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Sections C-III and C-IV

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FINAL REPORT

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Robert Thayer 1/21/95
Arnold J. Just 1/25/95
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THE EXTRACTION, CONCENTRATION AND DECONTAMINATION
OF Ba¹⁴⁰ FROM URANYL NITRATE
SOLUTIONS BY AN ADSORPTION PROCESS

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Experimental Work by: J. Schubert, J. V. Richter, and R. A. Duckett
of C-III, and W. E. Cohn, E. R. Tompkins,
J. X. Khym, S. Weiss and J. Teresi of C-IV.

Report Prepared by: J. Schubert

Report Submitted by: G. E. Boyd, W. E. Cohn and T. H. Davies

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ABSTRACT

An all-adsorption process has been developed for the extraction, concentration and decontamination of Ba^{140} from active uranyl nitrate solutions, and its chemical feasibility has been demonstrated on a laboratory scale. In a series of six flowsheet-test experiments consisting of an extraction cycle followed by two concentration-decontamination cycles an average over-all yield for Ba^{140} of 87% was obtained. This recovery was accompanied by a 200-fold total volume reduction and a removal of gamma-ray emitting contaminants to less than 0.5% of their initial amounts. A preliminary flowsheet for the large scale production of Ba^{140} has been presented.

The basic principles of this separations procedure are shown to be: (a) the selective ion-exchange adsorption of barium by one of the new resinous zeolites; (Amberlite IR-1), followed by: (b) the selective desorption and re-adsorption of Ba caused by its complex ion formation in ammonium citrate - citric acid solutions. Batch-type adsorption measurements and dynamic column studies have shown that both the equilibrium point and the rate for the adsorptions are favorable. In addition, a number of other important design features and results are discussed.

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I. INTRODUCTION

It is convenient to consider the adsorption process^{1,2} for the preparation of Ba¹⁴⁰ as consisting of three distinct operations; these are (1) extraction of the Ba from the UNH, (2) concentration, and (3) decontamination. Actually steps (2) and (3) are carried out nearly simultaneously so for the present they will be treated as a unit.

¹ The process for Ba extraction is genetically related to the all-adsorption process for the preparation of Pu as developed by the members of Section C-III, see, for example, CN-489, CN-1859.

² An all-adsorption method has been employed by W. E. Cohn and group to prepare curie amounts of Ba and Sr from UNH solutions (see 225-X77C). A flowsheet for the extraction and isolation of Ba¹⁴⁰ in 300 curie amounts has been presented in a memo to C. D. Coryell from W. E. Cohn, dated 11/4/44. However, information given with regard to volume reduction was not correct. From the results of the studies described in this report, the writer has introduced additional modifications as well.

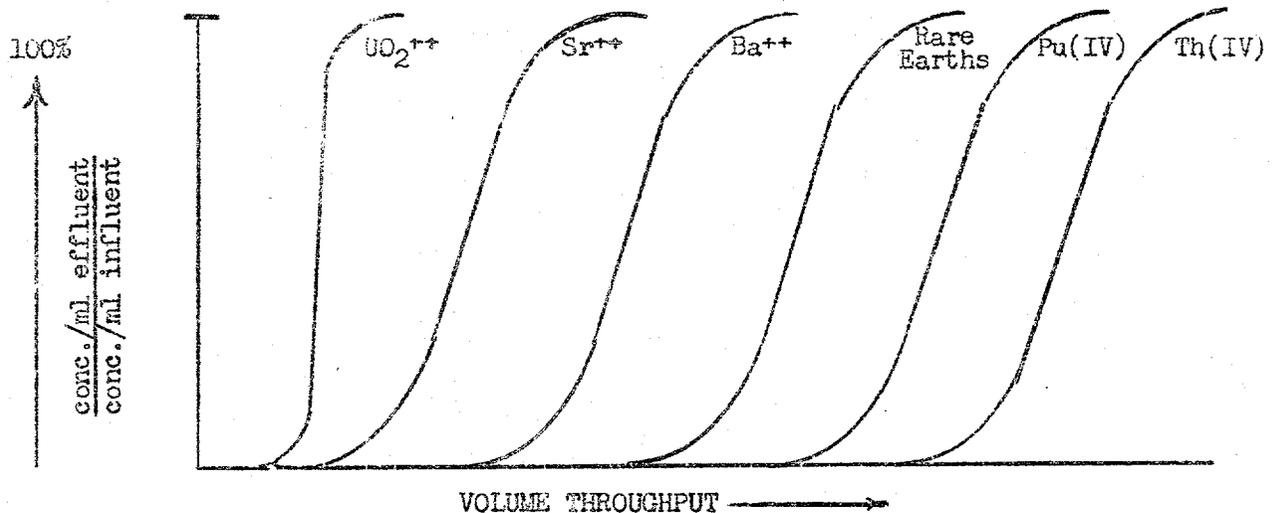
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II. QUALITATIVE DISCUSSION

(A) Extraction Step

When a solution of uranyl nitrate containing fission products is passed³ through a column packed with IR-1, nearly complete extraction of all the cations present except UO_2^{++} takes place through exchange with whatever cation is originally present in the exchanger⁴ and when the capacity of the bed for any single cation is reached then "breakthrough" occurs. The shape of the breakthrough curve and the point at which it occurs may be expressed as a function of two variables in the Schumann-Fumas theory and it may be shown that these are dependent upon chemical as well as physical factors.

It is found that the greater the adsorption affinity of a radioelement from UNH as determined, for example, from batch equilibrium experiments, the more delayed will be its breakthrough. Schematically the breakthrough of some cations from UNH is shown in Figure 1.



SCHEMATIC BREAKTHROUGH OF TRACER CATIONS IN UNH FROM BED OF AMBERLITE IR-1

FIGURE 1

³ Some of the terminology in common usage are as follows: (taken in part from Webster's "International" Dictionary) (a) ELUTE - to wash out; (b) ELUTION - the separation of material by washing; (c) ELUATE - collectively, the washings obtained by elution; (d) ADSORPTION - we will employ this term to describe the retention or extraction of cations by the ion exchanger; though it is understood ion-exchange is not a purely surface concentration phenomenon; (e) ADSORB - to hold by adsorption; (f) DESORB - has sometimes been used interchangeably for ELUTE; (g) EFFLUENT - that which flows out; (h) INFLUENT - that which flows in.

⁴ A discussion of the nature of Amberlite IR-1, its stability toward chemicals and radiation, and the principles governing its exchange equilibrium is given in CN-1873. The dynamics of ion-exchange adsorption are treated at length in CN-1859.

In the extraction of Ba¹⁴⁰, the UNH solution is allowed to trickle through the resin bed and the volume is regulated so that a minimum of barium is lost via breakthrough. The adsorbed UO₂⁺⁺ is eluted readily by washing with dilute H₂SO₄. The concentration of H₂SO₄ is not sufficiently high to remove the more strongly held Ba⁺⁺. Then, the Ba is eluted from the resin bed together with the other fission products by 5% citric acid at pH 6. The citric acid is quite effective in removing the adsorbed Ba because of the formation of a stable complex ion⁵.

(B) Concentration and Decontamination⁶

The pH of the 5% citric acid barium containing eluate is adjusted with hydrochloric acid to a pH of 2.5 and diluted ten fold. From such a solution the capacity of the exchanger is so great that a bed only one-tenth the volume required in the extraction step is used. The adsorbed activities consist of the alkaline earths and the rare earths. It was found that a 5% citric acid solution adjusted to a pH 3 will preferentially elute the rare earth activities. Hence, most of the unwanted gamma emitters are separated away from the Ba in this step. Subsequently, the Ba is eluted in a small volume (~3 column volumes) with 5% citric acid at pH 6.

⁵ J. X. Klym is responsible for the important observation that adjustment of the pH of citric acid solutions allows one to obtain efficient removal of adsorbed cations and specific separations as well from columns of IR-1.

⁶ These steps were established from experiments carried out by members of W. E. Cohn's group under the direction of E. R. Tompkins and G. W. Parker.

III. PRESENTATION OF FLOWSHEETS

In Flowsheet I is given the complete operations exactly as they were carried out for the processing of a fifth of a slug of U metal (.23 kgm). Four reproducibility cycles were run⁷. It was realized at the time, that while the operating conditions may not have been optimum, it was desirable to demonstrate the utility of the adsorption process. Additionally, the flowsheet operation was expected to yield information necessary to the design of more effective conditions.

Two additional cycles were run⁸ for the purposes of determining the gamma decontamination factors. These latter two cycles were operated with a few changes from the previous four, as noted in Table I which lists in detail the behavior of Ba in each step of the process. The overall average yield for the six runs is 87%.

Flowsheet II has incorporated in it the modifications which the small scale operations have suggested. In addition, the concentration of the starting UNH solution has been increased to 20 weight percent. The changes that have been made are based on experimental evidence as well as by calculating the operating characteristics, namely, breakthrough, from the Schumann constants. The flowsheet is also oversized by about ten percent in order to provide a maximum recovery of Ba.

Actual conditions of operation are highly flexible so that many variations from the designated flow rates, dilution factors and pH, for example, are possible without affecting the yield. A quantitative discussion utilizing the terms in the Schumann equation is given later.

⁷ Experimental work by E. R. Tompkins, J. Teresi, J. X. Khym and W. E. Cohn; analyses by J. W. Richter and Miss R. A. Duckett.

⁸ Experimental work by J. Teresi, J. Richter and J. Schubert. Fission product analyses for La, Zr and Cb made by Analytical Division.

