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भारत सरकार  
GOVERNMENT OF INDIA  
परमाणु ऊर्जा आयोग  
ATOMIC ENERGY COMMISSION

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USING PHOSPHOTUNGSTIC ACID

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## 1. INTRODUCTION

Caesium-137 is one of the major isotopes of long half-life which are formed in high yields as a result of nuclear fission of uranium-235. This fission product is of particular interest because of its valuable applications and is extensively used in interstitial and intracavitary therapy and in teletherapy units<sup>(1-6)</sup>. In several kilo curie quantities caesium-137 is widely used as irradiation sources for the preservation/pasteurisation of a wide variety of food materials and fruits, vegetables etc.<sup>(7-8)</sup>. The fact that caesium-137 requires substantially less shielding than cobalt-60 is specially advantageous in mobile irradiators.<sup>(9,10)</sup>

Several methods have been reported in literature for the separation and subsequent purification of caesium in different countries. Methods used generally are co-crystallisation<sup>(11)</sup>, solvent extraction<sup>(12)</sup> and precipitation<sup>(13,14)</sup> techniques. The choice of a particular method depends mostly on the nature and composition of the reprocessing waste solutions and on the operational facilities readily available.

With regard to the precipitation techniques, a number of reagents have been reported for the separation of caesium. These include sodium tetraphenyl boron, nickel ferrocyanide, chloroplatinic acid and phospho -tungstic acid<sup>(15)</sup>.

In the case of sodium tetraphenyl boron, the precipitate obtained is extremely fine and does not settle easily. Further, the

precipitation should be carried out at 0.1 - 0.2 M. nitric acid solutions. The method works efficiently only at pH values  $\sim$  0.5 which would involve considerable dilution of the original waste solution.

Separation of caesium with nickel ferrocyanide works efficiently only at pH 4-8 which again would necessitate the dilution of the reprocessing solutions.

In addition, all these methods would lead to contamination of the product with those fission products which are precipitated in the pH range 2-4 and also with iron and aluminium. Further, the removal of nitric acid from the concentrated fission product solution demands an additional handling step such as treatment with formaldehyde, sugar, etc. to decompose the acid. In addition, the cost of most of these reagents is highly prohibitive for use in large scale separations.

Phosphotungstic acid which is comparatively cheap has the advantage that it selectively precipitates caesium even from 2-4 M nitric acid solutions. This report deals with the precipitation of caesium as caesium phosphotungstate from fission product waste solution in acid medium and its subsequent purification. In an earlier attempt this procedure was used at Saclay for the separation of caesium and subsequently abandoned<sup>(16)</sup>. In this case, the precipitate of caesium phosphotungstate obtained was dissolved in baryta to convert the phosphate and tungstate into insoluble barium salts and caesium was left in the filtrate as hydroxide. This method has the draw back that it involves multiple precipitation techniques which makes its remote operation more complicated. Moreover, the action of atmospheric  $\text{CO}_2$  on baryta affects the efficiency of the process and necessitates

the use of deaerated reagents and if necessary, carrying out the reaction in an inert atmosphere.

The separation of phosphate and tungstate by anion exchange on De-acidite FF has been reported earlier<sup>(17)</sup>. However, the serious limitation for the use of organic resins in any unit process of ion exchange is their instability in the presence of high doses of ionising radiation. Changes in capacity, selectivity, rate of exchange and resin breakdown causing contamination with organic degradation products are some of the other drawbacks inherent with their use<sup>(18)</sup>. On the contrary, inorganic exchangers have been reported to be quite stable under such conditions<sup>(19)</sup>. In view of this, separation of phosphate and tungstate ions using a typical hydrous oxide like alumina was attempted and the results obtained with this are covered in this report.

## 2. EXPERIMENTAL

### 2.1 Reagents used

All reagents used in the experiments were of E. Merck or B.D.H. Anala R Grade. Alumina used was of chromatographic grade-Brockmann analysed.

