

by a short talk on the mathematics involved in the above technique.

The afternoon group discussions were on "The Structure of the Galaxy" in which the following specialists spoke on the subject mentioned against each: Dr. K. D. Abhyanker (Nizam's Observatory, Hyderabad) on "Kinematical Features of the Galaxy"; Dr. J. C. Bhattacharyya (Kodaikanal Observatory) on "Brightness Distribution of the Milky Way in the UV, Visual and Infrared Regions"; Dr. G. Swarup on "Radio Continuum and Line Radiation Characteristic of the Galaxy"; Dr. M. K. Vainu Bappu on "Optical Aspects of Spiral Structure of the Galaxy"; Mr. Ch. V. Sastry

on "Low Frequency Detection of Ionized Hydrogen Regions"; Dr. B. V. Sreekantan (Tata Institute of Fundamental Research, Bombay) on "Gamma-rays, X-rays and the Galaxy"; and Dr. R. R. Daniel (TIFR, Bombay) on "Cosmic Rays and the Structure of the Galaxy".

The evening lecture was given by Dr. V. Prabhakar Rao (Entomologist-in-Charge, Commonwealth Institute of Biological Control, Bangalore) on "Insect Control".

The Session concluded with an expression of thanks by the President Sir C. V. Raman, to all the Fellows, Invitees and Delegates who by making this "contact of minds" possible contributed to the success of the meeting.

DIFFERENTIAL INTERACTION OF MARINE HUMIC AND FULVIC ACIDS WITH ALKALINE EARTH AND RARE EARTH ELEMENTS

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ABSTRACT

Alkaline earth sulphates such as of Ba and Ra and rare earth hydroxides such as of Y, La and Ac were solubilized significantly by marine humic and fulvic acids in ammoniacal medium. Alkaline earth elements were associated with humic and fulvic acids as exchangeable cationic and/or cationic complexes whereas rare earth elements formed non-cationic complexes. Major fraction of humic acid precipitates in sea-water and this settling humic acid picks up only rare earth elements from alkaline earth-rare earth radioactive pairs. These rare earths were associated with humic acid as non-cationic complexes. The dissolved fraction of humic acid in sea-water also had the rare earths in non-cationic complex forms.

INTRODUCTION

HUMIC ACID (in ammoniacal medium) solubilises a large number of elements.¹ Solubilized Ba was found to be associated with the cation exchange sites of humic acid and the total solubilization of BaSO₄ was observed to be equivalent to the exchange capacity.¹ Solubilized transition and trivalent elements such as Zn, Mn, Cu, Co, Fe and Y are bound with the humic acid mostly as non-cationic complexes and small fractions were observed to be exchangeable on a cation column.

Humic acid precipitates in sea-water and picks up in the process a variety of major and trace elements present in the medium. In the light of the above observations and the presence of high concentrations of Mg and Ca, other alkaline earth elements are not expected to be significantly picked up by the settling humic acid. Results presented in Table I also support this contention. However, it has been observed that Y is almost quantitatively picked

up by the settling humic acid under similar conditions.¹

TABLE I*

Pick-up of ⁸⁵⁻⁸⁹Sr by humic acid (sea-water medium)

Time (days)	Activity in cpm per ml. in filtrate	
	Blank	Sample
0.17	1643	1633
7	1415	1370
15	1306	1293
22	1238	1230
33	1083	1074

* Humic acid sol.—12.8 mg. (exchange capacity 383 meq per 100 g.) in 100 ml ⁸⁵⁻⁸⁹ Sr (carrier content—1.86 mg.), spiked sea-water was left with intermittent shaking. Aliquots filtered from time to time, filtrate counts compared with that of the blank.

In this paper, further results are presented on the nature of this differential interaction of humic and fulvic acids with alkaline earth and rare earth elements. Discussions follow each of the experiments.

MATERIALS

The tracer experiments were carried out using the radioactive pairs ^{90}Sr - ^{90}Y , ^{140}Ba - ^{140}La and ^{228}Ra - ^{228}Ac . Humic and fulvic acids were prepared by alkaline extraction of a sample each of coastal marine sediment (CS) and shelf sediment I* (SSI) by the procedure as described in References 2, 3 and 4. Filtered† stock solutions had 0.95 mg. per ml. of humic acid and 0.11 mg. per ml. of fulvic acid. Interactions were studied in two media, viz., ammoniacal and sea-water.