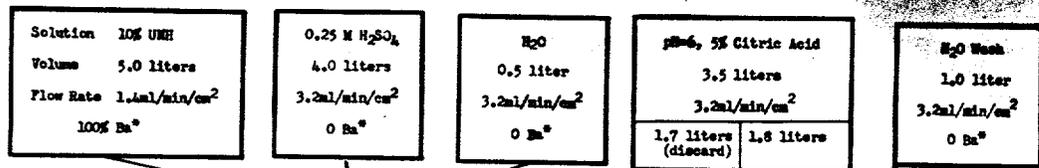


In general one may state that considerable latitude in flow rates is permissible. The process may be interrupted at any stage, the bed flushed with water, and the operation continued when convenient. The metering of the water which is needed to dilute the 5% citric acid to 1/2% for the concentration step is not critical because it is known from experiment that one gets just as efficient concentration from dilutions as low as 8 fold. Any dilution greater than tenfold actually results in more efficient adsorption. In addition a pH range of at least 1.8 units may be allowed, that is from 2.3 or less up to a maximum of 3.5.

It may be pointed out that Ba which may remain on the column from one cycle is retrieved in a subsequent cycle as can be seen from the extra high recovery observed in cycle 4, Table 1. The extraneous gamma activity was reduced to such a low value that accurate analyses were not possible. However, figures available for Zr and Cb indicated that these elements were reduced to less than 0.1% of their original value.

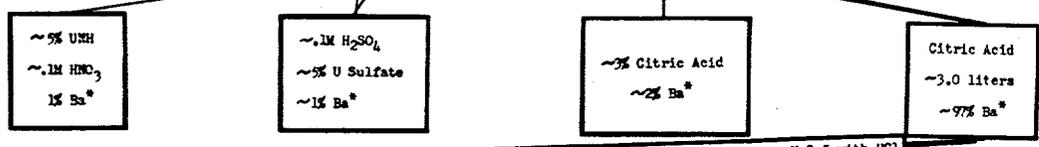
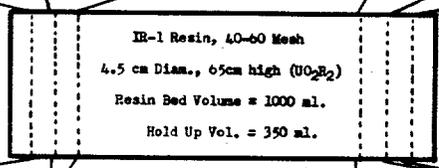
There are certain obvious variations in operation which may be made. For example, in the extraction step it may be desirable to operate a battery of columns, so that while one column is being loaded another is being stripped. Finally, the rare earth eluates, for example, may be stored after adjustment of pH, on a small column, thus simplifying storage problems.

Flow Sheet for the Extraction and Concentration of Ba⁺ from UNH on a Fifth of a Slug Scale. Yields Reported Averaged from 4 Cycles

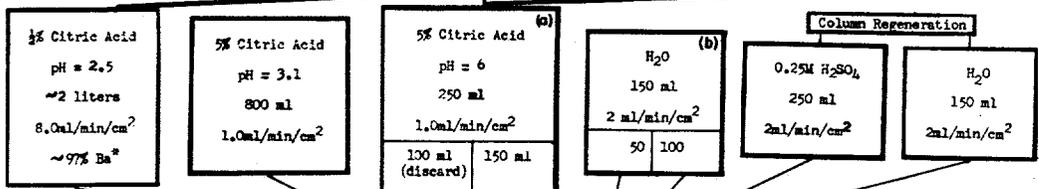


Extraction Step

Operation time about 8 hours

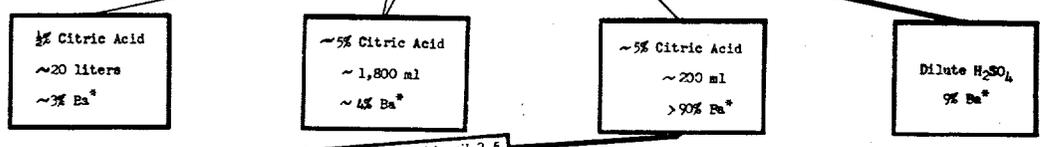
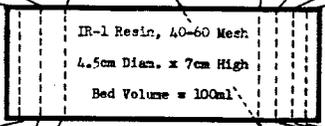


Diluted to 1/2% Citric Acid, Adjust to pH 2.5 with HCl

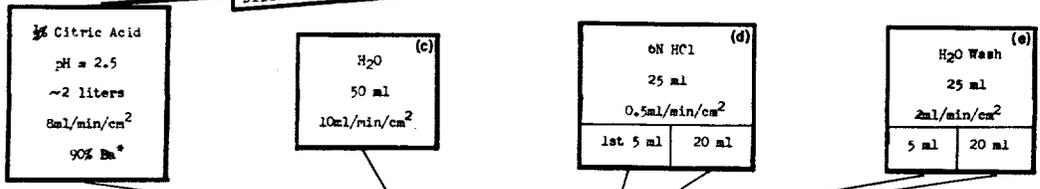


First Concentration Step

Operation time about 4 hours

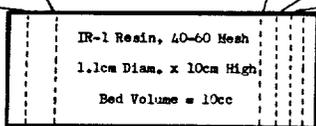


Diluted to 1/2% Citric Acid, pH 2.5



Second Concentration Step

Operation time about 4 hours

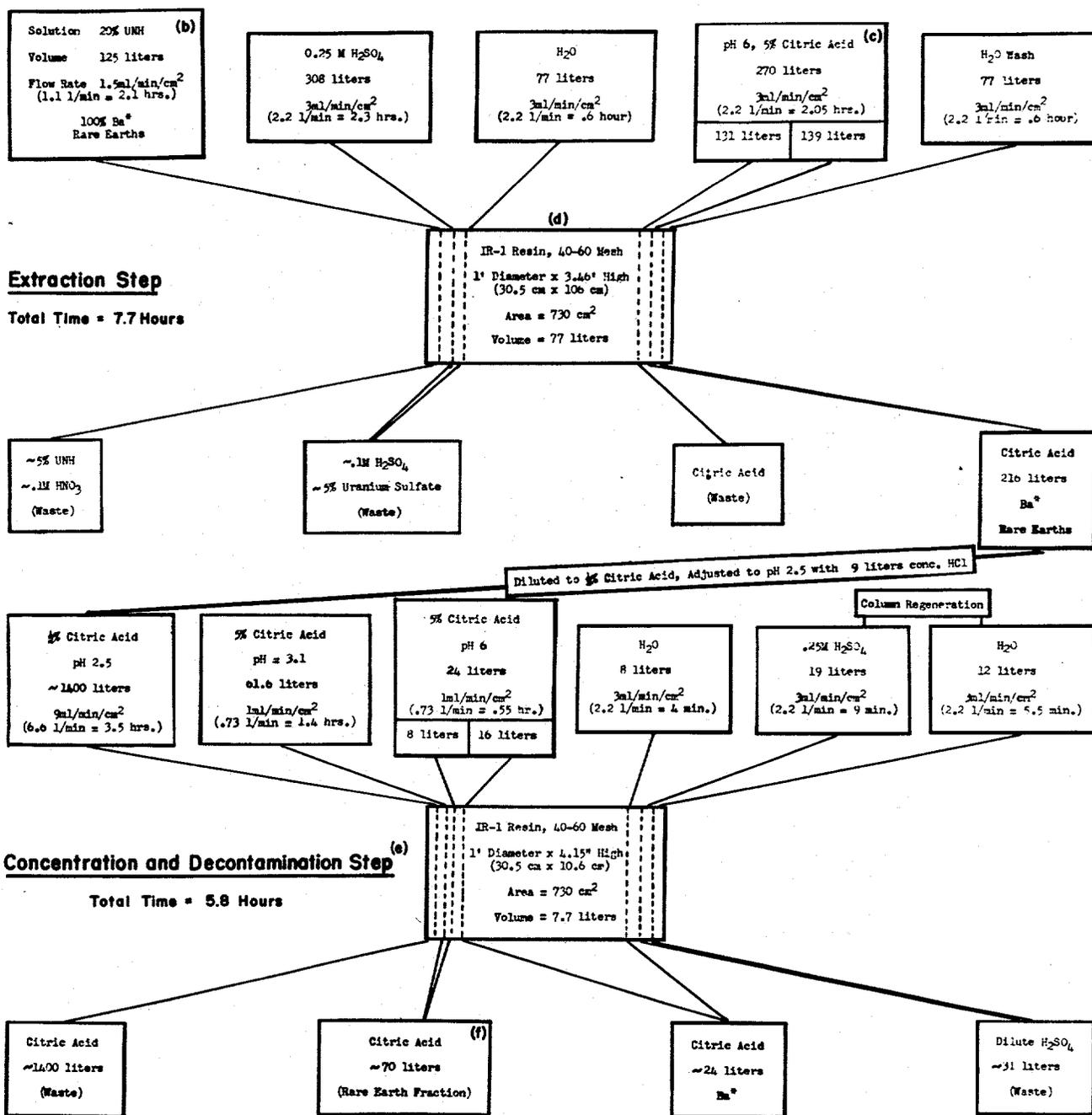


NOTES AND REMARKS: (a),(b) The volume of pH 6 citric acid should be increased to 300 ml (discard volume kept at 100 ml) and the subsequent water wash (b) added to (a); thus the % loss from (b) would be avoided.
(c) Another pH 3 wash can be inserted to increase the decontamination factor if desired.
(d),(e) The HCl was used for convenience. The H₂O washings are best combined with the effluent from (d).

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Flow Sheet II

Flow Sheet for the Extraction, Decontamination and Concentration of Ba* from 12 Slugs of U as Uranyl Nitrate.^(a)



NOTES: (a) Designed for 12 slug batches, each slug of uranium weighing 1.16 kgs. and contains ~0.3 mg. chemical barium.

(b) Density of 20 weight per cent UNH = 1.165, pH about 2.

(c) Concentration of citric acid given in volume per cent of the monohydrate citric acid. The pH is adjusted with NH₄OH.

(d) Volume of resin bed increased by 10%, that required for a/c₀ = .10. Mesh of resin given on basis of dry classification. One cc. of bed volume equals about 0.5 gm. dry resin. Liquid holdup of resin bed is approximately one-third bed volume.

(e) Repeat as many times as may be desired, each cycle uses a resin bed volume one-tenth that used in the preceding cycle until desired volume reduction attained.