### 2.2 Radioactive tracers

All the radioactive tracers used like caesium-137, tungsten 187, phosphorus-32, ruthenium-106, etc. were available with Isotope Division, BARC.

### 2.3 Apparatus

For all ion exchange studies glass columns of dimensions 20 cms (l) x 1 mm (d) were employed.

## 2.4 Counting

Gamma counting was done using a well-type scintillation counter and beta assays were carried out using standard Geiger-Muller/proportional counter set up. The spectra of the samples were analysed using 512 channel analyser, Model MTA-512 (Hungarian).

## 2.5 Procedure

2.5.1 Precipitation experiments: 1.0 ml of the caesium carrier (caesium carbonate- $\text{Cs}^+$  conc. 1.0 mg/ml) was taken in a 100.0 ml pyrex beaker and made upto 25.0 ml with 2M nitric acid. Phosphotungstic acid of known molarities in different amounts were added to the solution as required for the experimental conditions. The precipitate of caesium phosphotungstate was allowed to settle for about 60 minutes.

After settling it was filtered through a previously weighed sintered crucible (of porosity 4) applying mild suction. The precipitate was thoroughly washed with 2M nitric acid several times to remove excess reagent. This was finally dried at 110-120°C in an air oven for about 2-3 hours. The crucible with the contents was cooled in a desiccator and weighed.

## 2.5.2 Ion exchange column experiments

2.5.2. 1. 5 gms of chromatographic grade alumina was accurately weighed and slurried into the glass column in about 50.0 ml of distilled water. The column was provided with a glass wool padding at the bottom which acts as a support for the exchanger bed. Alumina bed was given a pretreatment with wash cycles using 200 ml. each of 0.1 M ammonium hydroxide, D.D. water, 0.1 M hydrochloric acid and D.D. water in that order successively.

The column was finally conditioned with dilute hydrochloric acid adjusted to pH 4 by dilution.

1-2  $\mu\text{Ci}$  of the respective tracer like tungsten-187, phosphorus-32 in the form of tungstate and phosphate was added to 50.0 ml of hydrochloric acid adjusted to pH 4 and was loaded on to the column at a flow rate of 0.3 ml/min. Before loading 1.0 ml of the solution containing the tracer was pipetted out and kept as reference. The effluent from the column was collected in a beaker. The column was washed with 10 column volumes of hydrochloric acid at pH 4. The washings and the effluent were mixed together, 1.0 ml from this was pipetted and counted against the reference to evaluate the absorption efficiency.

The experiment was repeated using the tracer for phosphate and tungstate separately and in the presence of each other under identical experimental conditions.

2.5.2. 2. A known amount of caesium carrier containing about 1-2  $\mu\text{Ci}$  of caesium tracer in a total volume of 25.0 ml was precipitated using phosphotungstic acid following the procedure detailed above.

The precipitate obtained after filtration, washing, etc. was dissolved in minimum quantity of 0.1 M sodium hydroxide and the pH of the resulting solution was adjusted to 4 using 0.1 M hydrochloric acid. To this solution was added 1  $\mu\text{Ci}$  each of phosphorus-32 and tungsten-187 tracers in the form of phosphate and tungstate, and passed through a column of alumina conditioned with hydrochloric acid adjusted to pH 4.

The effluent was checked by gamma spectrometry for purity of the products by identification of gamma peaks.

2.5.2. 3. Simulated fission product waste solutions having different compositions were prepared by dissolving appropriate amounts of the salts in water or nitric acid and finally adjusting the acidity to the respective molarities with nitric acid. (20) To 25.0 ml of the different types of the wastes  $1.0 \mu\text{Ci}$  each of the tracers of elements that are likely to be found in aged fission product solutions namely rubidium-86, strontium-85, + 89, cerium-141, ruthenium-106, zirconium-95, caesium-137 and sodium-24 were added and caesium was precipitated as caesium phosphotungstate using phosphotungstic acid. The precipitate obtained was filtered, washed and then dissolved in minimum quantity of 0.1 M sodium hydroxide. To the solution were added  $1 \mu\text{Ci}$  each of phosphorus-32 and tungsten-187. The pH of the solution was then adjusted to 4 using 0.1M hydrochloric acid and passed through the column of alumina conditioned with hydrochloric acid adjusted to pH 4. The spectrum of the effluent was examined using a 512 channel analyser.

