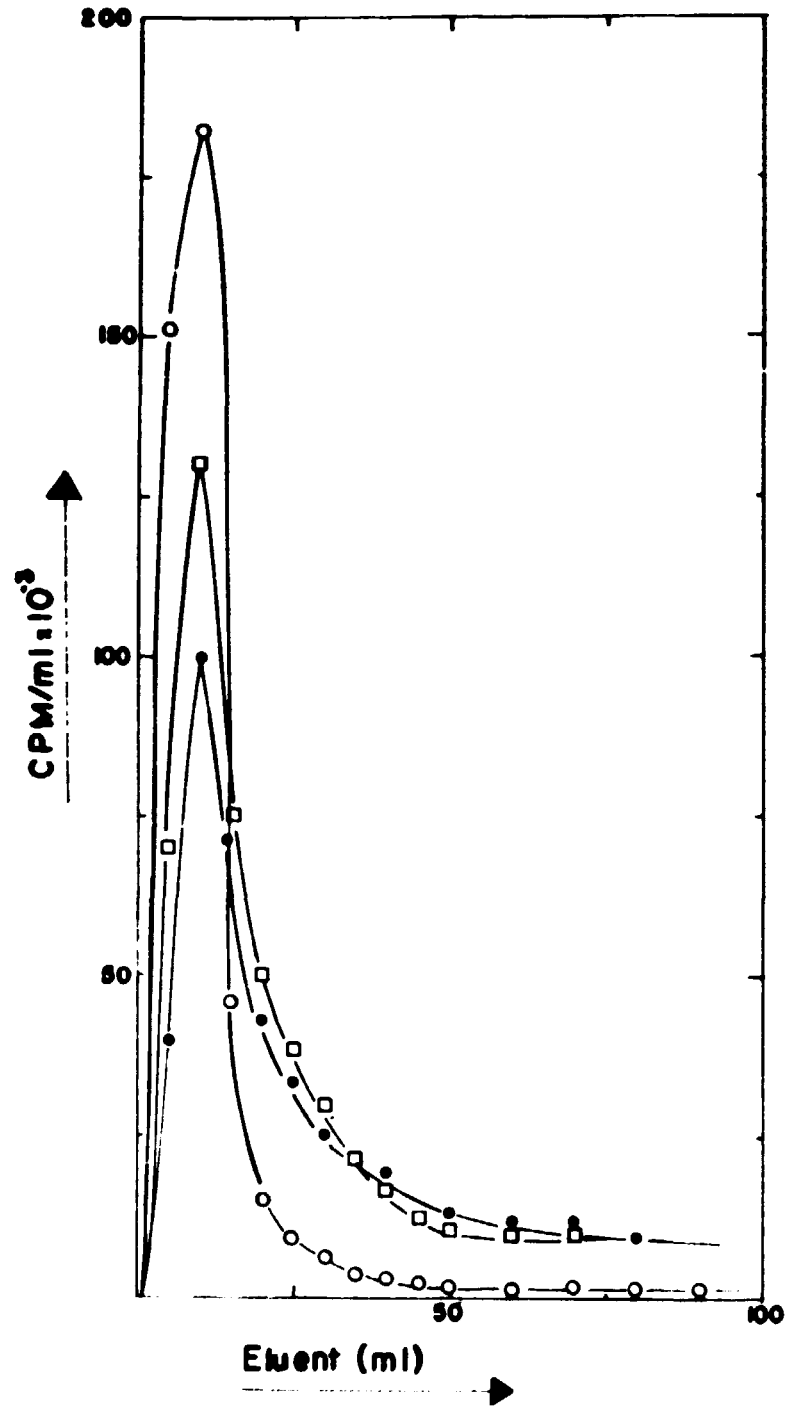


Figure 2 - Elution curves of cesium from R-AMP column. Column: 0.6 cm I. D. x 25 cm, with 4 ml of R-AMP; ○ 10M NH₄NO₃ - 0.2M HNO₃; □ 3M NH₄NO₃ - conc. HNO₃; ● 3M NH₄NO₃ - 3M HNO₃