(f) Stored on a resin column after adjustment of pH to 2.5.

TABLE I

SUMMARY OF BEHAVIOR OF Ba¹⁴⁰ IN THE INDIVIDUAL STEPS OF THE ADSORPTION PROCESS^a

Run No.	Extraction Step: % of Total Initial Ba in Given Eluate		Leadings and Tailings from Citric Acid Solution	1st Concentration Step: % of Total Initial Ba in Given Eluate			2nd Concentration Step: % of Total Initial Ba in Given Eluate		6 N HCl (overall yield) Observed
	H ₂ SO ₄ + H ₂ O Wash	5% Citric Acid, pH6		5% Citric Acid, pH2.5	5% Citric Acid, pH 3.1 and Tailings from pH 6	5% Citric Acid, pH6	5% Citric Acid, pH2.5	5% Citric Acid, pH3	
1	0	75	6.6	0.8	6.3	80.5	0.3	This step omitted	71
2	0.3	---	---	3	15	88.5	0.85	"	87
3	<1	102	0.5	4.6	5.9	102	---	"	97
4	<1	133	1.6	4.9	14.8	---	---	"	92
AVG.	ca 0.5	103	ca 3	3	11 ^b	90	0.5	"	87 ^c
A	0.8	93	0.1	0.6	7	92.1	1.4	1.7	89
B	0.1	98.5	0	5	3.5	92.6	2.7	5	86
AVG.	0.5	95.8	0.05	2.8	2 ^d	92.4	2	3.4	87.5

^aRuns made on fifth of a slug basis as shown in Flow Sheet I.

^bThe bulk of this activity came from the tailings of the subsequent pH 6 wash. The latter wash was 20% too low in volume. The volume was increased in cycles A and B with a resultant decrease in loss of Ba from this source.

^cDirect analysis of a combined mixture from the four cycles gave a yield value of 89%.

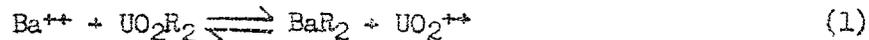
^dSee (b)

IV. QUANTITATIVE DISCUSSION

a. Extraction Step

1. Batch Equilibrium Studies:^{9,10} Adsorption of Ba from UNH.

The adsorption of Ba from UNH may be considered to take place with the uranyl form of the exchanger. We may write for the equilibrium:



where R is the monovalent behaving anionic part of the exchanger. The equilibrium constant for the reaction is:

$$K_c = \frac{N_{\text{BaR}_2} \times {}^m\text{UO}_2^{++}}{N_{\text{UO}_2\text{R}_2} \times {}^m\text{Ba}^{++}} \quad (2)$$

where N represents the mol fraction in the solid, and m the concentration in the solution in moles per 1000 gms of water. In exchange involving radio Ba it is apparent that $N_{\text{UO}_2\text{R}_2} = 1$, and since $\text{UO}_2\text{R}_2 \gg \text{BaR}_2$ the mol fraction $\frac{{}^m\text{BaR}_2}{{}^m\text{UO}_2\text{R}_2 + {}^m\text{BaR}_2}$ is simply equal to $\frac{{}^m\text{BaR}_2}{{}^m\text{UO}_2\text{R}_2}$, hence

$$K_c = \frac{{}^m\text{BaR}_2 \cdot {}^m\text{UO}_2^{++}}{{}^m\text{UO}_2\text{R}_2 \cdot {}^m\text{Ba}^{++}} \quad (3)$$

and

$$K_a = K_c \times \left(\frac{\gamma_{\pm}^{\text{UO}_2(\text{NO}_3)_2}}{\gamma_{\pm}^{\text{Ba}(\text{NO}_3)_2}} \right)^3 \quad (4)$$

where γ_{\pm} represents the mean activity coefficients of the ions in solution.

⁹ The experimental and theoretical background of the material given here is discussed in CN-1873.

¹⁰ Experimental work done by J. W. Richter.

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The value of the activity coefficient ratio approaches unity as the ionic strength, \mathcal{M} , of the solution approaches zero. A plot, therefore, of K_c vs. ionic strength or some function of the concentration will, upon extrapolation to infinite dilution, yield a value of K_a as shown in Fig. 2. Since the extrapolation is made from a part of the curve where experimental error is the greatest, the value of K_a can only be considered as approximate.

From the value of K_a we are enabled to calculate the mean activity coefficient of the tracer $\text{Ba}(\text{NO}_3)_2$. From (4) we have¹¹

$$\gamma_{\pm\text{Ba}(\text{NO}_3)_2} = \left(K_c / K_a \right)^{1/3} \times \gamma_{\pm\text{UO}_2(\text{NO}_3)_2} \quad (5)$$

The plot of γ_{\pm} vs. ionic strength is given in Figure 3. The known activity coefficients of pure $\text{Ba}(\text{NO}_3)_2$ and pure $\text{UO}_2(\text{NO}_3)_2$ are also given; thus illustrating the general effect that a bulk salt exerts on a foreign electrolyte which is present, in effect, at zero concentration.

In table II are given the values of K_c at different concentrations. The values recorded were read off the best smoothed curve through the experimental data which were precise to $\pm 5\%$.

¹¹ The presence of traces of other salts, do not affect the γ_{\pm} of UNH since the bulk of the ionic strength is entirely due to the UNH.

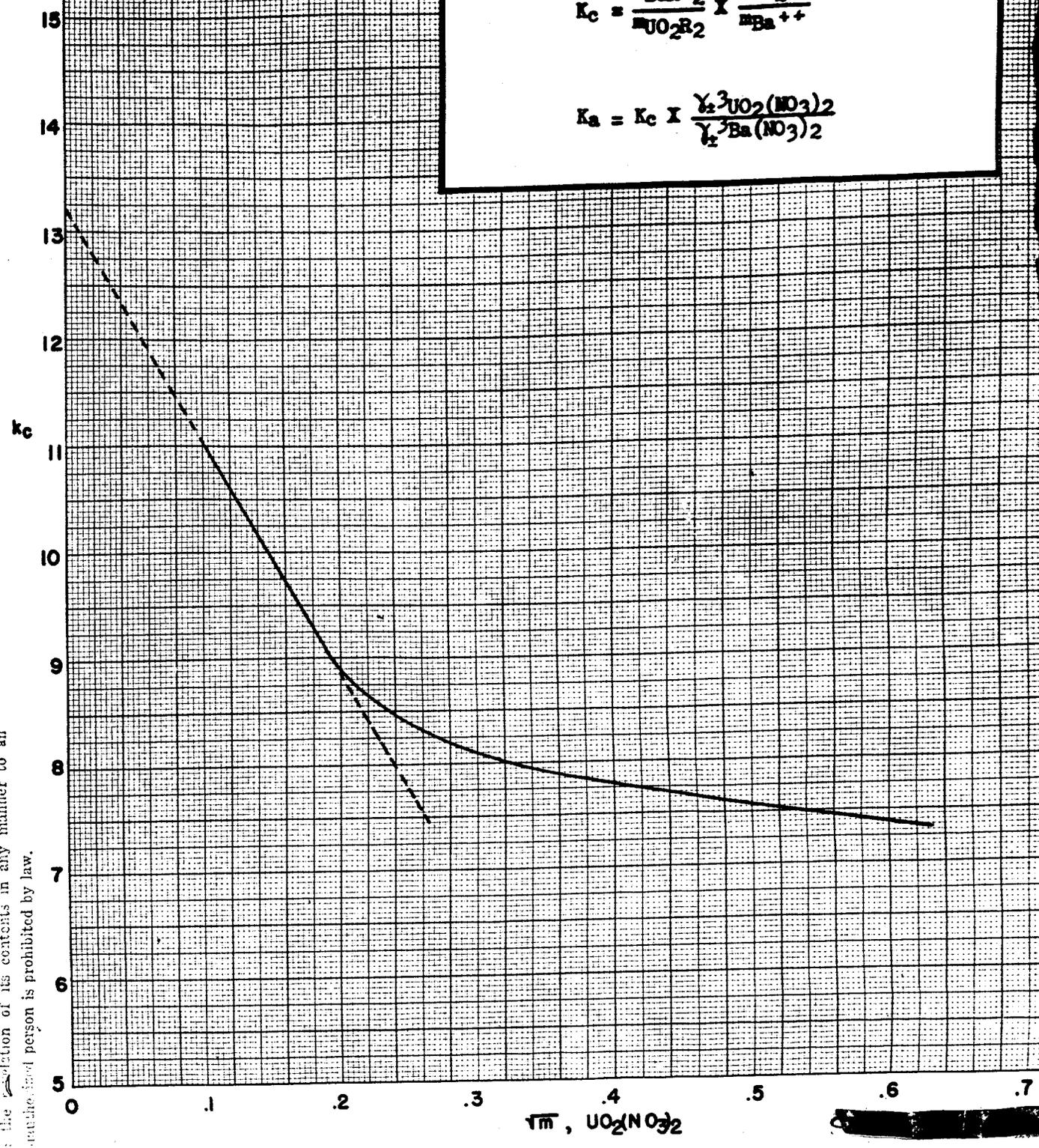
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Fig. 2
 Variation of Equilibrium Constant, K_c ,
 with Concentration for Reaction ($t = 25^\circ\text{C}$)