2.5.3 Determination of exchange capacity of alumina for phosphate and tungstate ions: Accurately weighed amount 5 grams of chromatographic alumina was taken and conditioned with hydrochloric acid adjusted to pH 4 following the procedure outlined as under 2.5.2.1.

100 ml of feed solution containing 2 mg/ml of phosphate/tungstate was prepared and to this was added  $100 \mu\text{Ci}$  of phosphorus-32/tungsten-187 tracer and pH of the solution was adjusted to 4 with hydrochloric acid and passed through the column of alumina at a flow rate of 0.3 ml/min. 1.0 ml fractions



to 1.0, where  $C$  is the count rate in cpm/ml at a particular instant and  $C_0$ , the original count rate cpm/ml.

The ratio  $C/C_0$  was plotted against the volume of the feed that has passed through. The breakthrough capacity for the exchanger under the experimental conditions was taken as the value corresponding to 1% breakthrough or to the value of  $C/C_0 = 0.01$ .

#### 2.5.4 Determination of the purity of the product

- (a) The product obtained was identified as caesium-137 by its characteristic gamma spectrum and compared to that of a standard source of known purity.
- (b) An aluminium absorption curve was also taken on a source prepared from the final product and compared against the standard.
- (c) A source prepared from the effluent was counted every day for one month and monthly readings were taken on the source for a period of 2 years to characterise the half-life of the product.

### 3. RESULTS AND DISCUSSION

Table-1 shows the effect of varying amounts of the precipitating agent on the yield of the precipitate. Addition of different amounts of phosphotungstic acid was carried out under otherwise identical conditions. As seen from the data, the yield of the product was influenced very little by increasing amounts of phosphotungstic acid beyond 61.6 mg per mg of caesium. This corresponds to 1 ml of 0.01 M phosphotungstic acid per mg of caesium. Hence the quantity of the precipitating agent used in the subsequent experiments was kept at this level.

Table-2 illustrates the influence of acidity of the medium in which the precipitation was conducted on the yield and nature of the caesium phosphotungstate precipitate obtained. In these experiments all the other conditions were kept constant and only the acidity of the precipitating medium was varied. As observed from the data, at low acidities like 0.5 M, the precipitate formed was microcrystalline and passed through a very fine filter like sintered disc-porosity 4. At acidities between 2.0M and 5.0M, yield of the precipitate obtained was fairly constant and equivalent to the amount that was expected theoretically confirming to the composition  $Cs_2HPTA \cdot 2H_2O$ . The increased yield at acidities 5.0M could possibly be explained on the basis that the precipitate formed was probably a mixture of  $CsH_2P_2TA$  and  $Cs_2HPTA$ . However, the fact that there is no difference in the yields or the nature of the precipitate in the acidity range 2.0M to 5.0M is indicative of the fact that the precipitation can be carried out under these conditions with good accuracy. This was further confirmed by another set of experiments wherein the completeness of the precipitation was checked radio metrically using caesium-137 as the tracer and complete mass balance was obtained in these cases. The behaviour of rubidium under these conditions is being investigated separately (21).

From the tracer experiments done to check the uptake of phosphate and tungstate in tracer amounts, it was found that these ions were quantitatively taken up by alumina separately and in the presence of each other. The spectra of the effluent showed the complete absence of tungsten-187 and beta assay indicated the absence of phosphorus-32 in the effluent. Subsequently the precipitation of caesium was carried out in the presence of caesium-137

tracer in the original solution and the precipitate obtained after dissolution was tagged with phosphorus-32 and tungsten-187 and passed through alumina to see whether the caesium-137 product as carried out under the suggested experimental conditions was likely to be contaminated with either tungsten-187 or phosphorus-32.