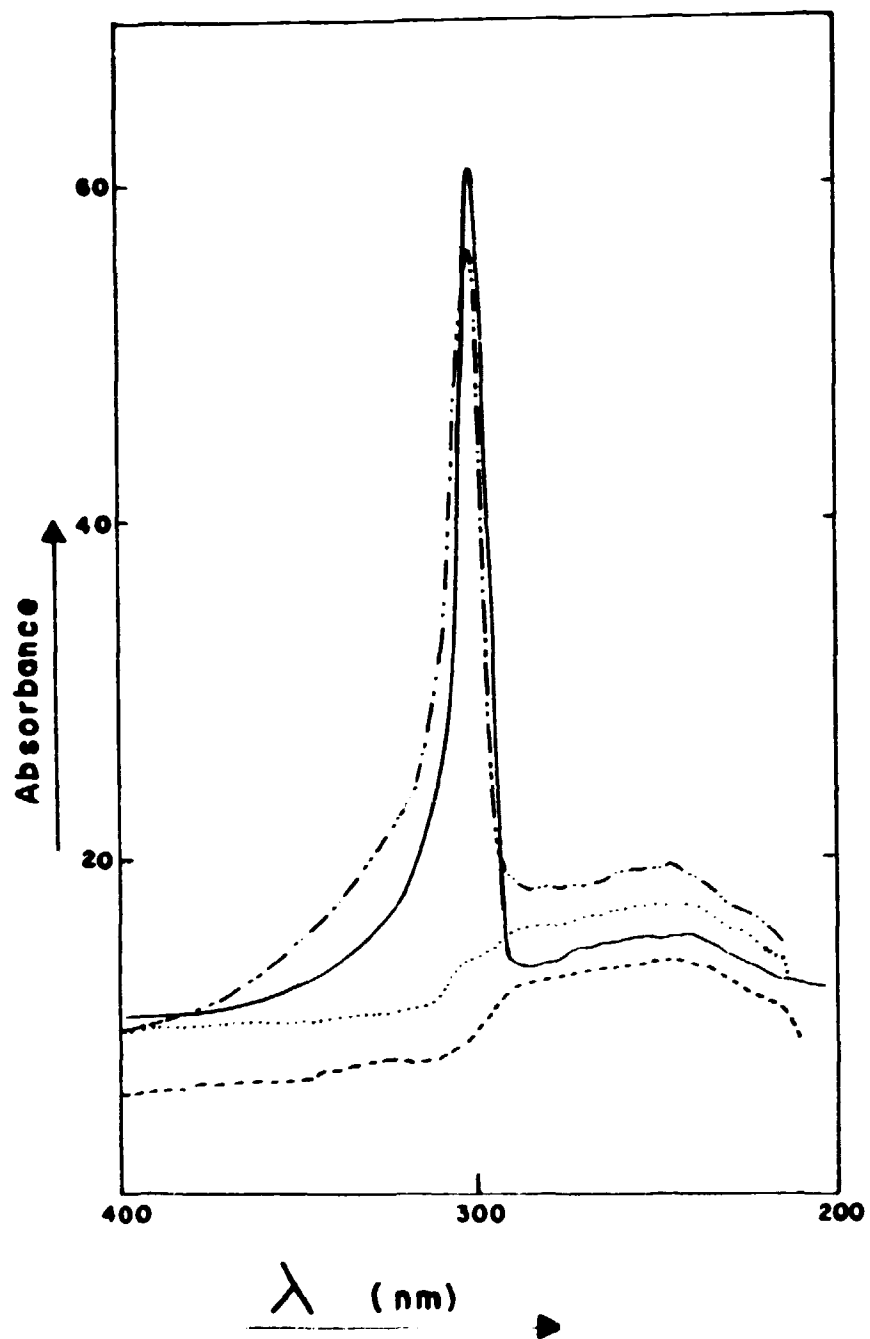


Figure 3 - Electronic adsorption spectra; — R-AMP; - - - AMP powder; - · - · resin in molybdate form; ····· resin in nitrate form

– reflection microscopy observation

The sample was prepared impregnating the compound over a lucite support by compactation until 150°C is reached. After cooling, the sample was polished and the micrography was obtained using metallographic microscopy. These micrographies showed the different patterns among resins in nitrate and molybdate forms and after AMP precipitation as well.