EXPERIMENTS AND DISCUSSIONS

Ammoniacal medium (in situ precipitates)

Experiment.—Two ml. of ammonia (6 N) and 1 ml. of 2% $(\text{NH}_4)_2\text{SO}_4$ were added to 1 ml. samples of humic (CS) and fulvic (SSI) acids. A known volume of the radioactive pairs containing known amounts of the inactive carriers of the elements was added to these solutions and to blanks. Volumes were made up to 5 ml. with distilled water and kept for a week with intermittent shaking, filtered and 1 ml. filtrates were counted for beta activity. One ml. aliquots were passed (0.2 ml. per min.) through Dowex 50 W X-8 cation column (2 cm. \times 1 cm.) conditioned to NH_4^+ form with 2.5 N ammonia. The column was washed with 2 column volumes of 2.5 N ammonia. *Effluents and washings* were evaporated and counted.

The activity retained in the column was eluted in each case with five column volumes of 4 M HNO_3 , the *eluate* evaporated and counted. The count rates of effluents and eluates were followed for decay and build-up. Results are given in Tables II and III, and in Figs. 1, 2, 3, 4 and 5.

Discussion.—The experimental procedures were such that Ba and Ra would have precipitated as sulphates and Y and La as hydroxides both from blank and sample solutions in the absence of solubilization. In the filtrate counts it is to be observed that whereas humic and fulvic acids solubilize all the ionic species, there is considerable depletion in the filtrate counts in the blank indicating the precipitation. The dissolved (solubilized) trace elements in blank are observed to be practically quantitatively retained on cation column (cf. Tables II and III). The effluents of humic and fulvic acids decayed with 64, 40 and 6 hours half-lives respectively of ^{90}Y , ^{140}La and ^{228}Ac . The eluates from the respective columns built up to saturation acti-

* 21 miles off-shore (at 50 m. depth).

† All filtrations in the work were made through 0.22 μ Millipore membrane.

TABLE II

Interaction of humic acid with alkaline earth and rare earth elements (ammoniacal medium)

	Activity in cpm per ml.					
	^{90}Sr - ^{90}Y		^{140}Ba - ^{140}La		^{228}Ra - ^{228}Ac	
	Blank	Humic acid	Blank	Humic acid	Blank	Humic acid
Added ..	7244 (2 $\mu\text{g. Sr}$, 1 $\mu\text{g. Y}$)	7244 (2 $\mu\text{g. Sr}$, 1 $\mu\text{g. Y}$)	8300 (2 $\mu\text{g. Ba}$, 1 $\mu\text{g. La}$)	8300 (2 $\mu\text{g. Ba}$, 1 $\mu\text{g. La}$)	223 (2 $\mu\text{g. Ba}$)	223 (2 $\mu\text{g. Ba}$)
Filtrate ..	3568	7293	96	2264	67	197
Influent ..	3568	7293	96	2264	67	197
*Effluent and washings	14	3508	6	1094	Nil	138
*Eluate	2164	..	671	..	60

* See Figs. 1, 2 and 3 for decay and build-up.

TABLE III

Interaction of fulvic acid with alkaline earth and rare earth elements (ammoniacal medium)

	Activity in cpm per ml.			
	^{90}Sr - ^{90}Y		^{140}Ba - ^{140}La	
	Blank	Fulvic acid	Blank	Fulvic acid
Added ..	7244 (2 $\mu\text{g. Sr}$, 1 $\mu\text{g. Y}$)	1448 (0.8 $\mu\text{g. Sr}$, 0.4 $\mu\text{g. Y}$)	8300 (2 $\mu\text{g. Ba}$, 1 $\mu\text{g. La}$)	4150 (1 $\mu\text{g. Ba}$, 0.5 $\mu\text{g. La}$)
Filtrate ..	3568	1406	96	329
Influent ..	3569	1406	96	329
*Effluent and washings	14	414	6	201
*Eluate	257	..	180

* See Figs. 4 and 5 for decay and build-up.