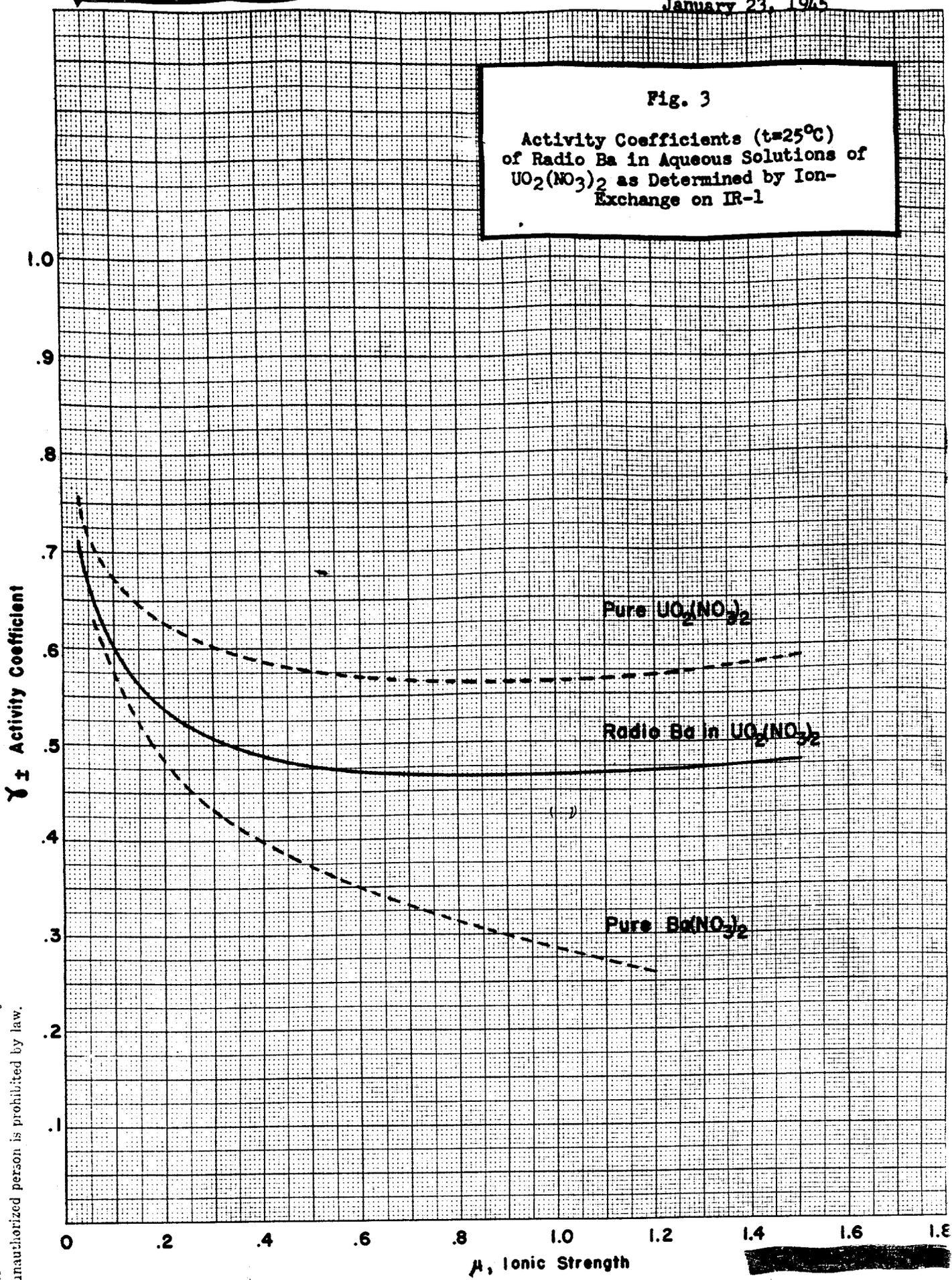
$$K_c = \frac{m_{\text{BaR}_2}^2}{m_{\text{UO}_2\text{R}_2}} \times \frac{m_{\text{UO}_2^{++}}}{m_{\text{Ba}^{++}}}$$

$$K_a = K_c \times \frac{\gamma_{\text{UO}_2(\text{NO}_3)_2}^3}{\gamma_{\text{Ba}(\text{NO}_3)_2}^3}$$



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Fig. 3
Activity Coefficients ($t=25^{\circ}\text{C}$)
of Radio Ba in Aqueous Solutions of
 $\text{UO}_2(\text{NO}_3)_2$ as Determined by Ion-
Exchange on IR-1



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TABLE II ^aEQUILIBRIUM DATA FOR THE REACTION $\text{Ba}^{++} + \text{UO}_2\text{R}_2 \rightleftharpoons \text{BaR}_2 + \text{UO}_2^{++}$

Molality (UNH) m	Ionic Strength μ	K_c	$\gamma_{\pm\text{UNH}}^b$	$\gamma_{\pm\text{Ba}(\text{NO}_3)_2}^c$	Calculated for Tracer in UNH $\gamma_{\pm\text{Ba}(\text{NO}_3)_2}$
0	0	13.2(ext.)	1.0	1.0	1.0
.01	.03	10.8	(.76)	.71	.71
.02	.06	10.0	(.72)	.63	.66
.04	.12	8.95	(.66)	.55	.58
.06	.18	8.4	(.63)	.50	.54
.08	.24	8.15	(.615)	.46	.52
.10	.30	8.0	.60	.43	.51
.2	.60	7.7	.57	.35	.47
.3	.90	7.55	.565	.30	.47
.4	1.2	7.3	.57	.26	.47
.5	1.5	7.05	.59	(.24)	.48

^a Values for K_c read off best smoothed curve through experimental data, observed average deviation $\pm 5\%$. Activity coefficient data given in parenthesis are extrapolated values.

The UO_2R_2 contained 1.19 m. mol UO_2^{++} per gram dried UO_2R_2 . The air dried UO_2R_2 contained 15.5% H_2O as moisture, mesh size, 60-80.

^b Robinson, et al., J. Am. Chem. Soc., 64, 1469 (1942)

^c H. S. Harned and J. C. Herker, Ibid, 55, 4838 (1933)

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Thus, the distribution is sufficiently in favor of the Ba so that the extraction can be expected to be quite efficient.

Effect of Hydrogen Ion Concentration

Up to a concentration of 0.15 M of free HNO_3 in 10% or 20% UNH there was little or no effect on the adsorption of Ba. With 0.2 M free HNO_3 , however, there appeared to be about a 15% decrease in capacity. In practice, it is preferable to keep the free HNO_3 as low as possible in order to minimize any chemical action on the resin. (See Appendix I, CN-1873).

Effect of Added Citric or Acetic Acids

Concentrations as high as 0.8 M of citric or acetic acids had no effect, within experimental error, on the adsorption of Ba from UNH. Both substances are weak acids and are practically unionized at the natural pH of 10 and 20% UNH solutions and thus contribute nearly nothing to the effective cation concentration of the solutions.

Effect of Increasing Ba Concentration and/or Extraneous Cation Concentration

At constant UNH concentration equation (3) simplifies to:

$$\frac{m_{\text{BaR}_2}}{m_{\text{Ba}^{++}}} = \lambda = K_c m_{\text{UO}_2\text{R}_2} \quad (6)$$

Now the efficiency of removal of Ba (i.e. % adsorbed for a given volume of solution and weight of exchanger) will remain unchanged as long as no appreciable change in the quantity $m_{\text{UO}_2\text{R}_2}$ takes place. When only radiochemical quantities of Ba are involved it is obvious that UO_2R_2 remains virtually unchanged. In the extraction step, as given in Flowsheet II we can calculate that for the ratio of solution to IR-1, the concentration of radio Ba ($\sim 10^{-11}$ M) can be increased to the order of 3×10^{-2} M with no change in the efficiency of removal.

In the same way, it can be shown that extraneous cations will have little or no influence on the Ba adsorption even if their concentration is of the order of 5% of the UNH concentration itself.

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2. Column Operation¹²

The breakthrough of Ba was studied as a function of UNH concentration and flow rate. The breakthrough characteristics were expressed in terms of the Schumann constants¹³ which are defined in the following equations:

$$k = y^v/x \quad (7)$$

where k = mass transfer coefficient, m.e./sec./cc. volume of bed/unit concentration difference between solid and liquid

v = fluid velocity, cc./sec./cm² cross-sectional area of bed

x = distance from top of column, cm. (bed depth)

further y = parameter in Schumann equation

$$h_s(1-f) = k T/Z \quad (8)$$

where h_s = storage capacity of solid, m.e./cc solid/unit concentration difference

f = fractional voids in bed (no units); = ca. 0.5 for IR-1

T = time in seconds

Z = variable in Schumann equation

Effect of UNH concentration: Figures 4 and 5

The storage capacity of the resin would be expected to vary as the inverse first power of the UNH concentration, disregarding activity effects. From Fig. 4 we have that $h_s(1-f) = 7.26$ from 0.22 M UNH. With 0.45 M UNH, all conditions of flow rate etc., being constant, $h_s(1-f) = 2.86$. This decrease in storage capacity is in agreement with that expected from the batch data as shown by calculating the storage capacity at .45 M from the data obtained with .22 M UNH. We may write, for the operational ranges involved, the expression:

¹² Experimental data by J. Schubert and J. X. Khym.

¹³ The practical application of the mathematical treatment of heat transfer to ion-exchange is described by R. H. Beaton and C. C. Furnas, Ind. Eng. Chem., **33**, 1500 (1941); an analysis of the Schumann equation as it applies to ion-exchange in radiochemical systems is given in CN-1859.

$$h_s(1-f)_{.45 \text{ M}} = h_s(1-f)_{.22 \text{ M}} \times \frac{\lambda_{.45 \text{ M}}}{\lambda_{.22 \text{ M}}} \times \frac{\eta_{.22 \text{ M}}}{\eta_{.45 \text{ M}}} \quad (9)$$

where η = viscosity in arbitrary units of the respective solutions; and λ is the slope of the adsorption isotherm as obtained from batch data. The viscosities of UNH solutions have been measured and may be found in MUC-7 DGE #196. Substituting the known values into (9) we have

$$h_s(1-f) = 7.26 \times \frac{7.2}{.45} \div \frac{7.7}{.22} \times \frac{10.0}{11.4} = 2.91$$

which is in excellent agreement with the observed values of 2.86.