– electron probe microanalysis

This method allows to obtain the P and Mo distribution inside the resinous structure by their characteristic radiations, PK α_1 and MoL α_1 (Figure 4) using the same sample used for the reflection microscopy analysis.

Applications of R-AMP Exchanger

The R-AMP column was applied to selectively retain cesium-137 from a mixture of fission-products as well as to prepare a barium-137m generator.

In order to study the cesium-137 recovery from fission-products mixture the behavior of some long-lived polyvalent products as ruthenium and rare-earths represented by europium was studied. Those elements showed a moderate retention on R-AMP column from 2M HNO₃ medium and their decontamination was obtained by washing the column with 1M HNO₃. In other experiments, 10 g U₃O₈ pellets were irradiated at IPEN reactor (MTR type) for 6 months. After 180 days cooling time, the pellets were dissolved with HNO₃. The solution was then adjusted to 3M HNO₃ and uranium extracted with TBP 30%-varsol v/v. To minimize the interference of elements such as Zr-Nb, the raffinate was treated with oxalic acid to complex them. The resulting solution was percolated through a R-AMP column to retain cesium-137. The final decontamination was obtained by washing a column with dilute H₂C₂O₄ and HF (Figures 5 and 6).

Generator systems for barium-137m were developed based on the very high affinity of long-lived parent ¹³⁷Cs for AMP exchanger and weak retention of short-lived daughter ^{137m}Ba. The experiments were developed fixing the cesium-137 on R-AMP column from nitric acid medium. The column was then washed with 1M HNO₃ and after secular equilibrium has been achieved, ^{137m}Ba was easily eluted with 0.1M or 0.3M HNO₃. The half-life determination of eluted ^{137m}Ba showed a low contamination of cesium-137 due to slight dissolution of the AMP. In order to determine the solubility of AMP and R-AMP in dilute acid medium, some experiments were done. These data revealed that the solubility increases with increasing contact time and it is higher at room temperature (~ 25°C) than at 0°C. The solubility of the AMP alone is higher than the AMP retained into the resin (R-AMP). Based on those properties a reliable generator system was obtained using a column containing ¹³⁷Cs charged on R-AMP at the upper portion of the column over a small amount of free R-AMP at the bottom to retain any cesium eluted with ^{137m}Ba. Successive elutions made with a 0.1M – 0.3M HNO₃ at ~ 10°C gave ^{137m}Ba completely free from the parent. It is recommended to keep the generator column inside a normal refrigerator (~ 10°C) when not in use.

Conclusion

Several AMP precipitation experiments on macroreticular anionic resin allowed to conclude that the best condition to synthesize this exchanger is at 60°C with four hours reactants contact time, the maximum yield of R-AMP being attained.

Analysis performed to characterize this exchanger confirmed the presence of AMP into the resinous structure, permitting thereby its use as cation exchanger. The R-AMP showed a capacity of 0.4 mEq/g of dry material.

