

THE SEPARATION AND DETERMINATION OF  $^{137}\text{Cs}$   
IN BIOLOGICAL MATERIALS

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II

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Albuquerque, New Mexico

1956

Submitted to the Faculty of the Graduate College  
of the Oklahoma State University  
in partial fulfillment of the requirements  
for the Degree of  
MASTER OF SCIENCE  
May, 1971

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#### ACKNOWLEDGEMENT

Sincere appreciation is expressed to my adviser, Dr. H. A. Mottola, whose patience and understanding made this work possible. His efforts throughout the study exemplified to me the finest in adviser-student relationships. Thanks are due also to Dr. O. C. Dermer, whose critical review was most helpful. And last but not least, my gratitude is expressed to my wife, Jean, who graciously agreed to suffer the privations of additional graduate work.

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## CHAPTER I

### INTRODUCTION

#### Importance of $^{137}\text{Cs}$ Determination in Biological Materials

The importance of  $^{137}\text{Cs}$  as a major fission product and public health hazard need not be emphasized. Because of its chemistry this isotope has been spread throughout the world and is to be found in air, soil, plant and animal life.  $^{137}\text{Cs}$  finds its way into man mainly through the ingestion of contaminated food products. The radiation dose suffered by a 70-kilogram adult is 0.06 rad per microcurie of intake<sup>18</sup>.  $^{137}\text{Cs}$  becomes distributed throughout the body uniformly and is eliminated mainly via urinary excretion with a 100-day biological half-life<sup>18</sup>.  $^{137}\text{Cs}$  has been determined in almost every conceivable material,<sup>14</sup> mainly by multi-channel gamma spectrometry, if the  $^{137}\text{Cs}$  activity is sufficient to permit resolution. The Los Alamos Biomedical Research group has determined the  $^{137}\text{Cs}$  content of thousands of humans over the past 20 years, mainly by whole body scintillation counting systems. In addition to  $^{137}\text{Cs}$  distributed by weapon fall-out,  $^{137}\text{Cs}$  is used in large quantities as a standard gamma source and in chemical tracer work. The likelihood of accidental human exposure becomes greater as more  $^{137}\text{Cs}$  is being used throughout the world. A rapid analytical procedure for determining  $^{137}\text{Cs}$  in urine would be valuable in assessing human exposure from excretion data. It is thought that any procedure suitable for use in separating and isolating  $^{137}\text{Cs}$  from

samples such as urine could be applied equally well to other biological and environmental samples, such as tissue, blood, plants, soils, etc.; however, this work is concerned only with the analysis of urine. The main problem in the determination of  $^{137}\text{Cs}$  at low levels in biological samples is its separation from bulk matter and other emitters, such as naturally occurring  $^{40}\text{K}$  and  $^{87}\text{Rb}$  as well as fission products.

Typical procedures for determining  $^{137}\text{Cs}$  in biological materials involve acid digestion and destruction of organic matter and the collection of cesium as silicotungstate or chloroplatinate for counting. These procedures are semiquantitative and time consuming, involve tedious precipitations necessary for purification, and require corrections for low yields.

The intent of this work was to investigate ion exchange and solvent extraction procedures that would be quantitative, rapid, effective in removing activity, and amenable to final determination of  $^{137}\text{Cs}$  by low background beta counting systems.

#### Analytical Approach to the Determination of $^{137}\text{Cs}$ in Urine

In reviewing the literature it was found that several derivatives of the 12-heteropolyacids have been used to isolate cesium from many interfering elements by cation exchange<sup>20</sup>. In fact, it has been known for some time that ammonium molybdophosphate (AMP) shows ion exchange selectivity for the alkali metal ions<sup>19, 20, 21</sup>. This material has been used mainly in England and continental Europe and for some reason has not been widely used in this country. Apart from the ammonium ions, only the large monovalent cations, viz.  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Tl}^+$ ,  $\text{Ag}^+$ ,  $\text{Hg}_2^{++}$  and some organic bases, have been found to form insoluble salts with

AMP<sup>20</sup>. The ion exchange reaction between alkali metal ions and AMP can be represented by:



where R represents the molybdophosphate anion and M<sup>+</sup> the metal ion.

The equilibrium expression is:

$$K = \frac{[MR][NH_4^+]}{[M^+][RNH_4]}$$

Where  $D_x = \frac{[MR]}{[M^+]}$  = distribution ratio =

$$\frac{\text{Quantity of x per unit Mass of AMP}}{\text{Quantity of x per unit Volume of Solution}}$$

If RNH<sub>4</sub> is present in so great excess that it can be regarded as constant, the expression reduces to:

$$\log D = \text{constant} - [\log NH_4^+]$$

Fortunately, the distribution ratio D for AMP and the above cations are in the order Cs<sup>+</sup> > Rb<sup>+</sup> > K<sup>+</sup> > Tl<sup>+</sup> > Ag<sup>+</sup> > Hg<sub>2</sub><sup>++</sup>. These relatively large D values are attributed to size and the unique structure of the molybdophosphate anion. Krtil<sup>13</sup> has investigated the exchange dependence upon the chemical environment, such as the HNO<sub>3</sub> and NH<sub>4</sub><sup>+</sup> concentrations. A plot of log D for cesium vs log [NH<sub>4</sub><sup>+</sup>] indicates a slope of -1 and thus suggests that strong ammonia solutions would decrease the D value for cesium and therefore be an effective eluting agent after exchange. The dependence of D for cesium on nitric acid concentration is nearly constant up to about 4M acid, where it shows a sharp drop.

If the D values for the alkali metals are sufficiently different, adequate separations should be possible by selective elution with NH<sub>4</sub><sup>+</sup> solutions. The really important separation is that of cesium from rubidium since other alkali metals would be less strongly held



and eluted long before rubidium. Good separations have been achieved between cesium and rubidium on relatively clean samples (low ionic strength)<sup>19,21</sup>, by the elution of rubidium with  $3M$   $NH_4NO_3$  and the elution of cesium with about  $15M$   $NH_4NO_3$ . The separation and determination of cesium in sea water<sup>15</sup>, in rain water<sup>6</sup> and urine<sup>17</sup> use this basic approach. In these cases, the AMP was utilized as a primary collection material and further purification was necessary.

In view of the above it was decided to consider the application of AMP as a collection and purification material in the determination of cesium in biological materials. It was not known whether biological samples would yield distribution ratios sufficiently large in order to permit a good separation from interfering elements or the necessary column parameters. Later work did indicate large D values for cesium, allowing good separation, but presented another problem in the excessive amount of saturated  $NH_4NO_3$  required to remove cesium after exchange. The possibility of using other eluting agents in less concentrated solution was studied without success. The recourse, then, was to dissolve the AMP containing cesium with strong base and equilibrate this solution with BAMBP, the only known extractant of cesium from strongly basic solutions<sup>4,24</sup>. The BAMBP extraction system was investigated and found to be adequate. The resultant organic extractant solution of  $^{137}Cs$  could then be counted directly by gamma spectrometry or the  $^{137}Cs$  back-extracted into highly acidic solution, concentrated by evaporation and determined by low level beta counting.

## CHAPTER II

### STRUCTURE OF AMMONIUM MOLYBDOPHOSPHATE

This compound is derived from a group of compounds known as the heteropolyacids. The heteropolyacids are compounds in which one atom of an element such as P, Si, B, or Al is combined with a number of atoms of an element such as W or Mo together with a relatively large number of oxygen atoms. Throughout the whole class of heteropolyacids they all have the same cation-cation ratios, are isomorphous and have similar chemical and physical properties. The best known compounds of this group are the silicotungstic, molybdosilicic, and phosphotungstic acids. The crystalline structure of these 12-heteropolyacids, which is the same for all of them, was clarified by Keggin<sup>12</sup> using X-ray powder photographs of 12-phosphotungstic acid. A molecule of this acid has the formula  $H_3(PW_{12}O_{40})$ . The anion  $[PW_{12}O_{40}]^{-3}$  consists of a central  $PO_4$  tetrahedron, surrounded by 12  $WO_6$  octahedra as a shell, linked together by shared oxygen atoms. (In order to see the unique structure of this molecule, a wooden model was constructed. This model is shown in Figure 1.) It can be seen that each  $WO_6$  octahedron besides sharing two oxygen atoms with octahedra in its own group of three also shares two oxygen atoms with octahedra in other groups. In each anion, each  $WO_6$  octahedron consists of one oxygen shared between three  $WO_6$  octahedra and one  $PO_4$  tetrahedron, four oxygen atoms shared between two  $WO_6$  octahedra, and one oxygen atom unshared with other polyhedra,