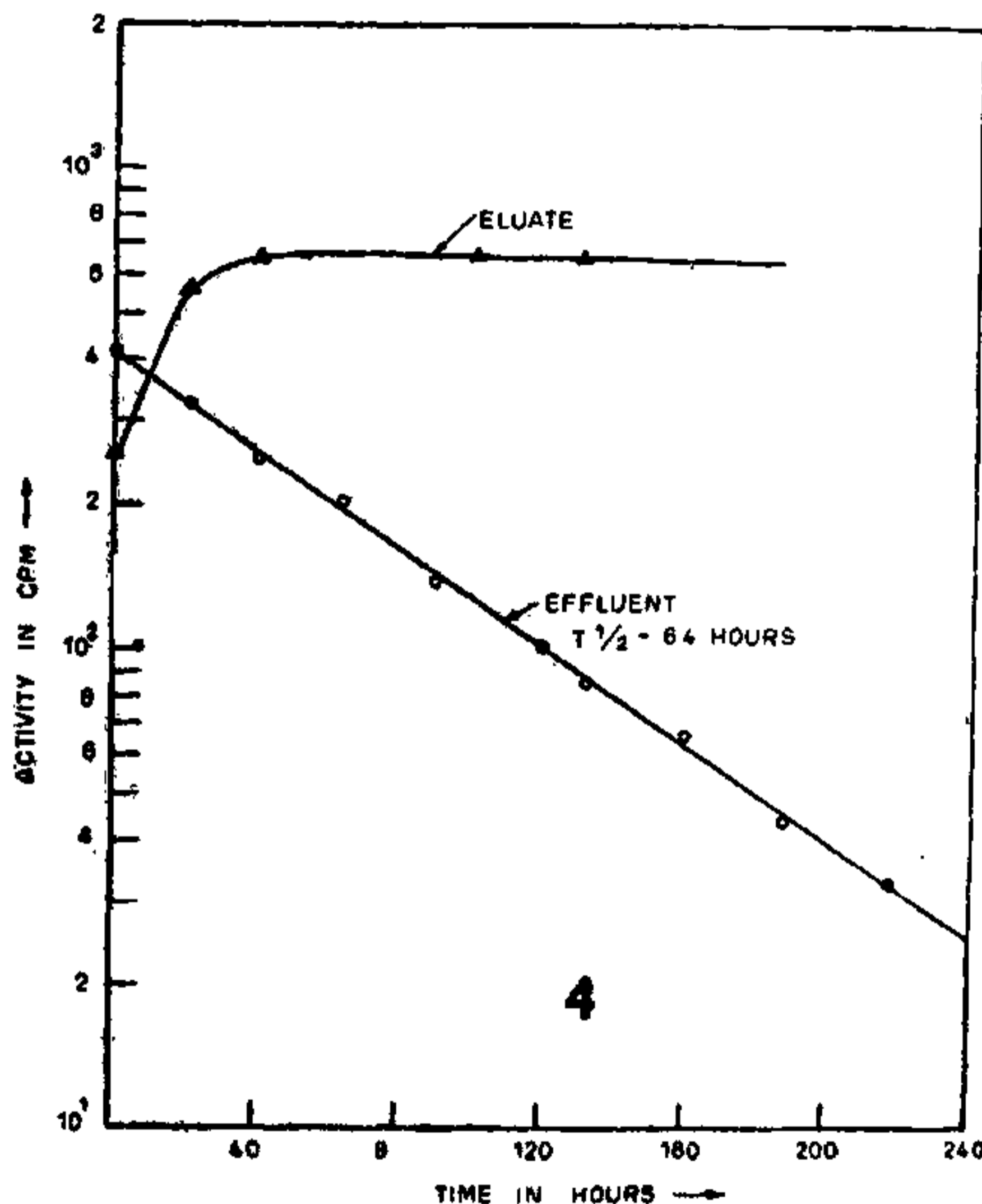
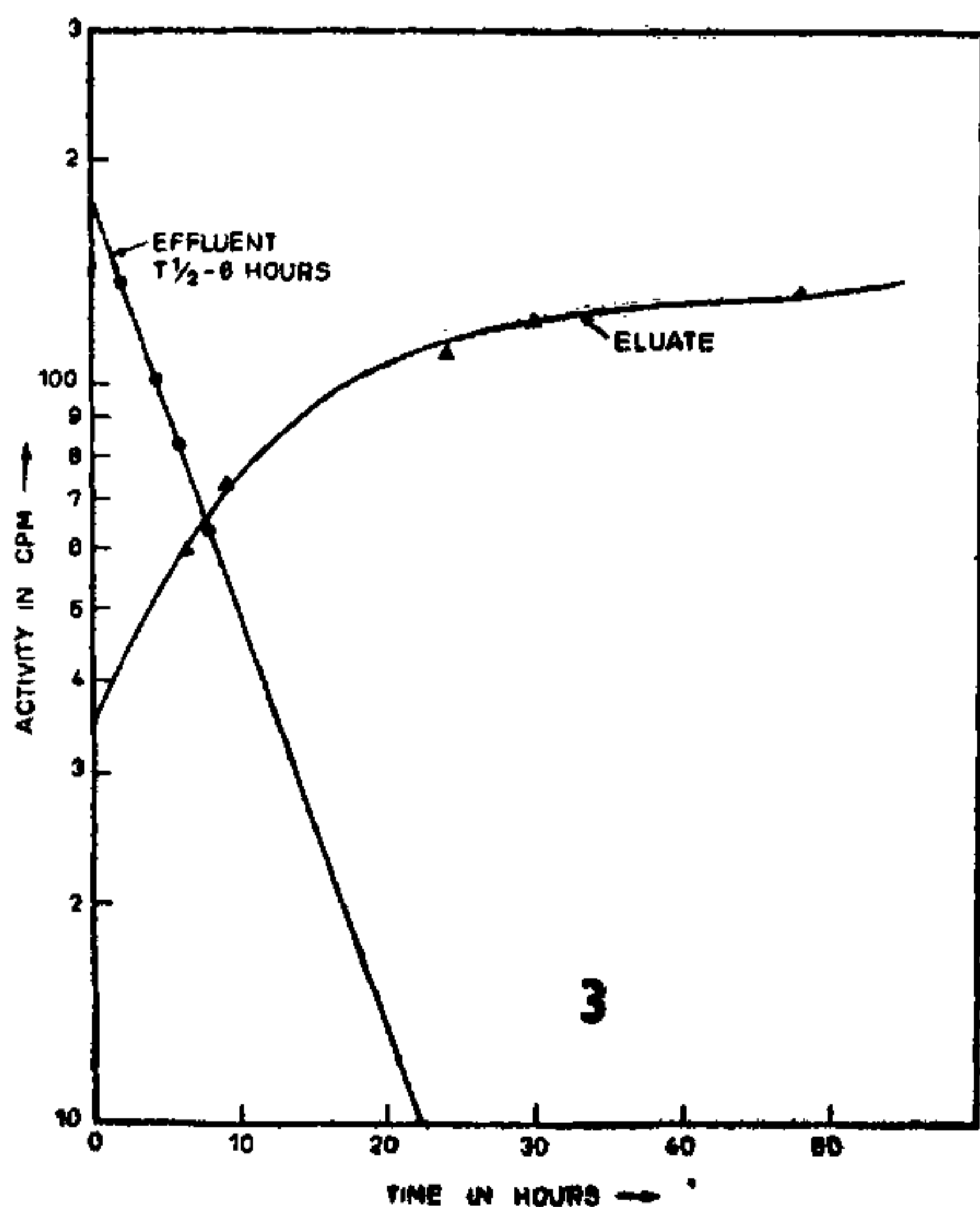
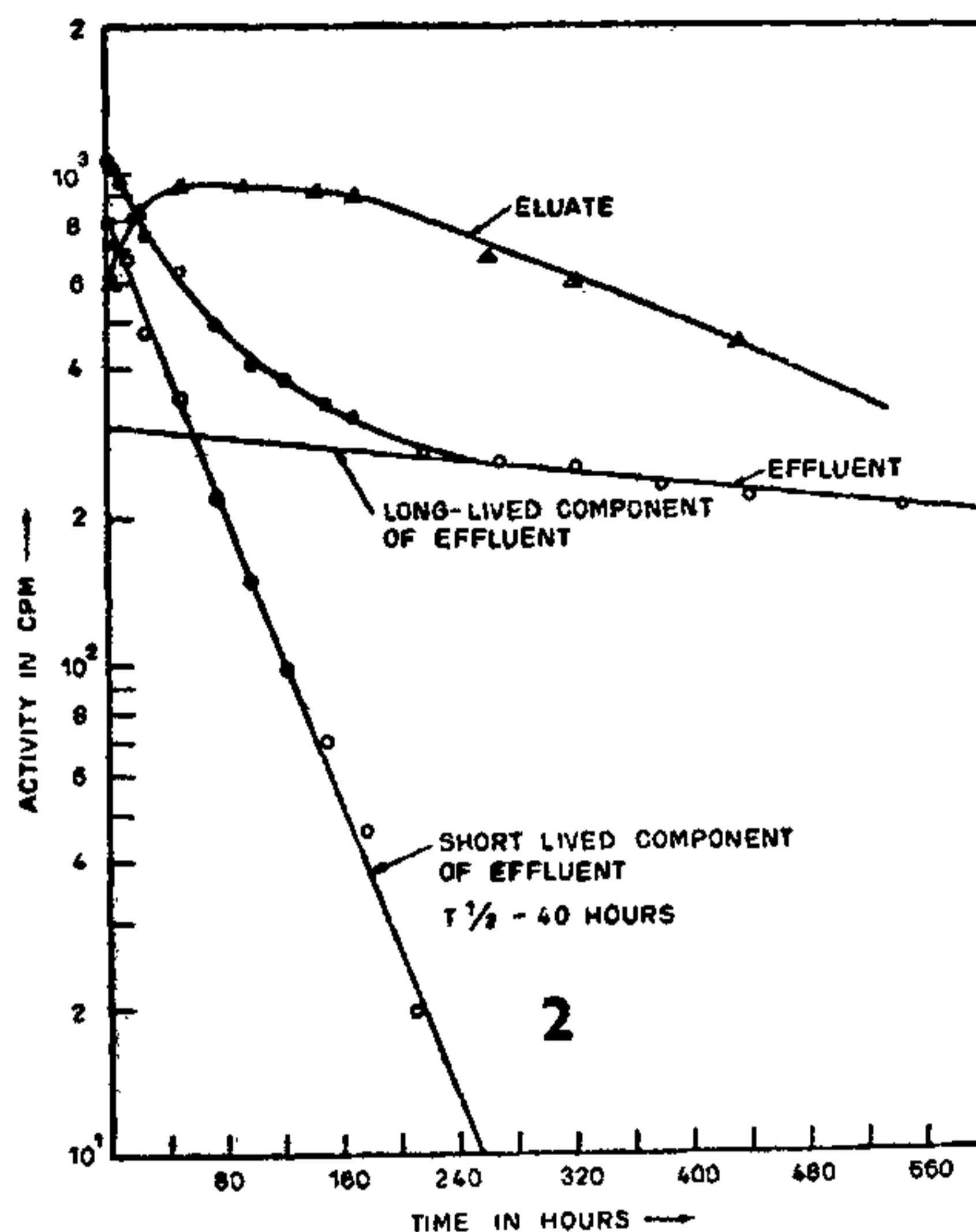