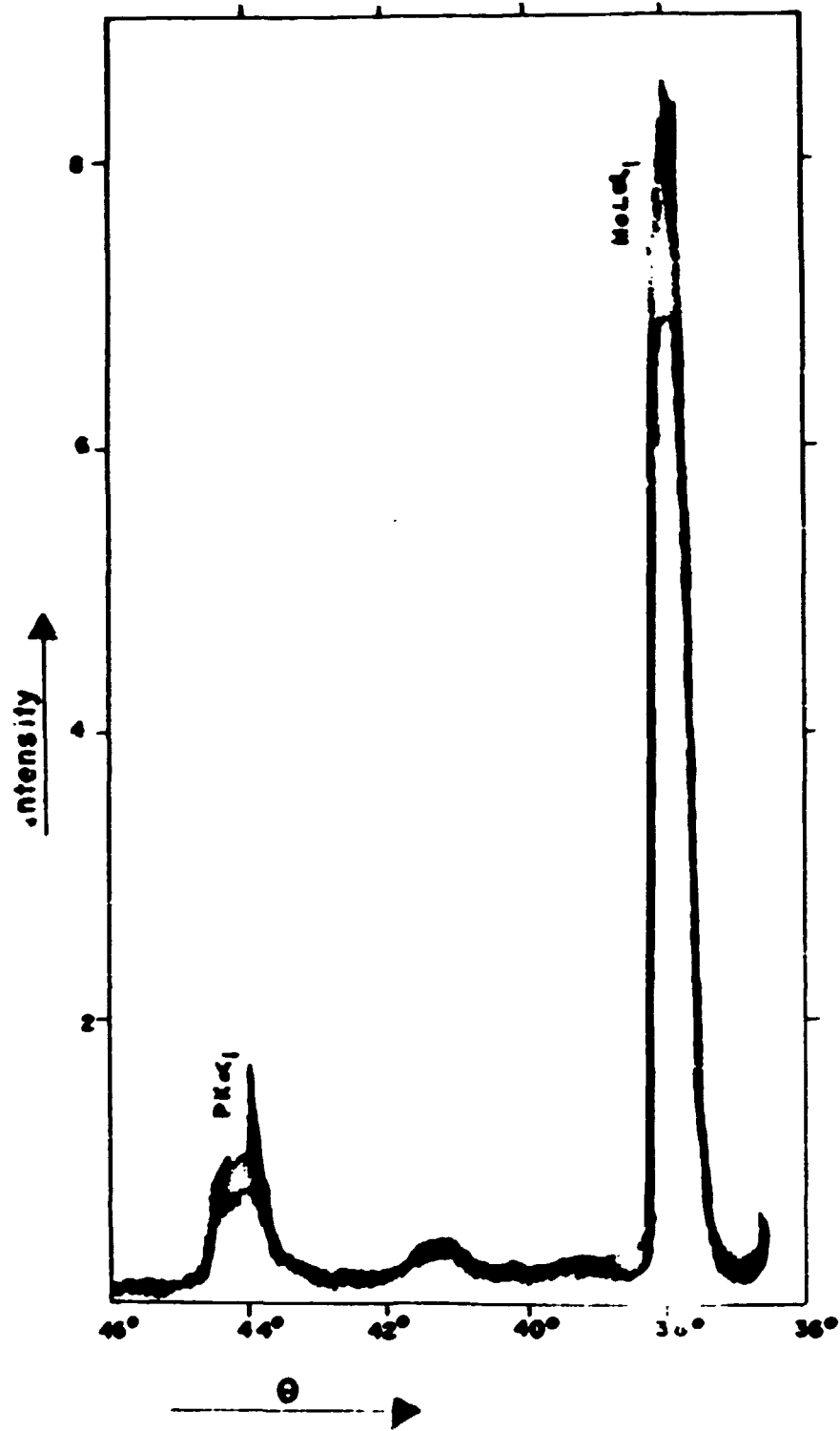


Figure 4 - Molybdenum and phosphorous characteristic radiations of R-AMP compound