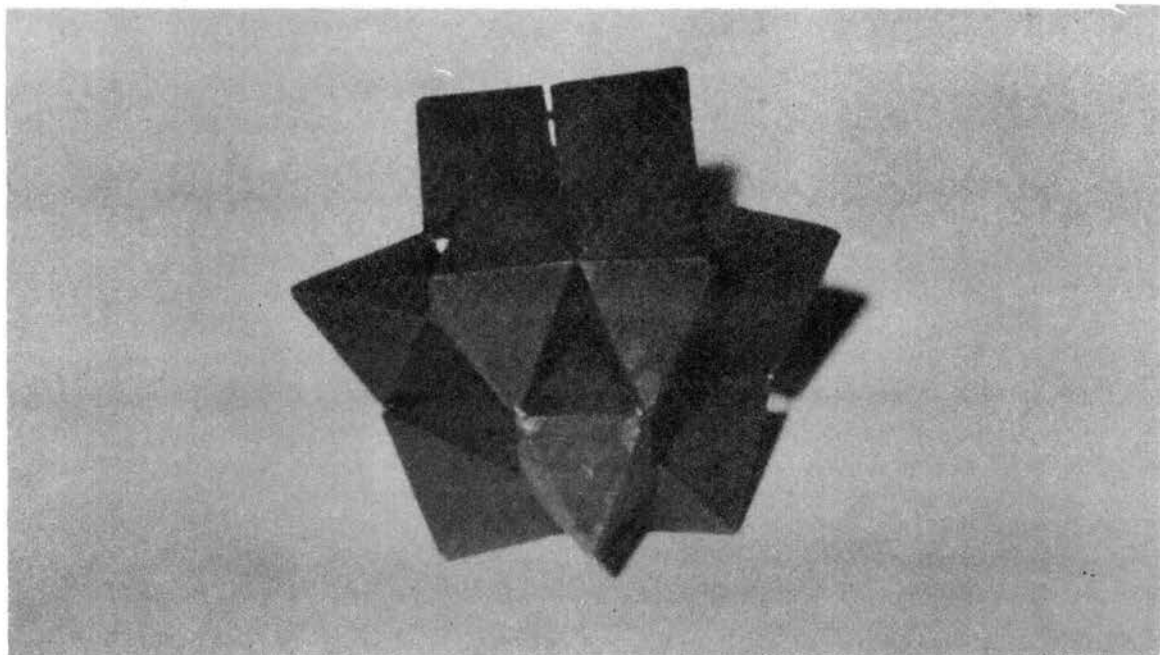


Figure 1a Model of the Phosphomolybdate Anion showing one flat face.

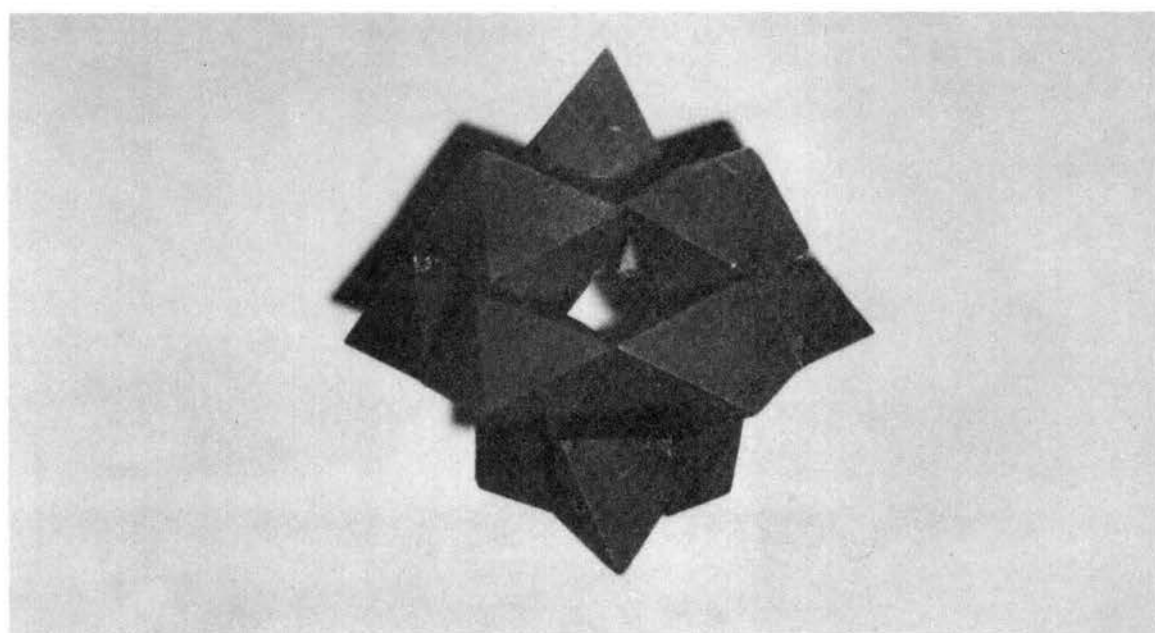
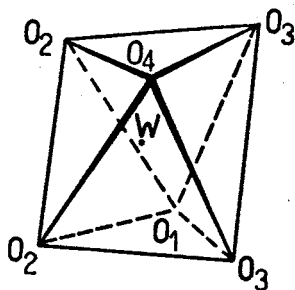


Figure 1b Model of the Phosphomolybdate Anion showing re-entrant face.

these oxygen atoms are symmetrically distributed about the central tungsten atom. It is also noted that two edges of each  $WO_6$  octahedron are shared with edges of two other octahedra. The oxygen atoms in each octahedron can be classified according to their position:



The O1 oxygen atoms are shared between three  $WO_6$  octahedra and one  $PO_4$  tetrahedron. The O2 atoms are shared between two  $WO_6$  octahedra. The O3 atoms are shared between two  $WO_6$  octahedra. The O4 atoms are unshared. The O1-O3 edges are shared between two  $WO_6$  octahedra. The surface presented by this molecule is interesting indeed. The surface consists of 6 cube faces and 8 octahedral faces. The latter can be divided into four flat faces and four re-entrant faces. Since these anions are complete structural units in themselves and when packed together in a crystal are not strongly linked to one another, the acids derived from them would be expected to be highly soluble and contain large amounts of water of crystallization. In the 5-hydrate packing, each of 4 flat faces is directly linked to a flat face of a neighboring anion and each of the 4 re-entrant faces is linked to a water molecule. These water molecules serve to bind together the re-entrant octahedral faces of adjacent anions. Therefore in the 5-hydrate structure<sup>11</sup> we have cubic packing, each anion having 14 neighbors. Four are linked directly, flat to flat, four indirectly through water molecules, and 6 are unattached leaving spaces large

enough for water molecules or other ions. The cesium salts of the 12-heteropolyacids form compounds that are isomorphous with the 5-hydrate acids and cesium ions replace water molecules in cube faces<sup>12</sup>. In addition to cesium there are a few other monovalent ions that are large enough to be packed stably into this structure<sup>19</sup>. These are  $K^+$ ,  $Rb^+$ ,  $Tl^+$ ,  $Ag^+$ ,  $Hg_2^{++}$ ,  $NH_4^+$  and cations derived from some organic bases. The ions evidently lower the crystal energy sufficiently to give salts insoluble in water. Owing to the dependence of crystal packing on size and also to ion exchange it becomes important to determine the sizes of spaces available. The interatomic distances are as follows<sup>12, 1</sup>.

- a. The  $PO_4$  tetrahedra in the center of the anion is undistorted; all edges are 2.80 Å.
- b. The  $WO_6$  octahedra are distorted, the shared edges (01-03) are 2.65 Å.

TABLE I  
OXYGEN-OXYGEN INTERATOMIC DISTANCES

01-02	-----	2.70 Å
03-03	-----	2.90 Å
02-02	-----	2.65 Å
03-02	-----	2.61 Å
02-04	-----	3.10 Å
04-03	-----	2.80 Å

In the 5-hydrate heteropolyacid, the packing is cubic, with the edge of the unit cube being  $12.140^{\pm .005} \text{ \AA}^3$ . Depending upon the orientation of the anions in the lattice, the maximum separation is believed to be about  $3.5 \text{ \AA}^3$ . The reported ionic radii of the monovalent ions that yield insoluble salts with the 12-heteropolyacids are shown in Table II.

TABLE II  
PAULING IONIC RADII FOR SOME IONS

<u>Ion</u>	<u>Radius (<math>\text{\AA}</math>)<sup>3</sup></u>
K <sup>+</sup>	1.33
Rb <sup>+</sup>	1.48
Cs <sup>+</sup>	1.69
NH <sub>4</sub> <sup>+</sup>	1.48 (ref 19)
Tl <sup>+</sup>	1.47
Ag <sup>+</sup>	1.26

While Cs<sup>+</sup> has the largest diameter and this undoubtedly accounts for the stability of cesium molybdophosphate, it would seem that other ions may fit more precisely in the AMP lattice; however, after consideration of the obvious next possibilities (Fr, Ba, tetraalkyl ammonium ions) room for exploration in this line seems limited. There seems little doubt that AMP and other heteropolyacid salts owe their cation exchange properties and high selectivity for certain monovalent ions to their unique crystalline structure. Another point worthy of

consideration still related to ionic size, but without direct geometric implications, is that Cs has a low enthalpy of hydration and if these water molecules are lost upon exchange with AMP, this would help explain the large selectivity of AMP for Cs over the other alkali metal ions of smaller size and higher enthalpy of hydration.