The justification for inserting the viscosities¹⁴ into equation (9) may be found in the correlation which exists between the diffusion coefficient of a radio element in solution of bulk electrolyte and the viscosity. A tracer cation in UNH behaves as an uncharged particle and as such its diffusion coefficient will vary in accordance with the Stokes-Einstein relation where $D \propto 1/\eta$, as discussed in CN-2197. It should be possible, then, to calculate the diffusion coefficient of a tracer cation in concentrations of UNH greater than 0.1 M as long as D is known for one concentration and the viscosity of any other concentration of bulk electrolyte. Since this point was not explicitly shown in CN-2197 it is of interest to illustrate the validity of the assumption (Table III).

¹⁴ It should be pointed out, for example, that at infinitely slow flow rates the viscosity term would not enter; but for the ordinary flow rates employed (i.e. contact times) it provides a fair correction factor for the non-equilibrium condition of the system.

TABLE III

THE RELATION BETWEEN THE DIFFUSION COEFFICIENT^a AND
 VISCOSITY FOR TRACER CATIONS IN $UO_2(NO_3)_2$ ($t = 25^\circ C$)

Cation	Conc. UNH(moles/l)	Visc.in m.poises	Diffusion Coefficient(cm^2/day)	
			D observed	D calculated
Pu	0.48	11.8	0.29	-
Ba	.48	11.8	.37	-
Zr	.48	11.8	.22	-
Pu	1.2	18.9	.21	.18
Ba	1.2	18.9	.26	.23
Zr	1.2	18.9	.13	.14

a Assumption is made that $D \propto 1/\eta$.

The agreement between the observed and calculated diffusion coefficients is within the experimental error of the measurements.

Now, the interior of the porous gel structure of IR-1 may be expected to be permeated with channels which contain solution. If the rate of adsorption of an element by IR-1 is determined by the rate of diffusion through these liquid filled capillaries, then it follows that the relative rates of adsorption from UNH solution would be determined by these viscosities. That such appears to be the case is shown graphically on page 29 in CN-1873, where the batch rate of adsorption data for Pu is given for three different concentrations of UNH. These data show that the rate of approach to equilibrium decreases with increasing UNH concentration; however, when corrected for viscosity the rates become about equal within experimental uncertainties. In effect, this result means that the rates of adsorption in UNH would be equal if the diffusion coefficient of the tracer element were the same.

Further work would be needed to establish a relation between the mass transfer coefficient k , and D , the diffusion coefficient, namely, that $k/D = \text{constant}$.

[REDACTED]

In Fig. 4 the breakthrough curve of UO_2^{++} from 20% UNH is given, partly because the appearance of UO_2^{++} serves as a monitor.

Flowsheet II has been designed to operate with 20% UNH because of the smaller volumes necessary to obtain a given amount of radio Ba.

It is of interest to observe that excellent agreement with the Schumann theory is obtained at very low C/C_0 values as is shown in Fig. 5. The data is from the same run as given for Curve III in Fig. 4.

Effect of Flow Rate: Figure 6

In the flow rate range studied, .0347 ml/sec/cm² to .00982 ml/sec/cm² y is nearly constant while k increases with the flow rate. Thus a 3.5 fold increase in flow rate results in a 3.2 fold increase in k .

These results are of the same order of magnitude as those reported for Pu(IV) in CN-1859 .

Miscellaneous Variables

While time did not permit the direct experimental investigation of variables such as bed height, mesh size of the exchanger and the like, we can, on the basis of previous studies summarized in CN-1859, forward generalizations and estimations of the probable effect of many factors which will serve as a working guide.

(a) Mesh size

No appreciable change in y is expected while k may vary inversely as the diameter of the exchanger. It is convenient to estimate the average particle diameter as the average screen opening through which the resin particles will pass. (dry screen basis). Hence, a knowledge of the product $k \times D$, enables one to estimate breakthrough characteristics for various particle sizes with sufficient accuracy for most purposes.

(b) Bed height

As a first approximation, we can say that k and $h_s(1-f)$ will remain essentially constant while y will vary directly with bed height as given in equation (7).

[REDACTED]

(c) Bed diameter

For the operational range involved k is expected to be independent of the bed diameter.

(d) Temperature

The storage capacity will, in general, decrease with increasing temperature. Taking the behavior of Pu as typical we may expect a decrease of 1-2% for each degree rise in temperature above room temperature. On the other hand, γ and k should remain essentially constant.

(e) pH, Extraneous Cations, Ba Concentration

See discussion under batch equilibrium.

(f) Behavior of Zr and Cb

Both Zr and Cb are adsorbed as radiocolloids principally (CN-1873, CN-2197). As a result they remain adsorbed in a narrow band at the very top of the resin bed. They may be removed preferentially, following the elution of UO_2^{++} by a 1/2% oxalic acid wash. Another scheme involves passing the active UNH solution through a small by-pass column which will serve to separate and concentrate the Zr and Cb. The Zr and Cb then can be recovered by eluting in a small volume of oxalic acid. Thus, a highly active preparation of Zr and Cb can be obtained as a by-product.

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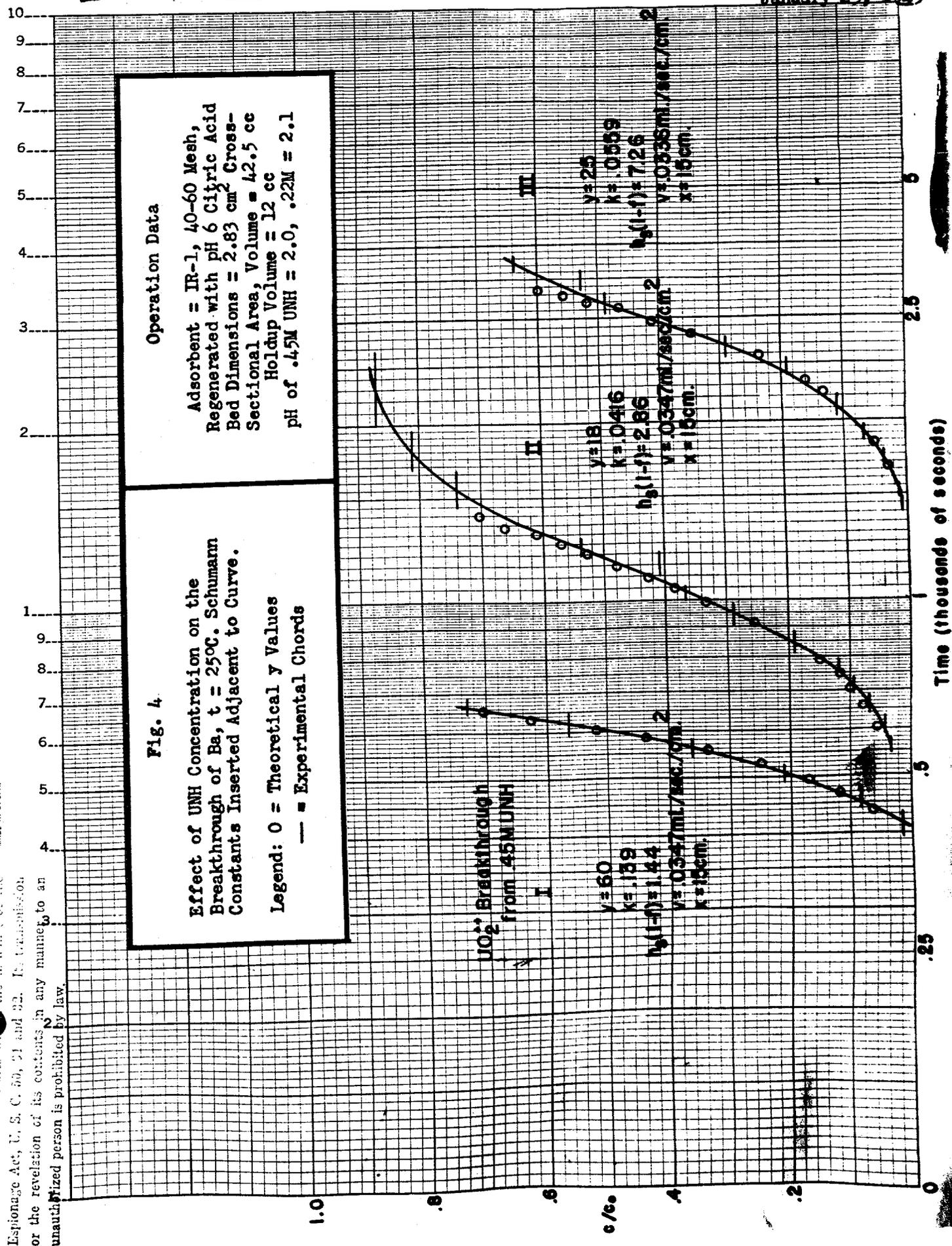


Fig. 4.
Effect of UNH Concentration on the Breakthrough of Ba, $t = 2500$. Schumann Constants Inserted Adjacent to Curve.