Figure-1 shows the spectrum of the tagged feed solution before passage through alumina bed. Figure-2 indicates the spectrum of the product after the alumina separation step and shows only the 0.66 MeV. photopeak corresponding to caesium-137.

The whole process was checked up finally by adopting the procedure using simulated fission product solutions having different compositions. These were tagged with tracers representative of elements that are likely to be present in aged fission product waste solutions.

Figure-3 represents a typical spectrum of the solution tagged with the tracers before the precipitation of Cs, Figure-4 represents the spectrum corresponding to the product obtained.

It is clearly seen that in the spectrum of the products after separation, only the predominant peak of caesium-137 at 0.66 MeV was present indicating a very good separation from all other fission products.

The breakthrough curves for phosphate and tungstate ions with respect to alumina are given in figure-5. The breakthrough curves exhibit more or less a sigmoid shape as seen from the figure. The breakthrough capacities of alumina for phosphate and tungstate ions were found to be 0.7 meq/g (21.2 mg/g) and 0.63 meq/g (103.5 mg/g) at pH 4.0.

The spectrum of the products in all the cases was found to be exactly identical to that of a standard caesium-137 source.

The aluminium absorption curve taken on the sample confirms the purity of the product as shown in figure-6.

The half-life of the source has been followed over a period of two years taking every day readings for an initial period of one month and monthly count rate for two years. The overall differences in the count rate correspond to only statistical variations and indicates pure caesium-137.

#### 4. RECOMMENDED PROCEDURE FOR CAESIUM-137 SEPARATION

On the basis of the results, the following procedure is recommended for the separation of caesium-137 from aged fission product waste solution.

Take a known volume of the reprocessing solution. Add the required amount of 0.01M phosphotungstic acid solution calculated on the basis that 1 ml of 0.01M phosphotungstic acid solution will be required for the complete precipitation of 1 mg of caesium from acid solutions.

Allow the precipitate to settle for an hour and filter it through a filter tube of porosity 4. Wash the precipitate thoroughly with large volumes of 2M nitric acid to remove the excess reagent and other ions.

After washing, dissolve the precipitate in a minimum amount of 0.1M sodium hydroxide solution. Adjust the pH of this solution to 4 with 0.01M hydrochloric acid. Calculate approximately the amounts of phosphate and tungstate that will be present in this

solution so that the quantity of alumina that will be required for their complete removal may be arrived at.

Chromatographic grade alumina should be used for the separation of phosphate and tungstate from caesium. Take an ion exchange glass column provided with glass wool packing at the bottom which acts as the support for the exchanger bed. Slurry the the exchanger down the column with water and wash it with 20 bed volumes of 0.1M ammonium hydroxide, distilled water, 0.1M hydrochloric acid and distilled water in that order mentioned. Finally condition the column with hydrochloric acid adjusted to pH 4 by dilution (20 bed volumes).

Pass the solution containing caesium, phosphate and tungstate (previously adjusted to pH 4) through the conditioned alumina column at a slow flow rate. Wash the column twice or thrice, with 10 bed volumes of hydrochloric adjusted to pH 4. Collect the effluent and the washings in a clean beaker and concentrate it to a minimum possible volume. Add a few ml of concentrated nitric acid to this and heat it for some time. Then boil the solution with concentrated hydrochloric acid thrice to convert the caesium into the chloride. Finally, evaporate the solution to near dryness, dissolve the product in dilute hydrochloric acid solution and supply caesium as caesium chloride in dilute hydrochloric acid solution.