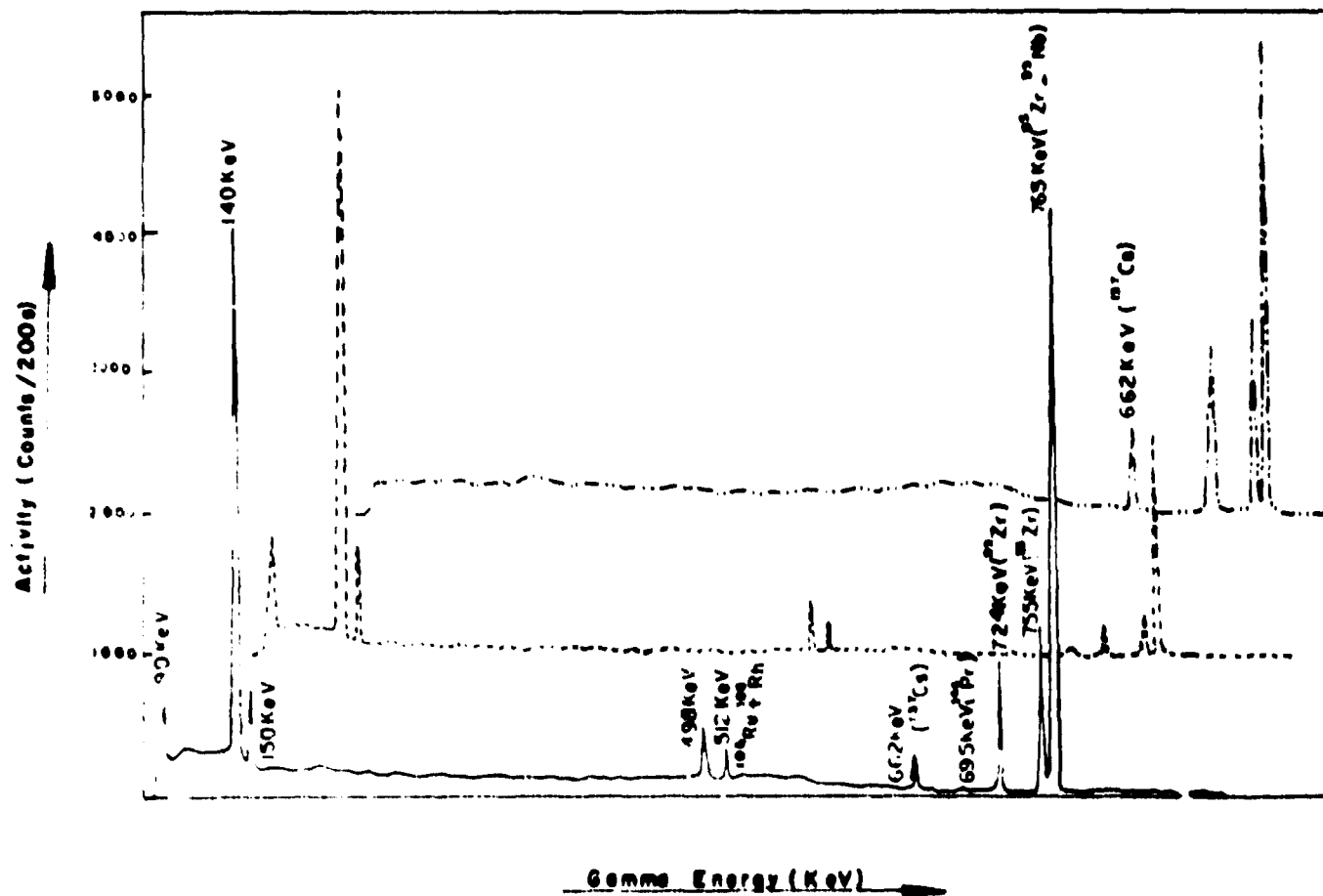


Figure 5 - Gamma-ray spectra showing cesium-137 retention from irradiated uranium solution on R-AMP column. Ge(Li) detector; ——— feed; irradiated U solution 1 ml (x 1); - - - - - effluent 1 ml (x 1); - . . . - . - charged R-AMP - 2 ml (x 4)