Operation Data
Adsorbent = IR-1, 40-60 Mesh, Regenerated with pH 6 Citric Acid
Bed Dimensions = 2.83 cm^2 Cross-Sectional Area, Volume = 42.5 cc
Holdup Volume = 12 cc
pH of $.45M$ UNH = 2.0 , $.22M = 2.1$

Legend: O = Theoretical y Values
— = Experimental Chords

UO_2 Breakthrough from $.45M$ UNH

I
 $v=60$
 $k=.159$
 $\ln(1-f)=1.44$
 $v=.0347 \text{ ml/sec/cm}$
 $k=15 \text{ cm.}$

II
 $v=18$
 $k=.0416$
 $\ln(1-f)=2.86$
 $v=.0347 \text{ ml/sec/cm}$
 $x=15 \text{ cm.}$

III
 $v=25$
 $k=.0559$
 $\ln(1-f)=7.26$
 $v=.0336 \text{ ml/sec/cm}$
 $x=15 \text{ cm.}$

Time (thousands of seconds)

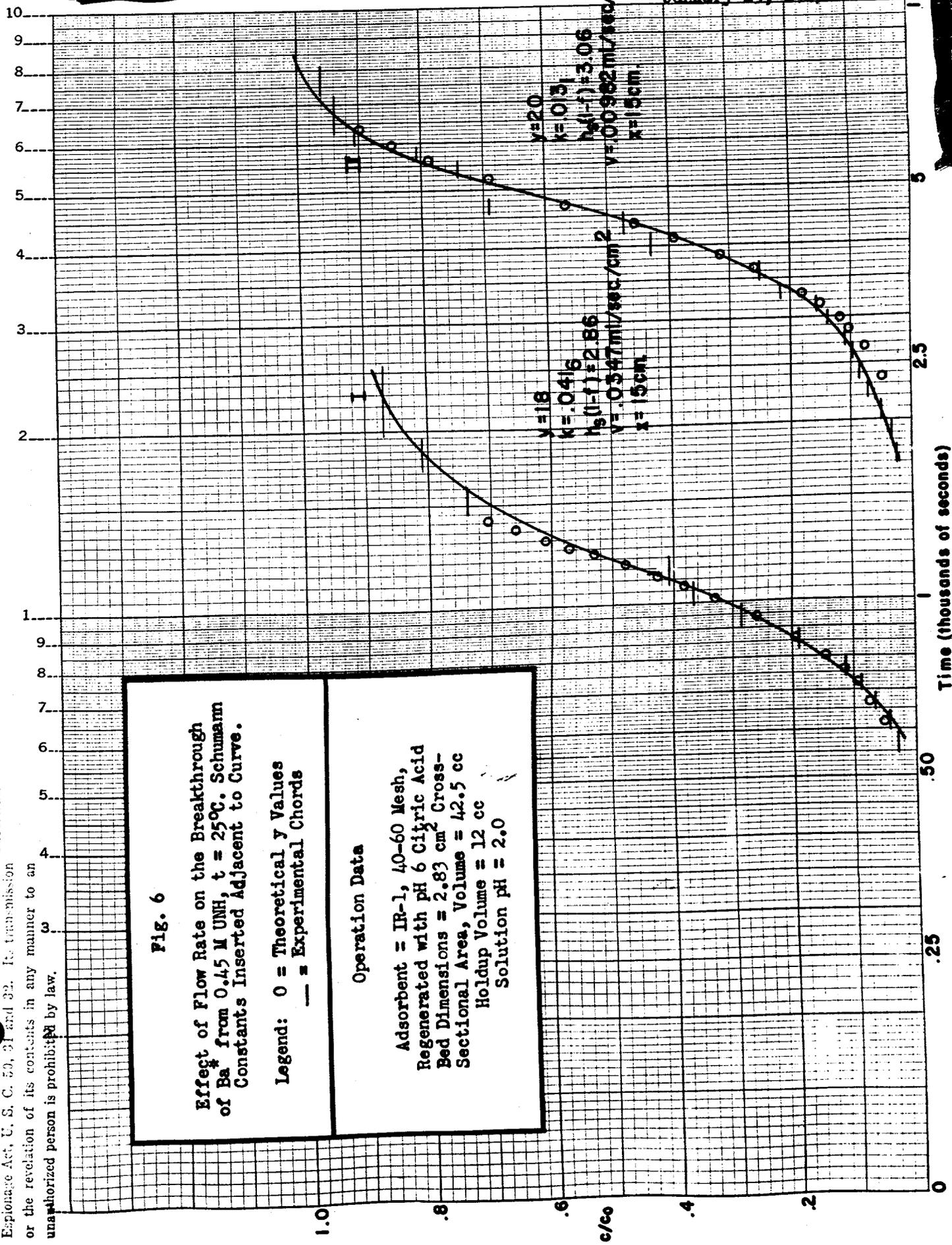


Fig. 6
Effect of Flow Rate on the Breakthrough of Ba from 0.45 M UNH, $t = 25^\circ\text{C}$. Schumann Constants Inserted Adjacent to Curve.

Legend: O = Theoretical y Values
 --- = Experimental Chords

Operation Data
 Adsorbent = IR-1, 40-60 Mesh,
 Regenerated with pH 6 Citric Acid
 Bed Dimensions = 2.83 cm² Cross-
 Sectional Area, Volume = 42.5 cc
 Holdup Volume = 12 cc
 Solution pH = 2.0

[REDACTED]

B. Concentration and Decontamination Steps: General Considerations

Citric acid is a fairly weak acid¹⁵ and hence under the conditions of the column operation the effective cation concentration (i.e. M^+) due to the citric acid alone, either from the 1/2 or 5% solutions is too low to have any appreciable effect on the barium adsorption. On the other hand, because of the complexing action of the citrate ion upon cations it becomes possible to adsorb or desorb a cation as the case may be, depending on the strength of the particular complex. One takes advantage of the relative dissociation constants of the complex ions to effect a separation and decontamination of Ba from other cations.

It is fairly well established that the formula of the divalent citric acid complex is the simplest possible, $M \text{ cit}^-$, and that their dissociation is:



Following the law of mass action we have

$$K_c = \frac{(M^{++}) (\text{cit}^{=})}{(M \text{ cit}^-)} \quad (11)$$

The relation of K_c to the thermodynamic dissociation constant, K_a , is given by

$$K_a = K_c \frac{\gamma_{M^{++}} \gamma_{\text{cit}^{=}}}{\gamma_{M \text{ cit}^-}} \quad (12)$$

It is apparent that the extent of complex formation depends on the citrate ion concentration. At $\text{pH} \sim 7$ all the citrate ion is in the form of the tertiary ion. Lowering the pH can be expected to have the same effect as decreasing the $\text{cit}^{=}$, and thus reducing the quantity of a cation which is complexed. At pH's where the $\text{cit}^{=}$ ion is reduced to a very small amount than the complexing ion is presumably H cit^- ; and at still lower pH's the H_2cit^- may be the principal complexing ion (CN-2575).

¹⁵ According to H.T.S. Britton, "Hydrogen Ions", p. 184, Vol. I, D. Van Nostrand Co., Inc., (1943), the dissociation constants of citric acid are: $K_1 = 1.0 \times 10^{-3}$, $K_2 = 2.5 \times 10^{-5}$, and $K_3 = 1.5 \times 10^{-6}$. It is presumed that the constants are for zero ionic strength.

[REDACTED]

[REDACTED]

The adsorption of Ba⁺⁺ and La⁺⁺⁺ from 5% citric acid as a function of pH is shown¹⁶ in Fig. 7. The concentration of NH₄OH added to adjust the pH was insufficient to cause the observed decrease in the adsorption of Ba⁺² or La⁺³. It is concluded that La⁺³ forms a considerably stronger complex¹⁷ than Ba⁺² because the bulk of the La⁺³ is complexed at a lower pH, i.e. less [ion] is needed to bind the La⁺³. It is understood that no adsorption of the complexed ion takes place because the resin will exchange only with cations.

The effect of pH on the concentration of cit⁼ may be expressed as follows:

$$\frac{[H^+]^3 [Cit^=]}{H_3 Cit} = K_1 K_2 K_3 = 6.1 \times 10^{-14} \quad (13)$$

When one calculates the [Cit⁼] from (13) it is found that a small change in pH in the region of ~pH 5-6 results in a large change in [Cit⁼]. The important conclusion to be drawn then, is that it would be preferable to design a separation process which operates at constant pH, say pH of 7, because the concentration of [Cit⁼] could be controlled quite easily within narrow limits. Such control is particularly important when it is desired to separate two substances whose complex dissociation constants do not greatly differ.

In Table III are recorded the dissociation constants of some complex citrates. An extended discussion of the complex citrates and the use of ion-exchange procedures for their determination will be presented in a forthcoming report. (CN-2575).

¹⁶ Experiment performed by J. W. Richter.

¹⁷ The writer believes that it is probable the trivalent citrate complexes are unionized, e.g. (La Cit).

[REDACTED]

TABLE III

DISSOCIATION CONSTANTS OF SOME METALLIC CITRATE
COMPLEXES^a

Cation	pK _a	Ionic Strength Originally Determined	Ref.
Ca ⁺⁺	3.9	.15	1
Sr ⁺⁺	3.5	.15, 1.0	1, 2
Ba ⁺⁺	(3.0)	-	3
Mg ⁺⁺	3.9	.15	1
Pb ⁺⁺	6.5	.03-.5	4
Rare Earths	>>Alkaline Earths	-	5

^a The dissociation constants have been calculated for zero ionic strength by assuming that the known variation of

$$\frac{\gamma_{Pb^{++}} \gamma_{cit^{3-}}}{\gamma_{Pb cit^{-}}}$$

with \mathcal{A} is the same for all the divalent citrate complexes (see reference 4).

- REFERENCES: (1) A. B. Hastings et al, J. Biol. Chem., 107, 351(1934); (2) Ion-exchange method at $\mathcal{A} = 1.02$. See page 53, CN-1873 for preliminary discussion. (3) Extrapolated from plot of pK_a vs. ionic radii of Ca⁺⁺ and Sr⁺⁺. C. D. Coryell suggested the plot of the log K_a or pK_a vs. ionic radii would be linear, at least in the case of the Ca, Sr, Ba triad. This relation has been verified for the F⁻ and SO₄⁼ salts by a plot of log K (solubility product) vs. ionic radii; also from preliminary ion-exchange data. (4) S. S. Kety, J. Biol. Chem., 142, 181(1942). (5) Estimated from the pH and total citric acid concentration at which the rare earths are eluted, using (13).