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REFERENCES

- (1) Isotopes and Rad. Technology, 1, (1), 99 (1963).
- (2) G.F. Behrens, Atomic Medicine, 3rd Ed., Williams & Wilkins Co., Baltimore (1959).
- (3) M. Brucer, Teletherapy Devices with Radioisotopes, Proc. of Int. Conf. on Peaceful Uses of Atomic Energy, Geneva, 10, 68-74 (1955).
- (4) R. Amlaric and J.P. Vigne, Le Caesium-137 in Teletherapie Gauthier, Villars, Paris (1962).
- (5) F. Comas and Brucer, Radiology, 69, 231-235 (1957).
- (6) M. Brucer, USAEC Report TID-5086 (1955).
- (7) B.D. Baines, Industrial Uses of Large Radiation Sources. Proc. of Conf. on the Application of Large Radiation Sources in Industry, Salzburg, Vienna, IAEA, 2, 243-264 (1963).
- (8) J.S. Cochran, Applications of Fission Products for Large Heat Sources, AED-Conf., 1966, 253-44 (1966).
- (9) C.E.A. Notes d'Information (18) 7, (1 November 1965).
- (10) M. Michaelis, Large Radiation Source in Industry, Proc. of Conf. on Large Radiation Source in Industry, Warsaw, 1959, IAEA, 2, 363-385 (1960).
- (11) S.J. Rimshaw, TID-7517, Part I-A, 303 (1956).
- (12) L.A. Bray, HW-SA-2982 (1963).
- (13) S.J. Beard and W.C. Schmidt, HW-81092 (1964).
- (14) J. Lefevbre and G. Aubertin, EUR-3473 (1967).
- (15) H.L. Finston and M.T. Kinsley, Radiochemistry of Caesium, NAS-NS-3035 (1961).
- (16) Raggenbass et al., Proc. of 2nd Geneva Conf. on Peaceful Uses of Atomic Energy, 1179 (1955).
- (17) K. Saddington, UNESCO/NS/NRC/16 (1957).
- (18) C.B. Amphlett, Proc. of 2nd Geneva Conf. on Peaceful Uses of Atomic Energy, 28, 17 (1955).
- (19) C.B. Amphlett, Inorganic Exchangers, 7, Elsevier Publishing Co. (1964).

- (20) L. Baestle, D. Van Dyeck, D. Huys and A. Guery, Proc. of 3rd Geneva Conf. on Peaceful Uses of Atomic Energy, 10, 772, (1964).
- (21) T.S. Murthy, K.R. Balasubramanian, M. Ananthakrishan and R.N. Verma (To be published).