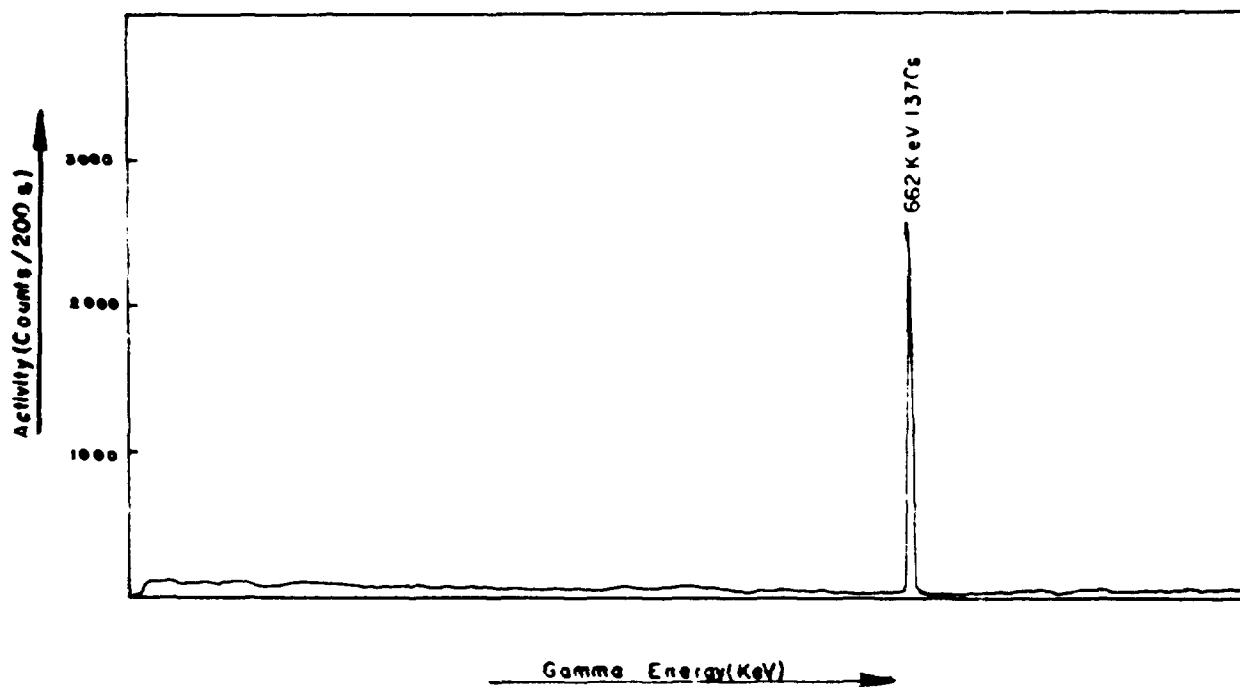


Figure 6 – Gamma-ray spectrum of radiochemically pure ^{137}Cs separated directly from an irradiated uranium solution with the aid of R-AMP column. Ge(Li) detector

The R-AMP is being successfully applied for the selective retention of cesium-137 from a mixture of fission-products. Among these, only ^{95}Zr - ^{95}Nb showed an appreciable retention on R-AMP column but they were easily decontaminated using oxalic or hydrofluoric acid as complexing agents.

Using a R-AMP (^{137}Cs) column a reliable $^{137\text{m}}\text{Ba}$ generator for many successive elutions was set up.

RESUMO

Apresenta-se neste trabalho uma nova técnica de preparação de fosfomolibdato de amônio, um trocador inorgânico útil à retenção seletiva de césio-137 de produtos de fissão. Devido a sua estrutura microcristalina, a utilização deste trocador em operações de coluna requer, normalmente, o uso de suportes como asbestos, sílica-gel e polímeros orgânicos.

O novo processo consiste no emprego de uma resina aniônica forte na forma molibdato, permitindo a precipitação de fosfomolibdato de amônio no interior do grão, mediante a adição de fosfato monobásico de amônio em ácido nítrico 7,5M. Obteve-se a melhor precipitação à temperatura de 60°C com um tempo de contacto de 4 horas, utilizando-se como suporte resina aniônica forte macroreticular, Amberlite IRA-900. O trocador formado nestas condições apresentou uma capacidade de troca de 0,48 mE/g e 100% de retenção de césio-137 de soluções 2M em HNO_3 .

Obtido o trocador num suporte compatível com o seu emprego em colunas cromatográficas, realizaram-se algumas análises de caracterização do composto: determinação da relação Mo:P, espectro eletrônico, espectro de absorção no infravermelho, diagrama de raios-X, análise por microscopia de reflexão e análise por microsonda eletrônica, confirmando a presença de fosfomolibdato de amônio na estrutura do grão da resina.

Estudaram-se, em seguida, as melhores condições de retenção de césio em coluna de R-FMA, hem como sua eluição. Foram igualmente investigadas as contaminações de alguns produtos de fissão polivalentes, tais como rutênio, terras raras e zircônio na sorção de césio-137 em coluna de R-FMA, em meio ácido. Aplicou-se este trocador na recuperação seletiva de césio-137 das soluções de urânio irradiado.

Destaca-se ainda a aplicação do R-FMA na preparação de uma fonte geradora de $^{137\text{m}}\text{Ba}$ (2,6 min), de importância didática na determinação de meia-vida.

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