Fig. 7

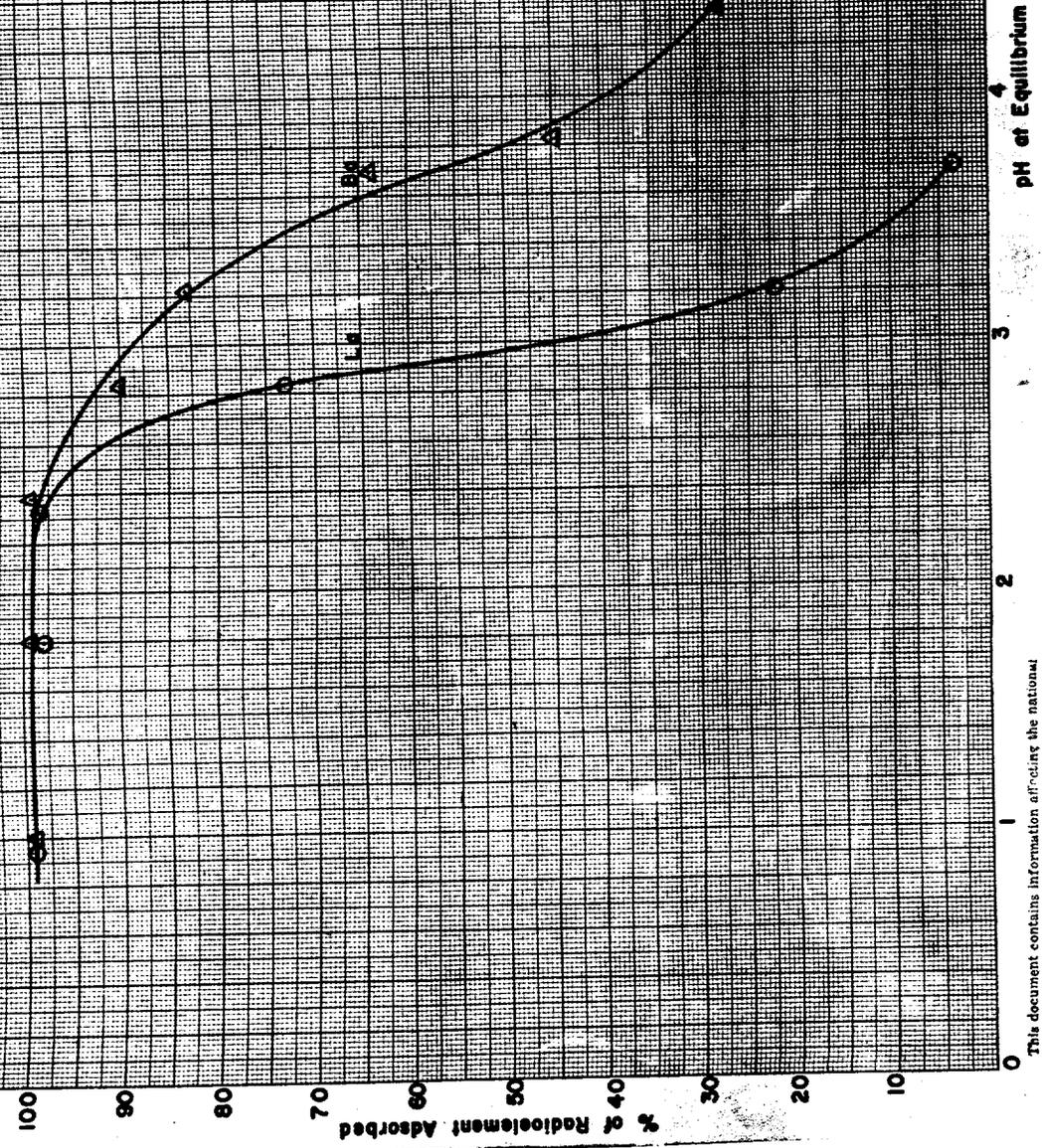
Absorption of Radio Ba and Radio La by IR-1 (HR)
 From 0.24 M (5%) Citric Acid as a Function of pH.
 Adjustment of pH Made with NH_4OH .

Experimental Conditions

0.5 gm. HR Shaken 2 Hours with 25 ml. of Solution.
 The HR was Air-Dried and Contained 2% H_2O . (60-80 Mesh)

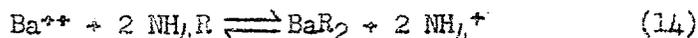
Composition of Citric Acid Solutions (0.24 M Citric Acid)

pH	Molarity of NH_4OH
1.79	0.0
2.32	.075
2.83	.15
3.21	.225
3.70	.30
3.92	.375
4.34	.45
4.73	.525
5.09	.60
5.56	.725
5.82	.80



Concentration Step

The eluate¹⁸ consisting of 5% citric acid (.24 M) at pH 6 is adjusted back to a pH of 2.5 and diluted ten-fold. The resulting 1/2% citric acid solution is passed through a small column of IR-1. The capacity of the IR-1 for the alkaline earths and rare earths under these conditions is so great that 200 column volumes of this solution is passed and only small loss of cations, ~3%, Table I, is encountered. The reason for the very high capacity is rather obvious; first, the cation contribution from the citric acid alone is insignificant; and second, the total effective cation concentration furnished by the NH₄⁺ (~.1 M) is also too low to appreciably affect Ba adsorption as a consideration of the equilibrium



shows.

The equilibrium constant, K_a , for the above reaction has been estimated from work to be described elsewhere to be about 15. Thus, a simple calculation shows that one gram of NH₄R will adsorb >98% of the Ba from 200 ml of a solution 0.1 M in NH₄⁺.

The breakthrough of Ba from 1/2% citric acid, at pH 2.5 was studied¹⁹ as a function of flow rate (Fig. 9). The variation of the terms, y and k with flow rate is in qualitative agreement with the Schumann theory.

Decontamination Step

A solution of 5% citric acid at pH 3 does not contain sufficient HCit²⁰ to complex the Ba or Sr, however the available HCit²⁰ is sufficient to complex the bulk of the rare earths.²⁰ Passage, then, of this solution preferentially elutes the rare earths, thus affecting a high degree of decontamination of the Ba. Since Sr is only a β -emitter it is not considered a contaminant. It is apparent that the removal of the rare earths is the result of complex ion formation only because the free cation concentration is far from sufficient to elute either the rare earths or the alkaline earths. The typical sharp elution curves obtained are shown in Figure 10.

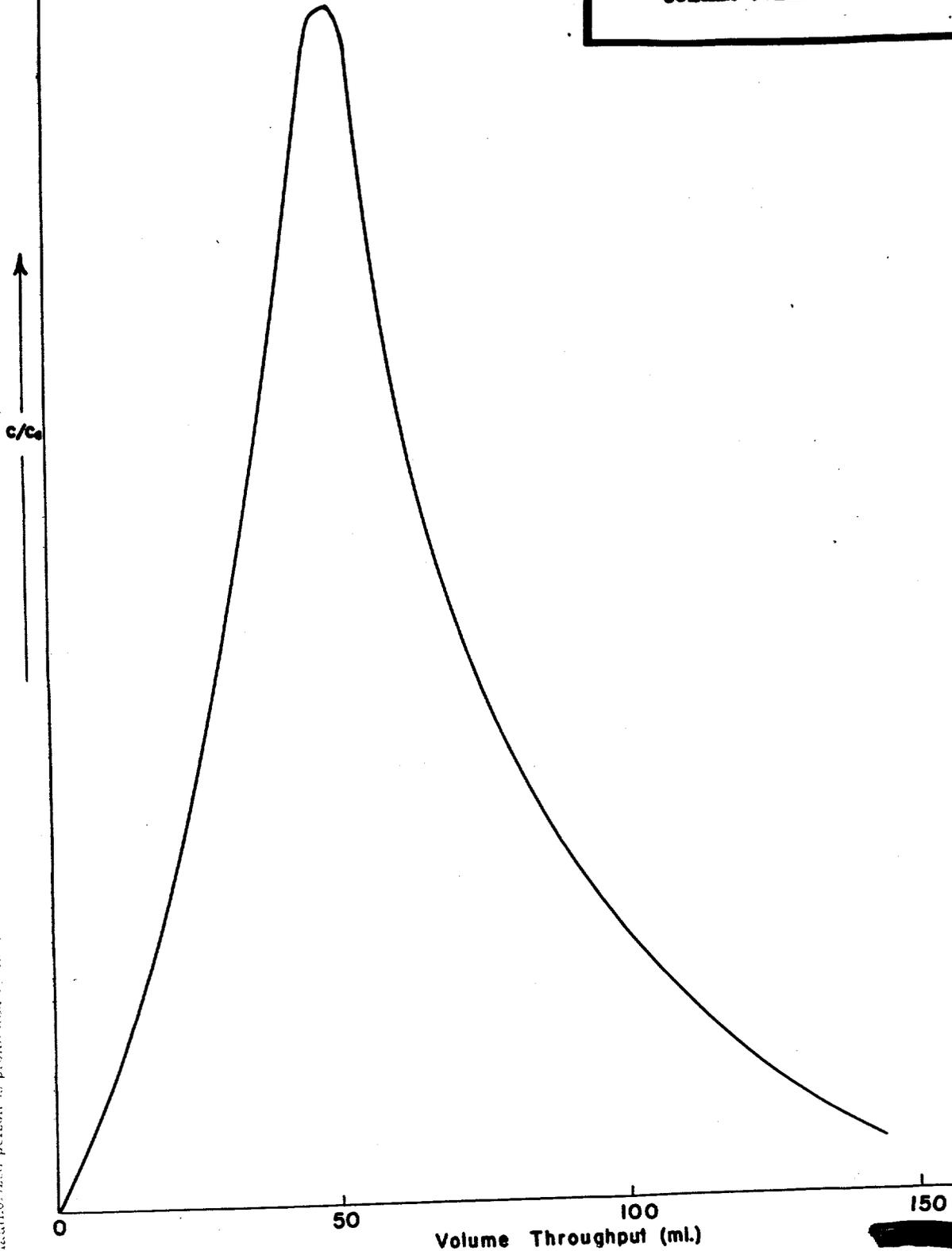
¹⁸ The efficiency of the pH 6, citric acid solution as an eluant for Ba is shown in Fig. 8.