Table 1

EFFECT OF VARYING AMOUNTS OF PTA ON THE YIELD

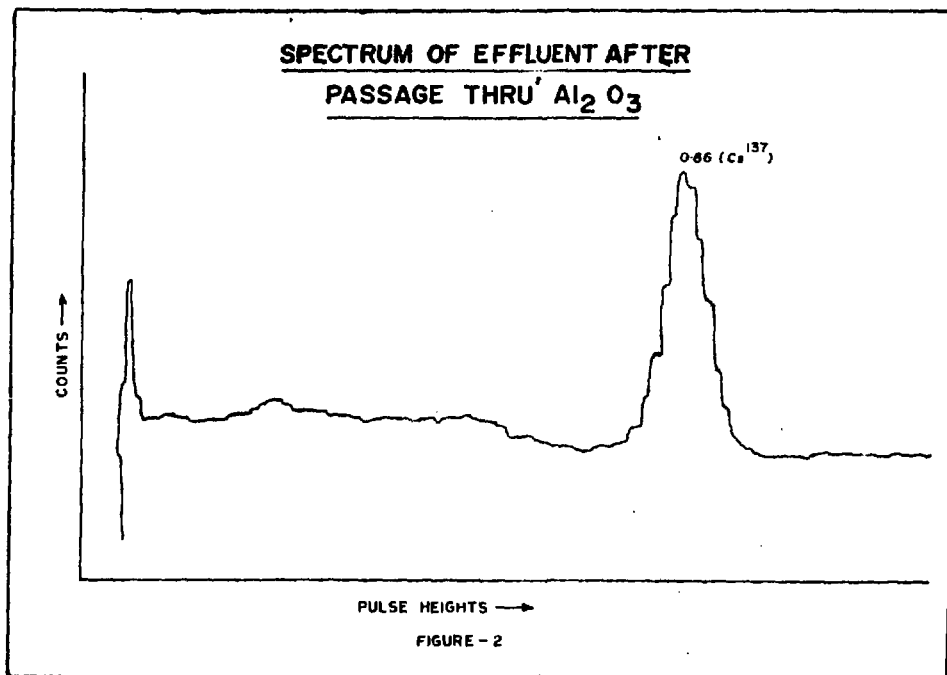
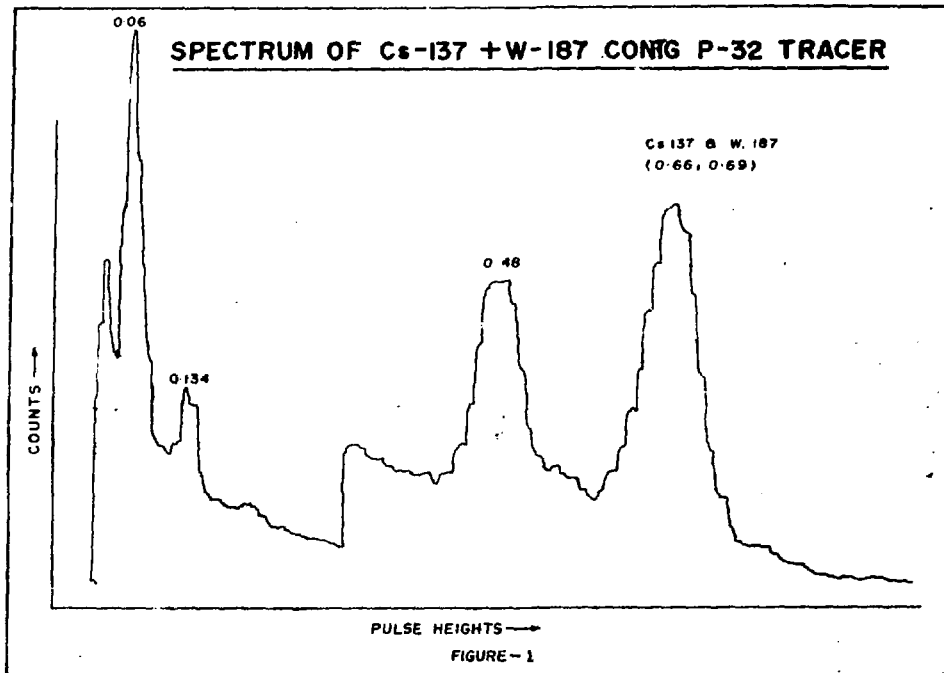
S.No.	Amount of PTA added (mgs)	Amount of Precipitate (mgs)
1	6.16	6.55
2	30.8	11.7
3	61.6	12.0
4	154.0	13.05
5	246.4	12.0
6	308	12.1
7	616	12.2
8	924	12.0

Table 2

EFFECT OF ACIDITY ON THE YIELD AND NATURE OF THE PRECIPITATE

S.No.	Molarity of HNO <sub>3</sub> (M)	Wt. of ppt. obtained (mgs)	Remarks
1	0.5		The precipitate passes through the tube.
2	1.0	10.75	
3	2.0	12.0	
4	3.0	11.58	
5	5.0	11.9	
6	6.0	14.4	{ The increased weight is probably due to the formation of Cs <sub>2</sub> HPTA at higher acidities.





**SPECTRUM OF WASTE (TYPE-1)**  
**TAGGED WITH  $^{141}\text{Ce}$ ,  $^{85}\text{Sr}$ ,  $^{137}\text{Cs}$  &  $^{24}\text{Na}$**