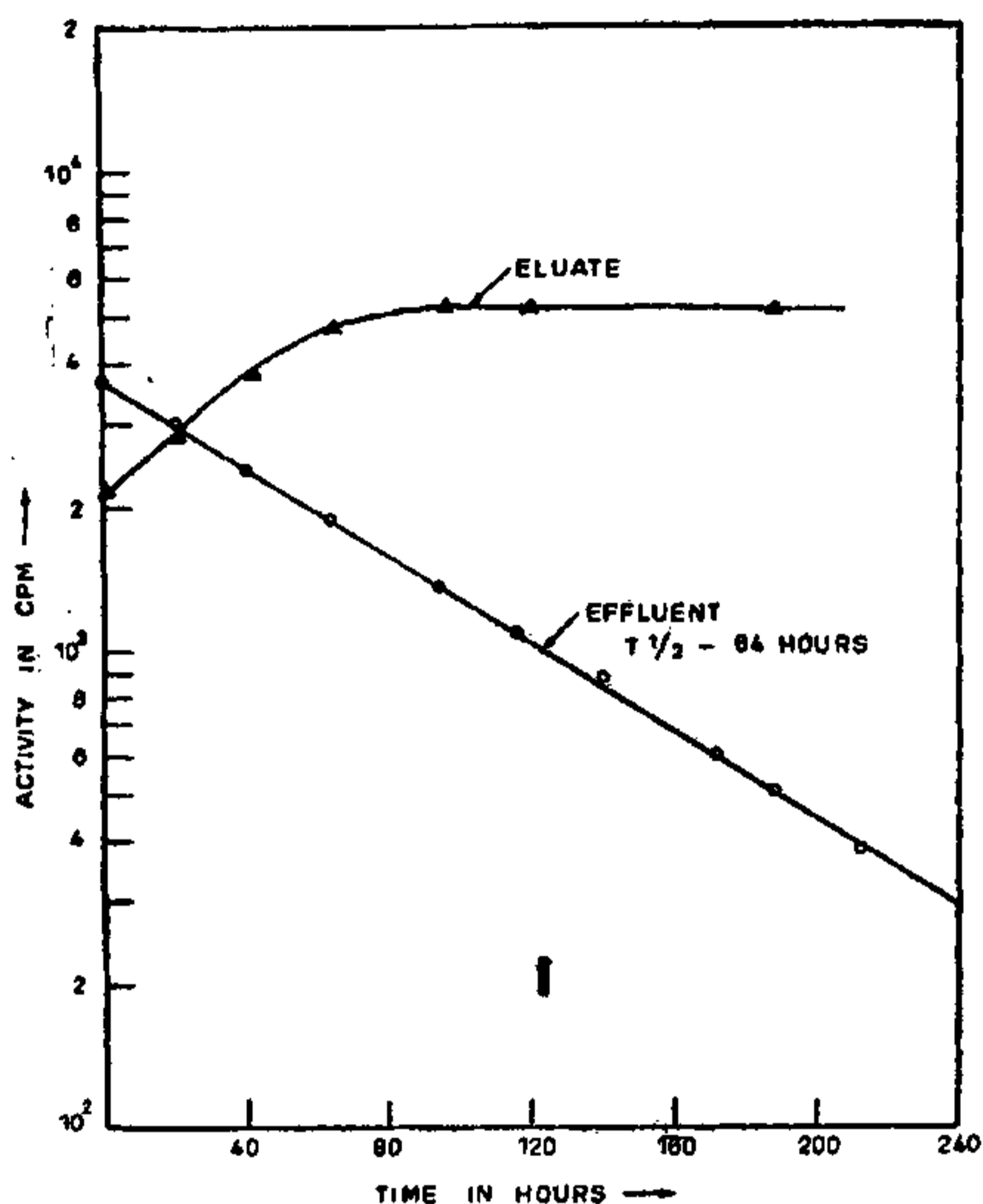
vities with time at rates required of ^{90}Sr , ^{140}Ba and ^{228}Ra . Thus, the effluents containing ^{90}Y , ^{140}La and ^{228}Ac were present as non-cationic complexes. And the Ba and Ra were associated with humic and fulvic acids in exchangeable cationic forms (cf. Figs. 1, 2, 3, 4 and 5).