¹⁹ The data presented were calculated from experiments performed by J. X. Khym.

²⁰ In this connection, it is interesting to note that separation of Y and Ce from one another on IR-1 by the use of citric acid solutions whose pH has been carefully adjusted is carried out routinely by members of W. E. Cohn's group.

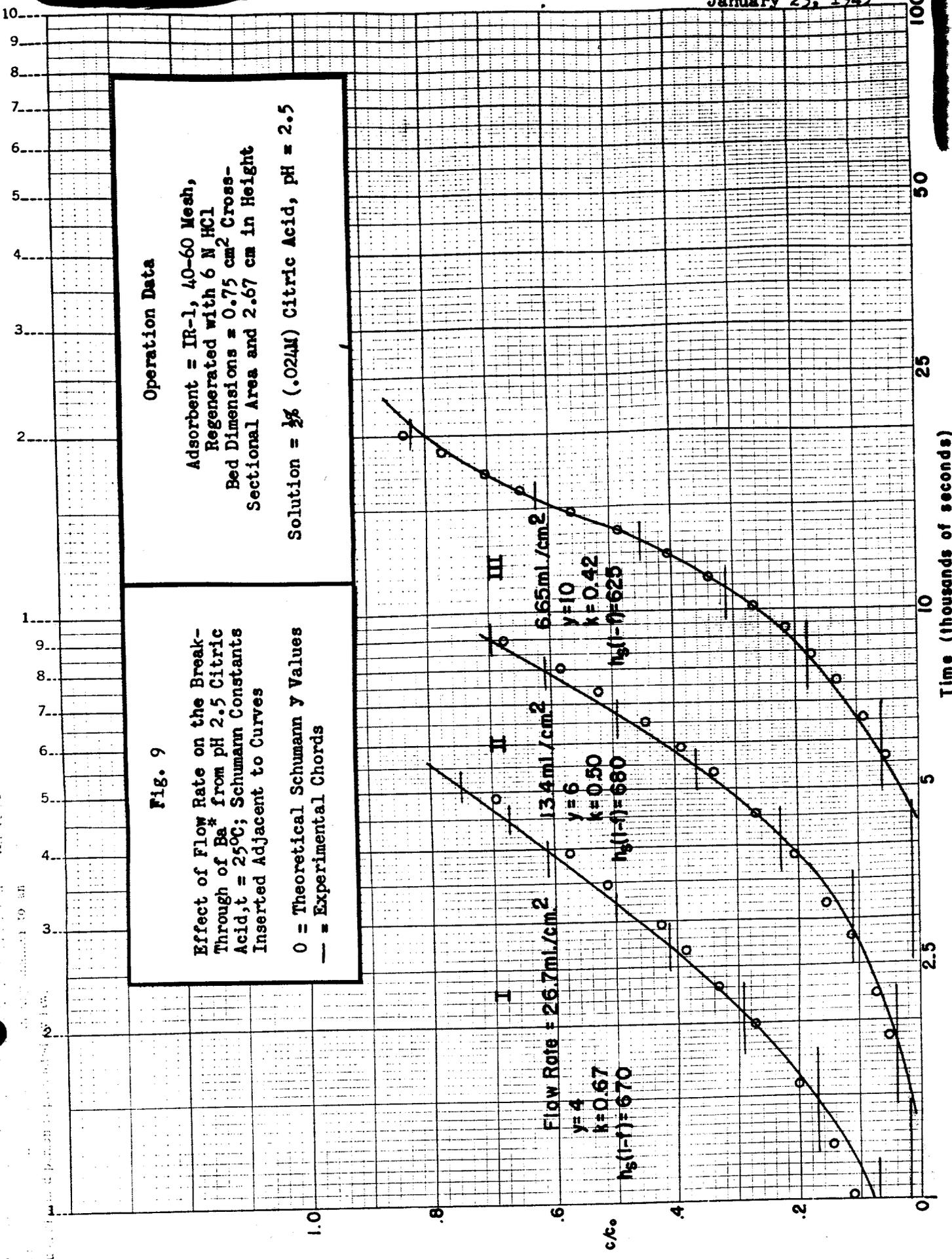
Fig. 8 (Semi-schematic)

Elution of Ba from IR-1 by 5%
Citric Acid at pH 6, $t = 25^{\circ}\text{C}$
Flow Rate = 3 ml/cm²/min
Column Volume = 43 ml.



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% of Total Activity Eluted

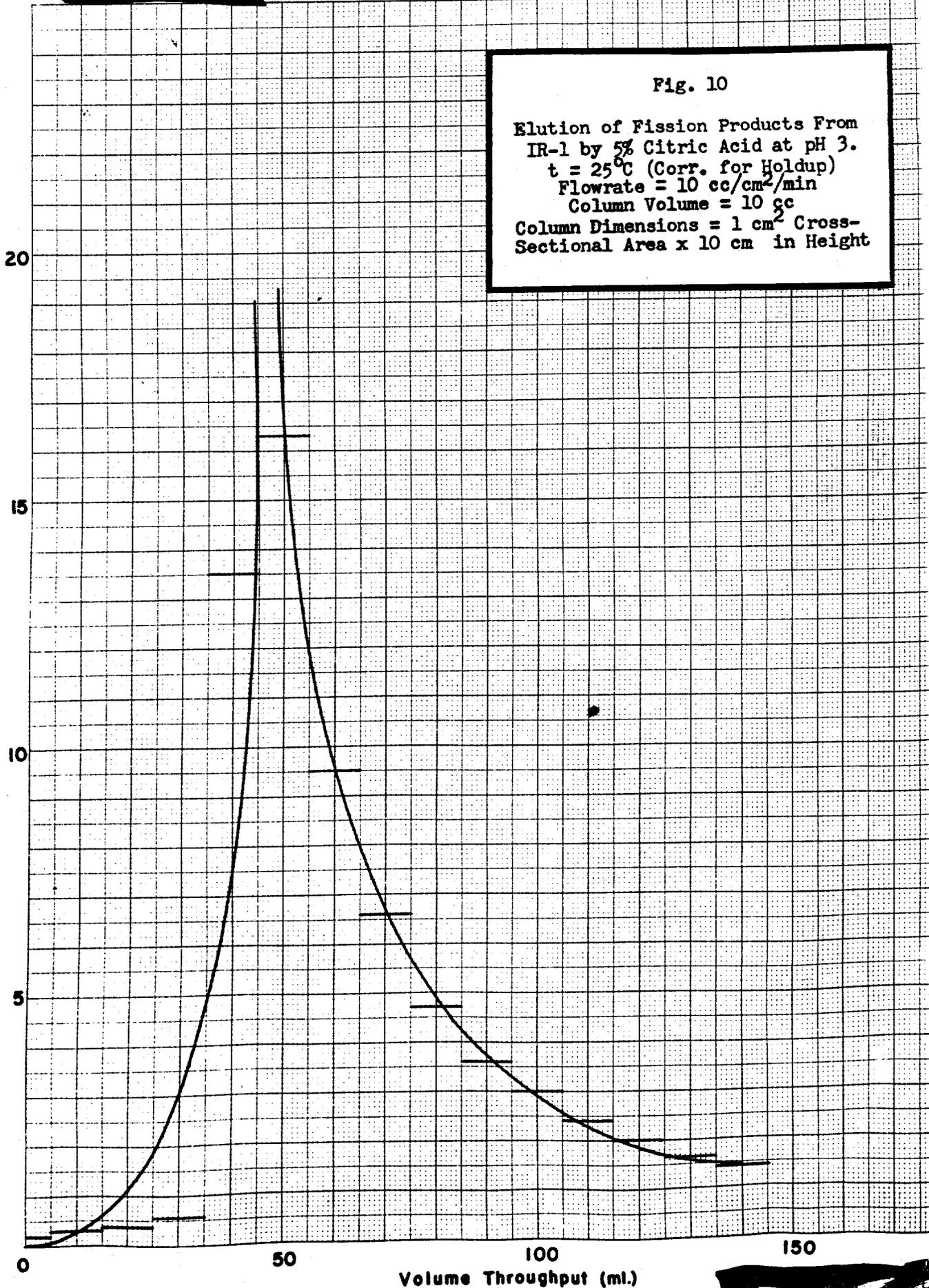


Fig. 10
Elution of Fission Products From
IR-1 by 5% Citric Acid at pH 3.
 $t = 25^{\circ}\text{C}$ (Corr. for Holdup)
Flowrate = 10 cc/cm²/min
Column Volume = 10 cc
Column Dimensions = 1 cm² Cross-
Sectional Area x 10 cm in Height

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Effective decontamination of Zr and Cb is accomplished at outset in the extraction step as described previously. After one concentration-decontamination cycle the Zr-Cb contamination is so low that accurate measurements are difficult. In cycle A, Table I, the initial total Zr activity amounted to 5.8×10^7 cts/min as compared with 25 counts/min in the final Ba containing solution. The initial Cb activity was 1.2×10^6 cts/min, the final activity was 25 cts/min. In cycle B, comparable results were obtained. The remaining gamma activity in the final Ba containing solutions, as far as could be determined, was due entirely to La which had grown from the Ba.

V. CONCLUSIONS

The extraction, decontamination and concentration of Ba^{140} from UNH solutions by ion-exchange adsorption on IR-1 has been demonstrated to be tenable and workable from both practical and theoretical considerations.

Future research for the preparation of Ba^{140} by adsorption should be directed toward (1) a systematic study of the mechanical variables in column operation, and (2) investigation of optimum chemical factors such as concentrations of eluting solutions and the like. Additionally, determinations of the dissociation constants of the citrate complexes of the fission cations would be of value.

Finally, a process for the separation of cations which employs citric acid solutions at constant pH appears, from a consideration of the equilibrium involved, to be so attractive as to be worthy of extensive investigations.