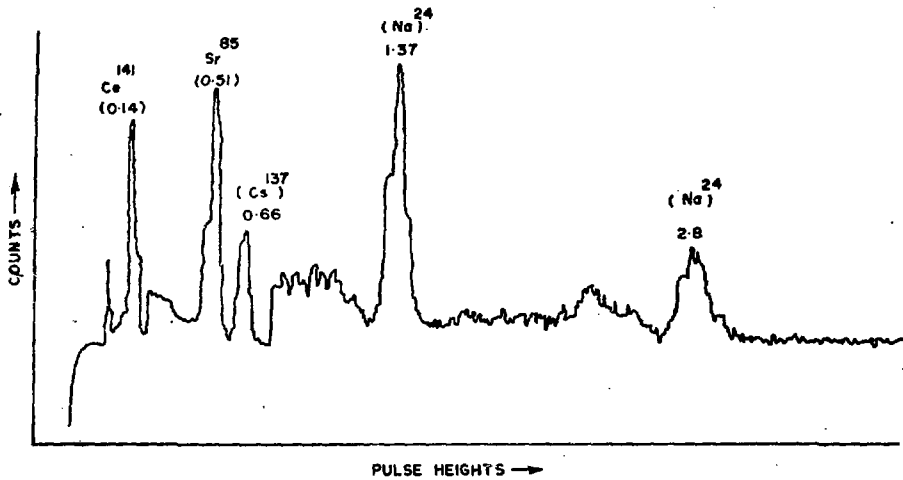


FIGURE - 3

**SPECTRUM OF WASTE (TYPE-1)**  
**AFTER THE EXPERIMENT**

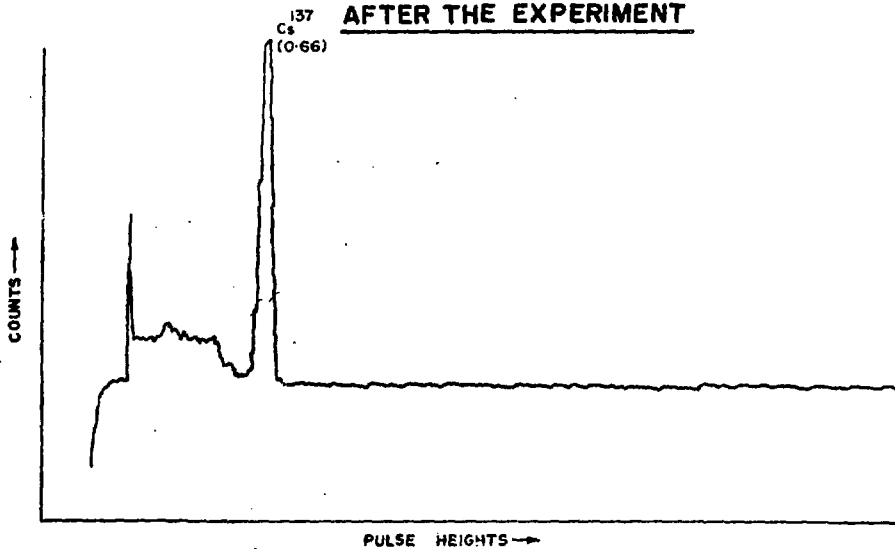
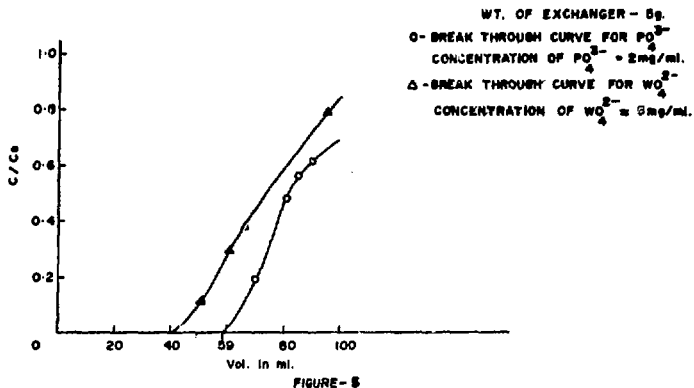


FIGURE - 4

### BREAKTHRU CURVES FOR PHOSPHATE AND TUNGSTATE ON ALUMINA



V24-II-71.

### β-ABSORPTION CURVE OF PRODUCT Cs-137 AND STANDARD Cs-137