$\Delta H_{\text{hyd}}^{(2)}$ (kcal mole <sup>-1</sup> )	<u>Li</u> <sup>+</sup>	<u>Na</u> <sup>+</sup>	<u>K</u> <sup>+</sup>	<u>Rb</u> <sup>+</sup>	<u>Cs</u> <sup>+</sup>	<u>NH<sub>4</sub></u> <sup>+</sup>
	-119	-93	-73	-67	-59	< -59
						(estimate based upon size)

## CHAPTER III

### ION EXCHANGE COLUMN DESIGN

In order to have an idea as to the characteristics of the desired column, a theoretical calculation was made based upon data that was available.

Ion exchange capacity of AMP = 1.57 meq/g

Particle size (r) = 74 microns = 0.0074 cm

Column cross section = 1.0 cm<sup>2</sup>

Fraction of volume containing AMP (B) = 0.5 estimated<sup>10</sup>

Diffusion rate ( $\bar{D}$ ) =  $3.7 \times 10^{-7}$  cm<sup>2</sup>/sec estimated<sup>10</sup>

Diffusion rate in liquid phase ( $D_m$ ) =  $2 \times 10^{-5}$  cm<sup>2</sup>/sec estimated<sup>10</sup>

Density of AMP = 5.5 g/cm<sup>3</sup>

Optimum volume distribution ratio ( $D_v$ ) = amount of ion in one ml of AMP/interstitial volume

Optimum flow rate (V) = ml/min

Of those estimated values  $D_m$  appears as the more reliable with B and  $\bar{D}$  probably less accurate.

1. Theoretical plate height (H). Using the derivation of Helfferich<sup>10</sup> the plate height is given by:

$$H = 1.64r + \frac{D_v}{(D_v+B)^2} \left[ \frac{0.142r^2 V}{\bar{D}} \right] + \frac{[D_v]^2}{(D_v+B)} \left[ \frac{0.266r^2 V}{D_m(1+70rV)} \right] + \frac{D_m B \sqrt{2}}{V}$$

These four terms reflect the parameters that affect the column. The first term is due to particle size dependence, the second to



particle diffusion, the third to film diffusion and the fourth to longitudinal diffusion. The usual procedure for evaluation is to double the first term, set all other terms equal to this double value, and then sum. Therefore:

$$H = 6(1.64r) = 0.073 \text{ cm}$$

2. Optimum volume distribution ratio ( $D_v$ )

The second term is set equal to the third term, the equation solved for  $D_v$ , and this evaluated.

$$D_v = \frac{0.142 D_m}{0.266 \bar{D}} = 29$$

3. Mean molar distribution ratio ( $D_x$ )

$$D_x = \frac{D_v}{B} = \frac{29}{0.5} = 58$$

4. Optimum flow rate (V)

$$V = \frac{3.28 D_m (D_v + B)^2}{0.266 D_v^2 T} = 2.1 \text{ ml/min}$$

5. Relative peak retention ( $\alpha$ )

$$\alpha = \frac{D_{v,CS} + 1}{D_{v,Rb} + 1}$$

Unfortunately, the individual distribution ratios ( $D_v$ ) for cesium and rubidium are not known and must be derived by other means. The best approach relies on previous elution data,<sup>19</sup> since  $V_{\max} = V_{T,b}(D_v + B)$ , where  $V_{t,b}$  is the total bed volume and  $V_{\max}$  is the volume of eluant required to elute the ion at the highest concentration (ie, maximum peak height). Using values from Figure 2 of Smit's work<sup>19</sup>:  $V_{\max}(\text{RB}) = 0.15 \text{ ml}$  and  $V_{\max}(\text{CS}) = 0.7 \text{ ml}$  and  $D_{v,Rb} = 8.6$   $D_{v,CS} = 44$

The relative peak retention ( $\alpha$ ) is: 4.7

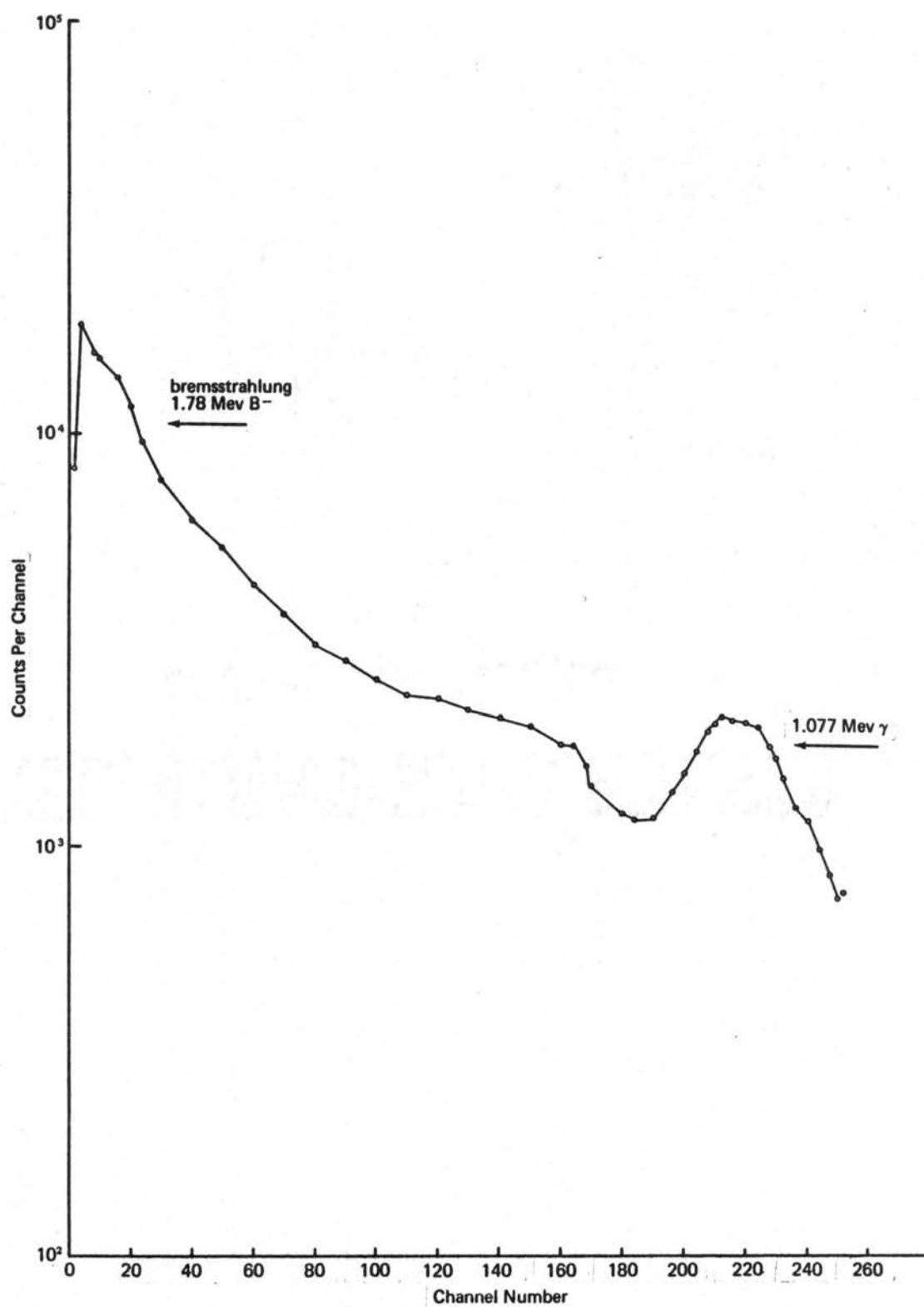


Figure 2 GAMMA ENERGY SPECTRUM FOR THE  $^{86}\text{Rb}$  STANDARD SOLUTION

## 6. Number of theoretical plates (N)

Glueckauf<sup>8</sup> has developed the interrelationship of product purity, relative peak retention, and number of theoretical plates. If we set the maximum allowable Rb concentration at 0.01%, representing a large separation factor, reference to Figure 3 of Glueckauf's work indicates 25 plates are required. The length of the column (L) = NxH = 1.8 cm and a 1-cm<sup>2</sup> cross section gives 1.8 cm<sup>3</sup> of AMP. However, this calculation is based upon pure AMP, and it is known that some substrate such as asbestos is required in order to obtain sufficient porosity for adequate flow<sup>6,15</sup>. On the assumption that one part asbestos and two parts AMP (by weight) would be required, 1.8 cm<sup>3</sup> of AMP corresponds to 10 g. A 5 g amount of asbestos corresponds to 2.5 cm<sup>3</sup> in a 1-cm<sup>2</sup> cross section column. The effective plate height H\* now may be calculated as:

$$H^* = \frac{L}{N} \frac{4.3}{25} = 0.17 \text{ cm}$$

## 7. Elution

$$V_{\max}(\text{Cs}) = V_{t,b} (Dv+B) = 96.8 \text{ ml}$$

$$V_{\max}(\text{Rb}) = V_{t,b} (Dv+B) = 20.7 \text{ ml}$$

## 8. Band width (W)

$$W(\text{Cs}) = \frac{4V_{\max}}{\sqrt{N}} = 77.5 \text{ ml}$$

$$W(\text{Rb}) = \frac{4V_{\max}}{\sqrt{N}} = 16.5 \text{ ml}$$

## 9. Time required (T)

$$T = \frac{(V_{\max}(\text{Cs}) + V_{\max}(\text{Rb}))}{V} = 56 \text{ min}$$

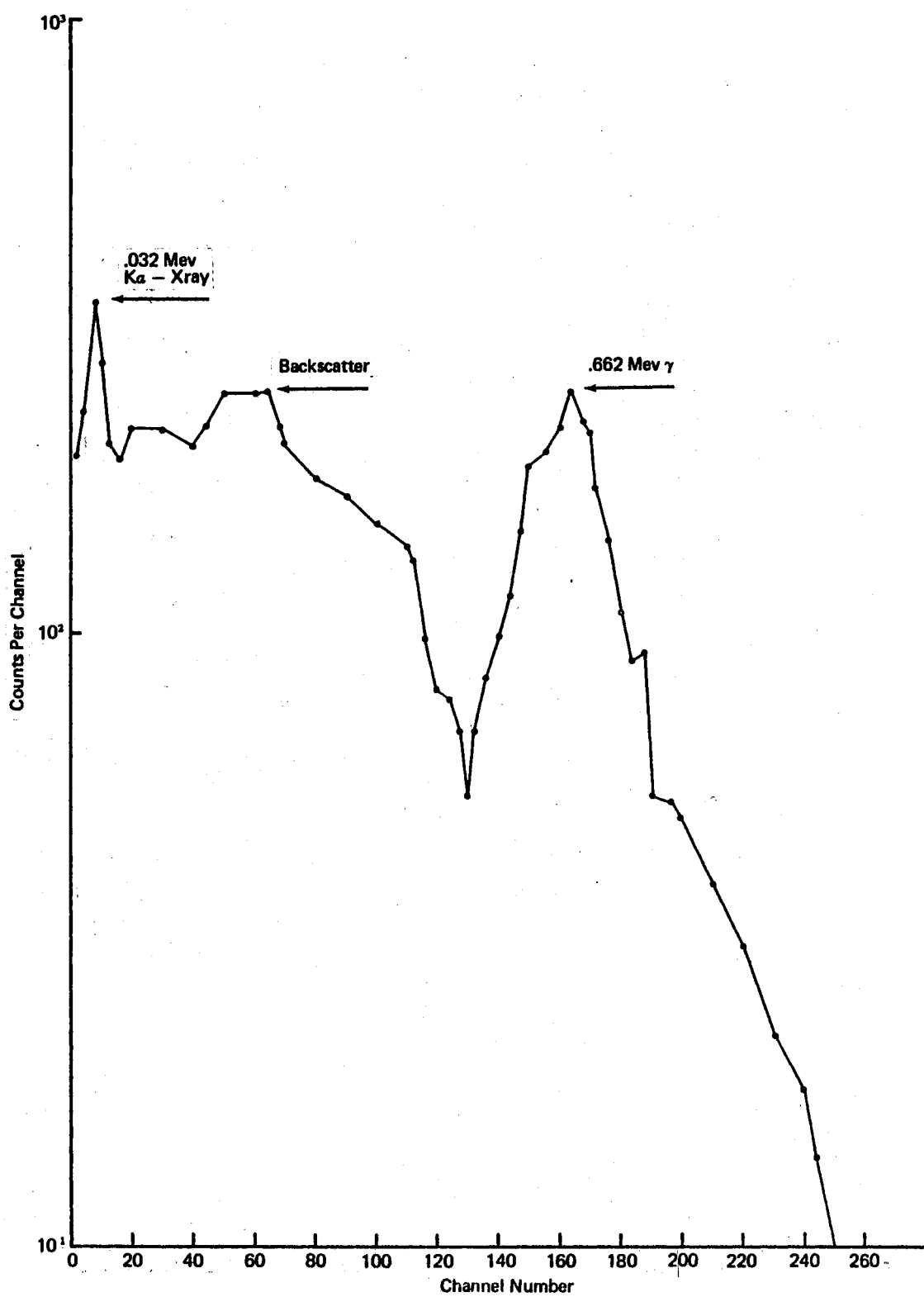


Figure 3 GAMMA ENERGY SPECTRUM FOR THE  $^{137}\text{Cs}$  STANDARD SOLUTION

These theoretical calculations were used to set up the initial experimental conditions for elution. A comparison will be presented later of theoretical and measured values. The two critical parameters, number of plates and relative peak retention, are thought to be reasonable and should give a good separation of Rb and Cs. It is generally accepted that overdesign is necessary and this was taken into account by imposing a high degree of separation (0.01%), consequently the calculated parameters cannot be considered attainable or to be expected but as guides for further refinement of conditions as adjusted to empirical behavior.

## CHAPTER IV

### EXPERIMENTAL

#### Materials and Equipment

##### A. Equipment

Ainsworth Analytical Balance, type 21N.

Beckman Zeromatic pH meter.

Multi-Channel gamma spectrometer, Nuclear Data Inc., series 1100 with 3" X 3" well-type NaI crystal.

##### B. Materials

Fisher certified A. C. S. grade chemicals:

Ammonium Nitrate

Phosphomolybdic Acid

Sodium Hydroxide

Phosphoric acid (ortho, 85%)

Nitric acid (71%)

Ammonium Hydroxide (29.6%)

<sup>86</sup>Rb isotope - New England Nuclear standard NE-072: 10 microcuries as RbCl in 0.5 N HCl.

<sup>137</sup>Cs isotope - New England Nuclear standard NE-018: 10 microcuries as CsCl in 1.0 N HCl.

Methylamine Hydrochloride. Eastman Organic Chemical, white label.

Asbestos - acid-washed selected fiber. Fisher Scientific Co.

BAMBP - K & K labs #23937

(4-~~sec~~-butyl-2-(~~d~~-methylbenzylphenol)

#### Preparation of Ammonium Molybdophosphate (AMP)

The exchange properties of the AMP used, known to depend on the method of preparation<sup>20</sup>, were shown to be comparable to the material used by previous workers. This was ascertained by equilibration experiments in which reported D values were duplicated.

#### Preparation

A saturated solution of phosphomolybdic acid ( $20 \text{ MoO}_3 \cdot 2\text{H}_3\text{PO}_4 \cdot 48\text{H}_2\text{O}$ ) was prepared in about 2 liters of distilled water. The acid was only slightly soluble but the addition of about 5 ml of ~~cond~~  $\text{H}_3\text{PO}_4$  and heating improved the solubility. A saturated solution of  $\text{NH}_4\text{NO}_3$  (ca 15 M) was prepared and added to the phosphomolybdic acid solution in excess. The AMP precipitate was filtered with (Whatman #42) paper under suction. The precipitate was washed repeatedly with 0.1 M  $\text{NH}_4\text{NO}_3$  until the supernatant liquid showed a pH greater than 3. The AMP was then dried at  $100^\circ\text{C}$  for 8 hours. The fine yellow powder produced was passed through a 200-mesh screen. The particle size was less than 74 microns.

#### Determination of Distribution Ratios (D)

#### Sample Preparation

Sample type I: 200 ml of fresh urine was evaporated to dryness with 5 ml concentrated  $\text{HNO}_3$ . Ashing with addition of small

portions of concentrated  $\text{HNO}_3$  was repeated until a white residue remained. The residue was then dissolved with 200 ml of 0.1M  $\text{NH}_4\text{NO}_3$  and the pH adjusted to 1 with  $\text{HNO}_3$ .

Sample type II: 200 ml of fresh urine was ashed as for type I. The residue was then dissolved with 100 ml of 0.1 M  $\text{NH}_4\text{NO}_3$  and the pH adjusted to 1.

Sample type III: 200 ml of fresh urine was ashed as for type I. The residue was then dissolved in 100 ml of distilled water and the pH adjusted to 1 with  $\text{HNO}_3$ .

Sample type IV: raw urine was made 0.1 M in  $\text{NH}_4\text{NO}_3$  and the pH adjusted to 1 with  $\text{HNO}_3$ .

Sample type V: raw urine was adjusted to pH = 1 with  $\text{HNO}_3$ .

Sample type VI: 0.1M  $\text{NH}_4\text{NO}_3$  was adjusted to pH = 1 with  $\text{HNO}_3$ .

#### Equilibration Time

Since it was not known how long the equilibration would take between cesium and the AMP a series of samples of type I were shaken for 60, 30, 15, and 1 minute with 0.5 g AMP. Analysis of the aqueous phase showed the D values to remain essentially constant throughout these times. Thereafter all samples were shaken with AMP for 1 minute for equilibration.

#### Procedure

A 10-ml sample of each type was pipetted into 250-ml glass-stoppered Erlenmeyer flasks; 0.5 g of AMP was then added to each flask. Standard amounts (activities) of  $^{86}\text{Rb}$  and  $^{137}\text{Cs}$  were added to the flasks with the aid of a micropipette. (The  $^{86}\text{Rb}$  and  $^{137}\text{Cs}$  activities



were added separately and evaluated individually.) Each sample was shaken and the phases were allowed to separate for several hours. Since adequate separation was possible, resort to filtration or centrifugation was not necessary. A 5-ml aliquot of the clear aqueous phase was transferred to a soft glass test tube for counting.

#### Counting Procedure

Energy spectra of the  $^{86}\text{Rb}$  and  $^{137}\text{Cs}$  (Figures 2, 3) standard solutions were obtained with a 256-channel gamma spectrometer, equipped with a well-type 3" X 3" NaI crystal. The spectra revealed adequate purity of the isotopes. The  $^{137}\text{Cs}$  samples were counted for 2000 seconds (live) and the integral counts were obtained by arithmetic summation of the counts in channels 140-180 (4KEV/channel). These counts were compared to a known activity of  $^{137}\text{Cs}$  placed in 5 ml of sample type I. For the  $^{86}\text{Rb}$  samples the same procedure was followed except the summation was taken from channels 196-236. Counting statistics as discussed in reference (7) were taken into consideration but the counting error, being smaller than other errors affecting D values, was finally neglected.

#### Data

$$D_x = \frac{\text{Activity per gram AMP}}{\text{Activity per ml of sample}}$$

TABLE III  
EXPERIMENTAL DISTRIBUTION VALUES

Sample type	D (Cs)	D (Rb)	$\frac{D (Cs)}{D (Rb)}$
II	2100	98	21
III	4200;4030	358;417	12;10
IV	1840;1890	82;97	22;20
V	2966	338	9
VI	6770	277	24

#### Discussion of Experimental Results

It is of interest to compare these values with those in the literature. Only two are available on sample type VI<sup>19</sup>, where the reported values of D(Cs) and D(Rb) are 6000 and 230 respectively. The correlation is satisfactory, however, a value of 6000 may be suspected of having undergone rough rounding off. Perhaps the investigators involved experienced such variability in their values that they rounded them off to 2 significant figures, and the result should have been reported as  $6.0 \times 10^3$ . It is interesting to note the rather large D values for these types of samples. Since D values drop roughly from 6000 to 1500 in going from 0.1M  $\text{NH}_4\text{NO}_3$  to sea water, one would expect an increasing salt content to further reduce the D value. This is evidently not the case and each sample type must be evaluated individually.

The dependence of D(Cs) upon the ammonium ion concentration has been determined by Krtil<sup>13</sup>. A plot of  $\log D$  vs  $\log C_{\text{NH}_4\text{NO}_3}$  yields a

straight line with a slope of -1. The ammonium ion dependence is borne out in the above samples and those samples without added  $\text{NH}_4^+$  yield significantly higher D values. The analysis of sample type III appears to be the most advantageous. After ashing, the concentration of the sample is doubled, no  $\text{NH}_4\text{NO}_3$  is required, and the method yields a large D value. The analysis of raw urine is not normally performed for esthetic reasons, but from the D values above there is no reason why this analysis cannot be done in an emergency.

It should also be noted that even though AMP prepared by different techniques may yield variable D values<sup>20</sup> and the same effect is observed if different amounts of AMP are taken for batch equilibration, those variations will be within one order of magnitude.

#### Elution

Prior to elution of rubidium and cesium, it was found that use of a column 1 cm<sup>2</sup> in cross section could not be packed well and thus led to very low flow rates. A 6.25-cm<sup>2</sup> column was substituted in which flow rates could be maintained between 3 and 4 ml per minute. Also it was found that the parameter B had been overestimated. The bed height after settling was 6.5 cm, which corresponds to a total bed volume of about 41 cm<sup>3</sup>. Since 4.3 cm<sup>3</sup> of dry AMP and asbestos was added, B becomes 0.105. The material does appear to pack better in large columns.

#### Elution Procedure

To a 6.5-cm<sup>2</sup> column 10 grams of AMP and 5 grams of asbestos were added as a slurry in 0.1 M  $\text{NH}_4\text{NO}_3$ . The column was shaken for complete

mixing and allowed to settle overnight. After the column was drained, activities of  $^{86}\text{Rb}$  and  $^{137}\text{Cs}$  were washed onto it with 100 ml of sample type III. The  $^{86}\text{Rb}$  was eluted with  $3\text{M}$   $\text{NH}_4\text{NO}_3$  and the  $^{137}\text{Cs}$  eluted with saturated (ca.  $15\text{M}$ )  $\text{NH}_4\text{NO}_3$ . The elution curve is shown in Figure 4. The eluate was collected in tubes 1-140, each tube representing 5 ml. The radioactivity in the tubes were counted in a multichannel analyzer already described and the activities of each were monitored at the gamma peak maximum for each isotope. The results show an excellent separation of Rb and Cs. The curve is also evidence of complete  $^{40}\text{K}$  removal, the main offender in biological samples. The Rb tail persisted when using  $3\text{M}$   $\text{NH}_4\text{NO}_3$  and fell to background only after the addition of saturated  $\text{NH}_4\text{NO}_3$ . This suggests that  $3\text{M}$   $\text{NH}_4\text{NO}_3$  is a little too weak for the purpose and another elution was carried out using  $4\text{M}$   $\text{NH}_4\text{NO}_3$ . The results of this elution are shown in Figure 5. This resulted in improvement and  $4\text{M}$  was used in subsequent separations. A comparison of these elution parameters with design predictions is now in order.

TABLE IV

A COMPARISON OF MEASURED AND CALCULATED ELUTION PARAMETERS

Measured Values	Estimated Values	Calculated Values
$V_{(\text{max})}(\text{Rb}) = 70 \text{ ml}$	--	20.7
$V_{(\text{max})}(\text{Cs}) = 145 \text{ ml}$	--	96.8
$D_v(\text{Cs}) = 33$	--	44
$D_v(\text{Rb}) = 15$	--	8.6
$D = 0.105$	0.5	

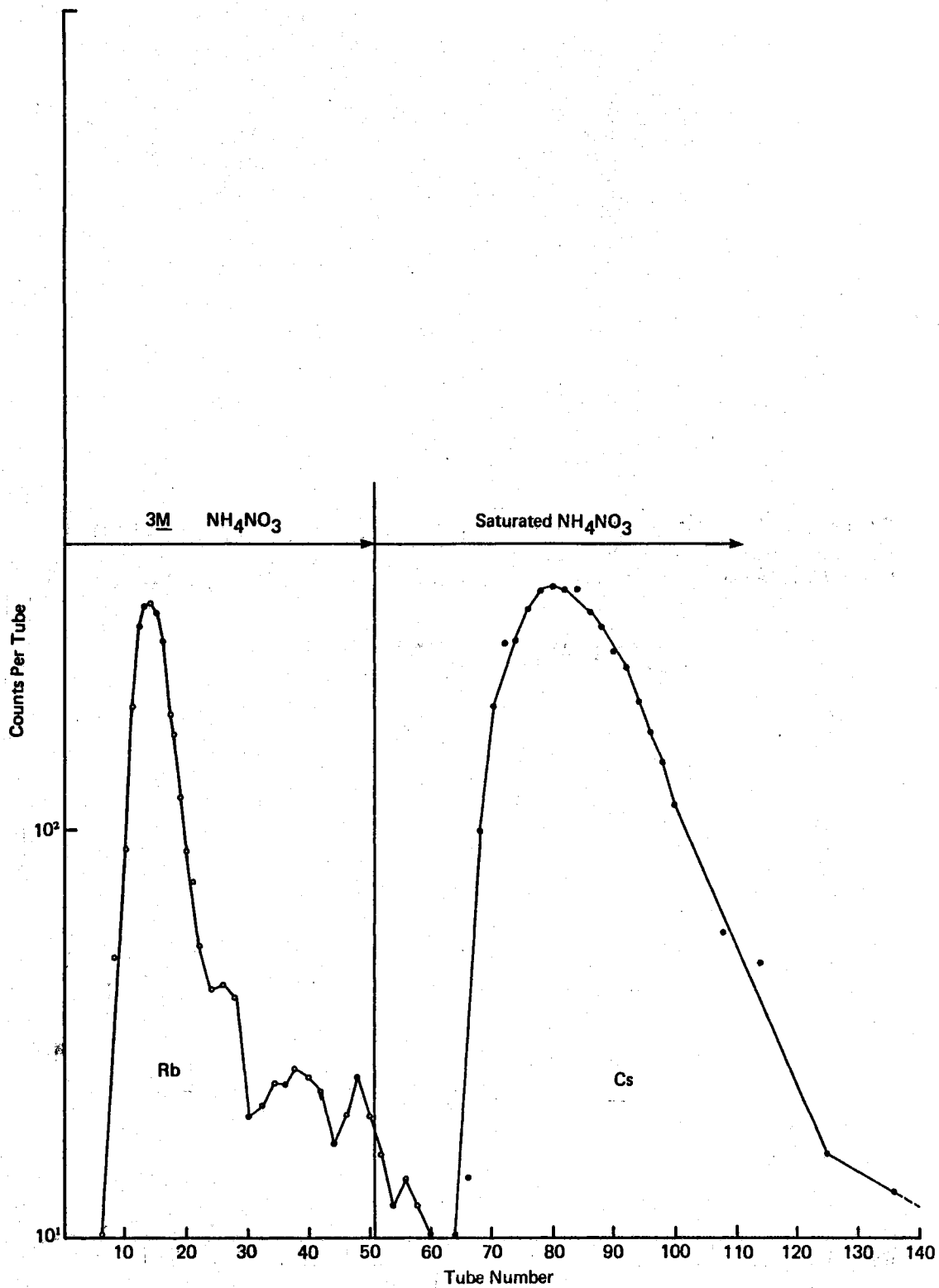


Figure 4 ELUTION CURVE FOR  $^{86}\text{Rb}$  AND  $^{137}\text{Cs}$  ACTIVITIES USING 3M  $\text{NH}_4\text{NO}_3$  AND CONCENTRATED  $\text{NH}_4\text{NO}_3$

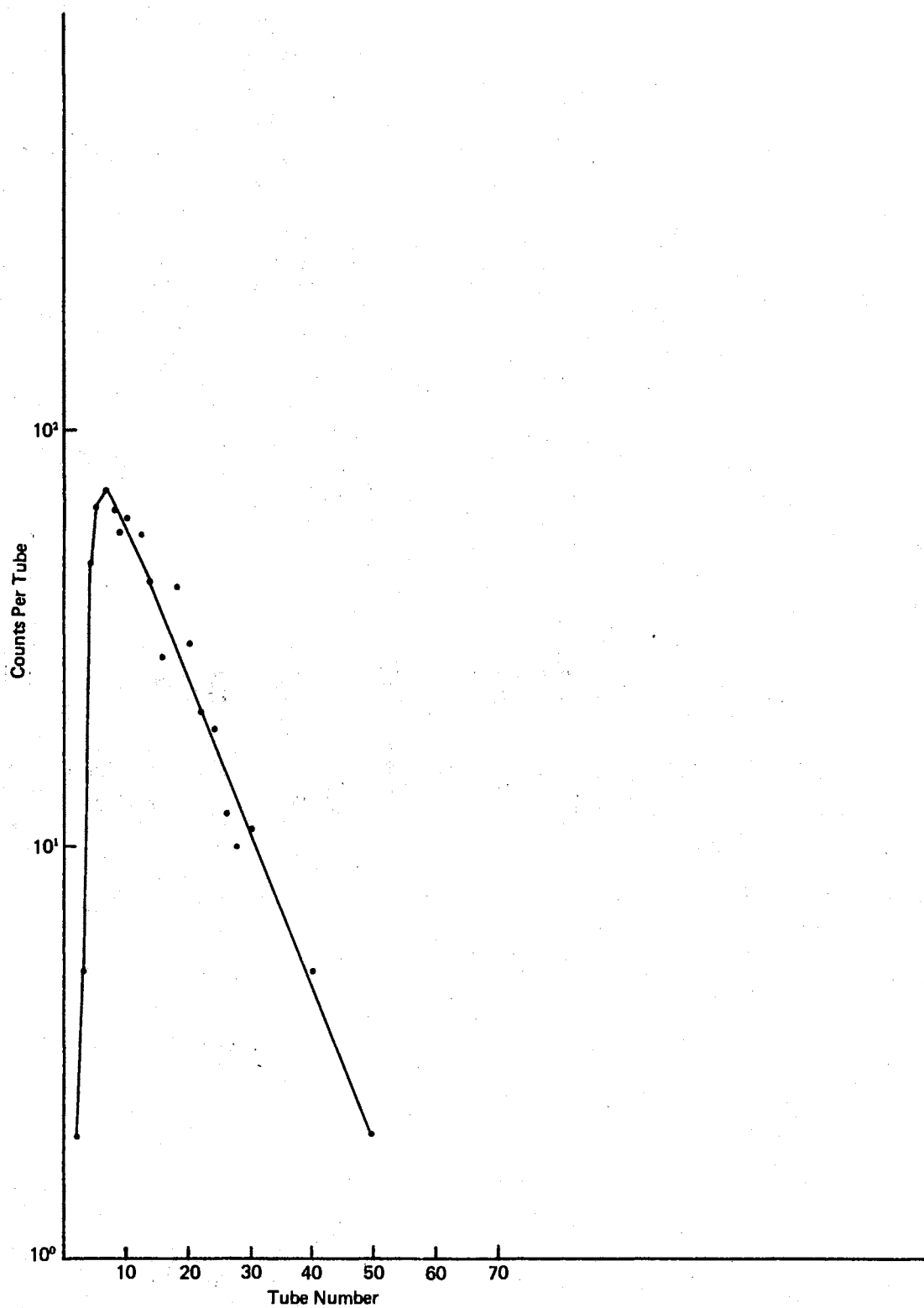


Figure 5 ELUTION CURVE FOR  $^{86}\text{Rb}$  USING  $4\text{M NH}_4\text{NO}_3$ .

Considering the many assumption and overdesign in the theoretical calculation, the correlation is satisfactory, and points out the usefulness of prior calculations, following Helfferich's pattern, before performing an ion exchange elution.

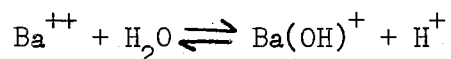
#### New Eluting Agents

The large volume of saturated  $\text{NH}_4\text{NO}_3$  required for the elution of Cs is clearly undesirable. This rather viscous solution would present significant difficulties in final counting. Due to the strong size dependence of AMP and exchangeable ions, it was thought that ions derived from substituted amines larger than  $\text{NH}_4^+$ , might displace Cs more effectively. The column was prepared as described above and standard activities were added, followed by 100 ml of sample type III. A saturated solution of methylamine hydrochloride was added to the column and the eluant monitored for  $^{137}\text{Cs}$  activity. In the 200 ml of eluant that was collected, no  $^{137}\text{Cs}$  was detected; thus indicating the unsuitability of this material as an eluting agent. Sizewise, hydroxyl ammonium ion would qualify as a potential eluting agent, but its strong reducing action prevents its use in the presence of AMP. It is possible that these ions are too large to fit into the crystal lattice space between two AMP molecules. Their ionic diameters are not known, but one can estimate the diameters of the nonsolvated free bases from the reported bond lengths.<sup>3</sup>



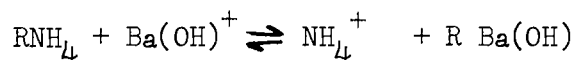
These diameters would permit incorporation into the AMP lattice, but once protonated and solvated their sizes are apparently larger, since they did not elute Cs after several column volumes. It should be noted that salts of the heteropolyacids have been prepared from organic bases<sup>20</sup> such as 8-quinolinol. Although Cs has shown a favorable distribution ratio in batch determination employing long contact times with AMP, the exchange is believed to take place on the surface only and the Cs is readily eluted with a few column volumes of dilute ammonium nitrate solution. So it is likely that other salts could be formed with different organic bases, but the problem is fitting an ion into the AMP lattice once it has formed, and not the formation of a new ion exchange material.

In reviewing all known metal cationic diameters it is noted that only francium has a diameter larger than Cs. Unfortunately Fr does not exist as a stable isotope and the use of active Fr would interfere with the final Cs determination unless counted by gamma spectroscopy, which would defeat the purpose of this work. Another possibility considered was the use of barium as an eluting agent. An exchange between barium and AMP has been observed<sup>21</sup> and is believed to take place via a monovalent hydroxide complex:





and the exchange reaction is:



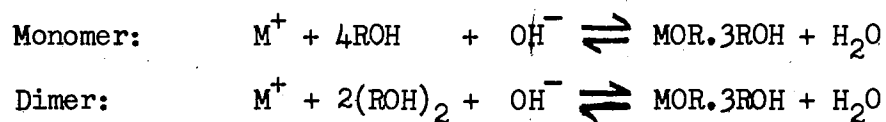
This mechanism explains the observed dependency of barium absorption on both hydrogen and ammonium ion concentrations<sup>21</sup>. Such a mechanism would require both low  $\text{H}^+$  and  $\text{NH}_4^+$  concentrations since the stability constant for the  $\text{Ba}(\text{OH})^+$  complex is quite low ( $\log K = 0.7 @ \text{pH} = 3$ )<sup>21</sup>. Elution curves show that barium can be eluted with dilute  $\text{NH}_4\text{NO}_3$ ; therefore barium cannot be used to elute potassium, rubidium, or cesium.

In summary, the use of new eluting agents for cesium on AMP did not appear fruitful and other means had to be used to collect cesium in a form suitable for counting.

#### Solvent Extraction Using BAMBP

BAMBP extraction systems have been studied by Oak Ridge scientists<sup>4,24</sup> with a view toward applying them to the removal of fission products from nuclear fuel. It was thought that this reagent could be utilized for the extraction of Cs from strongly alkaline solutions containing as much as 10 grams of AMP. The dissolution of AMP by a strong base such as NaOH would reduce the time and volume required to remove the Cs as already pointed out. BAMBP can be classified as a hindered phenol, with a slight solubility in aqueous alkali, limited association through hydrogen bonding, and predominance of the dimer as the principal species. Alkali metal extraction by BAMBP involves cation exchange with a phenolic proton to form an alkali phenolate, which is solvated with additional phenol molecules. At high hydroxide concentrations, water is also extracted since it

competes with the phenol molecule as the solvating species. The degree of extraction of the alkali ions decreases rapidly with decreasing ionic size. Extraction measurements<sup>4</sup> have shown an inverse first-power dependence upon the  $H^+$  concentration in the pH range 7.6-10.6 and a third-power dependence upon the concentration of BAMBP in the range 0.1-1 M. The extraction depends upon the equilibrium between the monomer and dimer of BAMBP, which, as expected, has been found to depend upon the concentration of BAMBP.



At formal concentrations of BAMP greater than 0.6 M the dimer predominates. One also sees here that increasing the hydroxide concentration would shift the equilibrium to the right. The ability of BAMBP to extract Cs preferentially over the other alkali metals is thought to be due to the smaller hydration energy that has to be overcome. The mole ratio Cs:BAMBP has been found to be 1:4 in the organic phase<sup>4</sup>, as shown by the equations.

The distribution of Cs and Rb between 0.5 M BAMBP in kerosene and 1 M NaOH was investigated. In Figure 6, the distribution ratios are shown vs. pH for the above system. A value of 0.5 was found for the slopes of these lines. The use of 6 M NaOH solutions resulted in a dark viscous third phase with reduced distribution ratio. This phase is thought to have contained hydrated sodium ions and BAMBP. The BAMBP was evidently consumed in the extraction of sodium and an insufficient concentration for Cs extraction was left. Whether BAMBP would extract Cs in the presence of a large amount of AMP was then investigated.

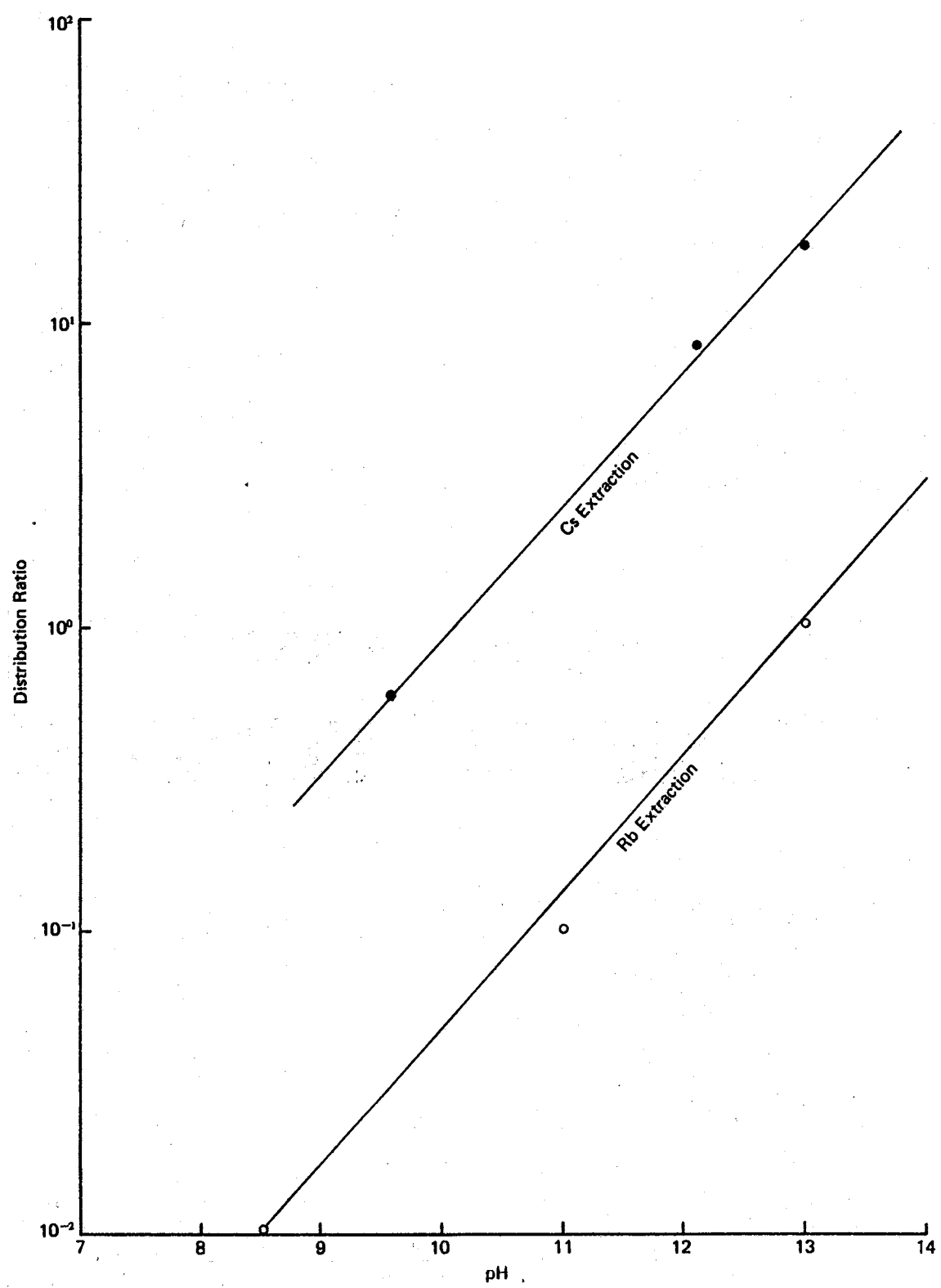


Figure 6 DISTRIBUTION RATIOS Vs pH FOR <sup>137</sup>Cs EXTRACTION BY .5M (BAMBP)

It was found that 20-30 ml of 6 N NaOH was sufficient to dissolve 10 grams of AMP and a series of these samples were prepared with the pH adjusted from 7 to 13. It was found that Cs was indeed extracted, the bulk of the AMP being left in the aqueous phase. There was no third phase observed. The distribution ratio was at maximum for both Cs and Rb at pH 12.5, with values of 10 and 1 respectively.

Undoubtedly this extraction can be optimized by increasing the BAMBP concentration and using diluents other than kerosene. For instance it has been reported<sup>4</sup> that cyclohexane provides larger D' values. For the present work, the use of 0.5 M BAMBP in kerosene and the aqueous phase at a pH of 12.5 appeared adequate. A distribution ratio of 10 for Cs requires multiple extraction to achieve adequate recovery, however. From the relationship:

$$\% \text{ extracted} = \left[ \frac{D'}{D' + \frac{V_{aq}}{V_{org}}} \right] \times 100$$

$$\text{where } D' = \text{Distribution ratio} = \frac{\sum [M^+]_{org}}{\sum [M^+]_{aq}}$$

and  $V_{aq}$  = volume of aqueous phase

$V_{org}$  = volume of organic phase

the number of extractions required for a certain recovery can be calculated.

$$\frac{W_n}{W_o} = \left( \frac{V_{aq}}{D'V_{org} + V_{aq}} \right)^n$$

where  $W_n$  = weight of solute remaining after n extractions

$W_o$  = initial weight of solute in aqueous phase.

Thus, if the desired recovery is 98%, D is 10 and if  $V_{aq}$  and  $V_{org}$  are

40 and 10 ml respectively, the number of extractions becomes three.

#### Recommended Procedure

To a measured volume of urine (up to 2 liters have been handled successfully), add 20 ml of concentrated  $\text{HNO}_3$ . Dissolve the white residue in distilled water (one-half the original volume) and adjust the solution to a pH of 1, using  $\text{HNO}_3$ . Prepare the ion exchange column by using 10 grams of AMP and 5 grams of asbestos. Make this mixture into a slurry with 0.1M  $\text{NH}_4\text{NO}_3$  and pour onto a 6.25-cm<sup>2</sup> by 50-cm column. A wad of glass wool at the bottom and finally one at the top of the column were found to be beneficial in preventing loss of AMP and entrainment in the solution to be added. Allow the AMP and asbestos to settle for several hours, then add the sample to the column in portions, maintaining a flow rate through the column of about 3 ml per minute. Allow the column to drain, then elute interfering elements using two 100-ml portions of 4 M  $\text{NH}_4\text{NO}_3$ . Add 6 M NaOH in 10-ml portions until the AMP is completely dissolved. Collect each portion in a 125-ml separatory funnel. It should be noted that NaOH will dissolve the AMP by percolating it through the undisturbed column but smaller volumes can be obtained by breaking up the partly dissolved bed with a glass rod, to allow greater contact. The solution is now adjusted to a pH of 12.5 using  $\text{HNO}_3$  or NaOH as required. Extract the sample 3 times with 10-ml portions of 9.5 M BAMBP in kerosene. For a Cs measurement by beta count, the organic phases can be combined and back-extracted into strong acidic solutions. Final transfer is to a steel counting planchet using a small dropper, each portion being evaporated under an infra red lamp. Alternatively,

if gamma activity counting is employed, the total organic phase can be counted directly. The recovery using this procedure was found to be 93% of the activity added initially. The small Cs loss is attributed to solution transfers and possibly adsorption of Cs on glass or asbestos surfaces.

The gamma energy spectra of  $^{137}\text{Cs}$  following analysis is compared with the energy spectra of the  $^{137}\text{Cs}$  standard solution in Figure 7.

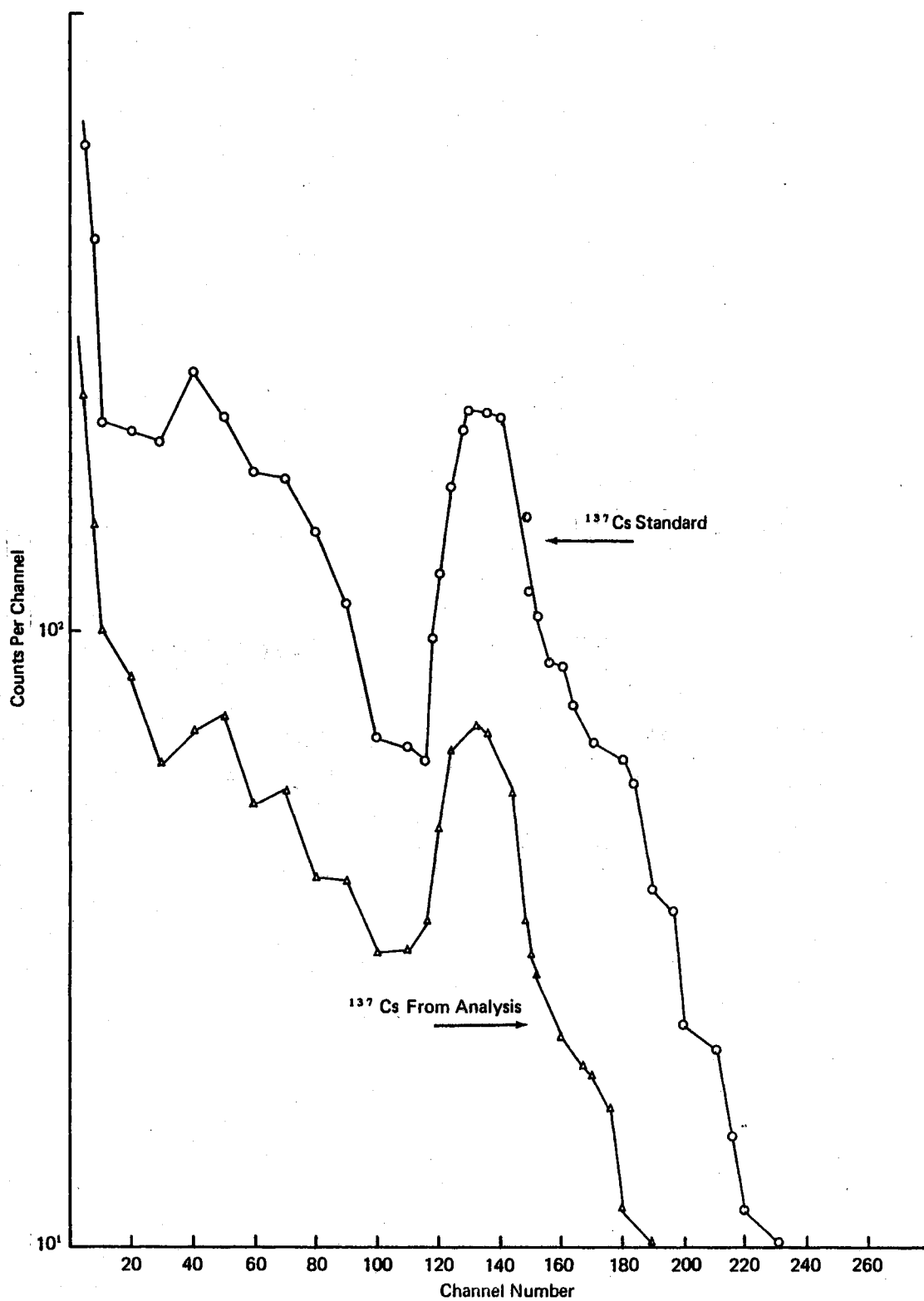


Figure 7 GAMMA ENERGY SPECTRUM OF  $^{137}\text{Cs}$  AFTER ANALYSIS

## CHAPTER V

### CONCLUSIONS AND RECOMMENDATIONS

An analytical procedure has been developed for the determination of  $^{137}\text{Cs}$  in biological materials. Application of the procedure was demonstrated on human urine. In arriving at a final procedure, the literature was reviewed for ion exchange and solvent extraction systems that might be applied with modifications to the problem at hand. The ion exchange material chosen for study was ammonium molybdophosphate since its usefulness in separating the alkali metals had been demonstrated on samples of low ionic strength. The structure of AMP was considered in order to determine a basis for its exchange properties. The ion exchange properties of AMP were found to depend upon ionic size of an exchangeable univalent metal,  $\text{NH}_4^+$  solution concentration, and pH. A column design calculation was made in order to determine the necessary conditions to effect a good separation of cesium and rubidium. Even though rubidium concentrations are quite low in biological samples, a good separation would require complete removal of  $^{40}\text{K}$  and other interfering activities. The theoretical calculations were useful and a trial elution of  $^{137}\text{Cs}$  and  $^{86}\text{Rb}$  resulted in good correlation with them. Distribution ratios were obtained using raw and ashed urine samples and were found to be surprisingly large in comparison with published values. Column parameters and procedures were adjusted to give a maximum rubidium



contamination of 0.01%. Several elutions were performed showing excellent separation. Because of the large D values obtained for cesium, unsuitably large quantities of saturated  $\text{NH}_4\text{NO}_3$  were required for elution. Other eluting agents were considered and tried in order to improve the efficiency of elution of cesium but were not fruitful. The solvated methylammonium ion is possibly too large to fit into the AMP lattice. In order to collect the cesium from the column in reasonable volume, a BAMBP extraction system was investigated. The AMP containing cesium was dissolved in strong base and the solution equilibrated with 0.5 M BAMBP in kerosene. Fortunately, AMP did not interfere. Rubidium was extracted only one-tenth as much as Cs, which further reduces any possible rubidium contamination. A final procedure was described for urine samples. It is believed that this method can be applied to a host of biological and environmental samples, and these applications can be tested quickly by batch equilibration of AMP with the sample in question.

#### Recommendations

1. AMP is a valuable ion exchange material for the alkali metal ions. Its application to other biological and environmental samples should be investigated.
2. Large sample volumes take a long time for percolation through the column so ways to improve flow rates without loss of resolution should be investigated.
3. The size and solvation energies of exchangeable ions on AMP should be investigated and a systematic search for new eluting agents be continued.

4. The solvent extraction of Cs from strongly basic solutions containing AMP should be studied in an effort to improve the distribution ratio. It is believed that there are optimum hydroxide ion and BAMBP concentrations as well as a host of non-polar solvents to try as the BAMBP carrier.

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VITA

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