Humic and fulvic acids are not only solubilizing agents, but there are selective interactions for the two groups—alkaline earths and rare earths. Pillai *et al.*'s³ finding that Ca was not detected in the ash of drastically electro-dialysed humic acid is also in line with the present observation. However, the sorption of trivalent elements in exchangeable form is not completely excluded, since Pillai *et al.*'s³ also observed that a mixture of humic and fulvic

acids purified by simple dialysis and filtered has about 10% of its Fe^{+3} content as exchangeable on cation column.

Sea-Water Medium

Experiment.—Humic acid (CS) adjusted to pH 7.9 by NaOH and filtered was used.



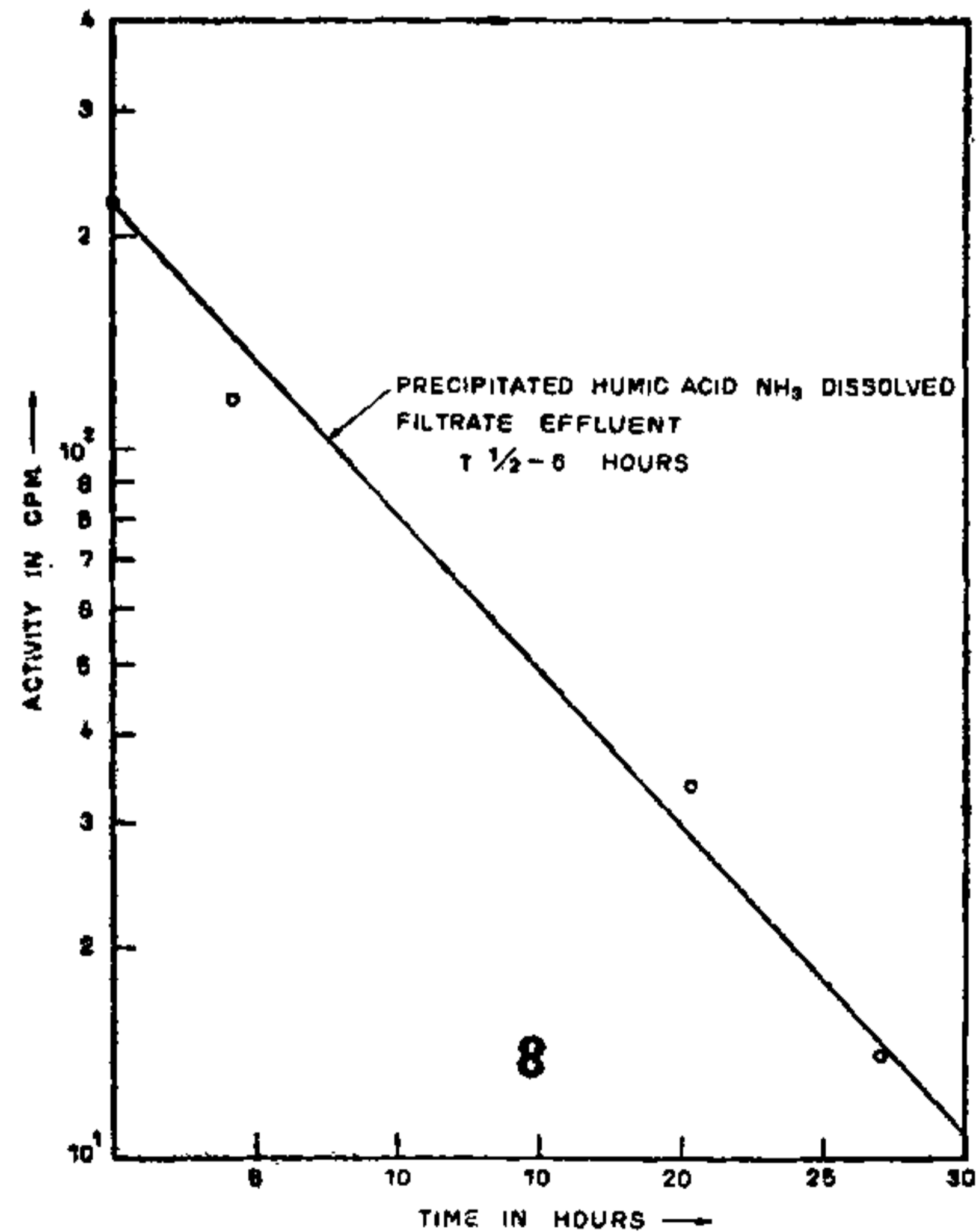
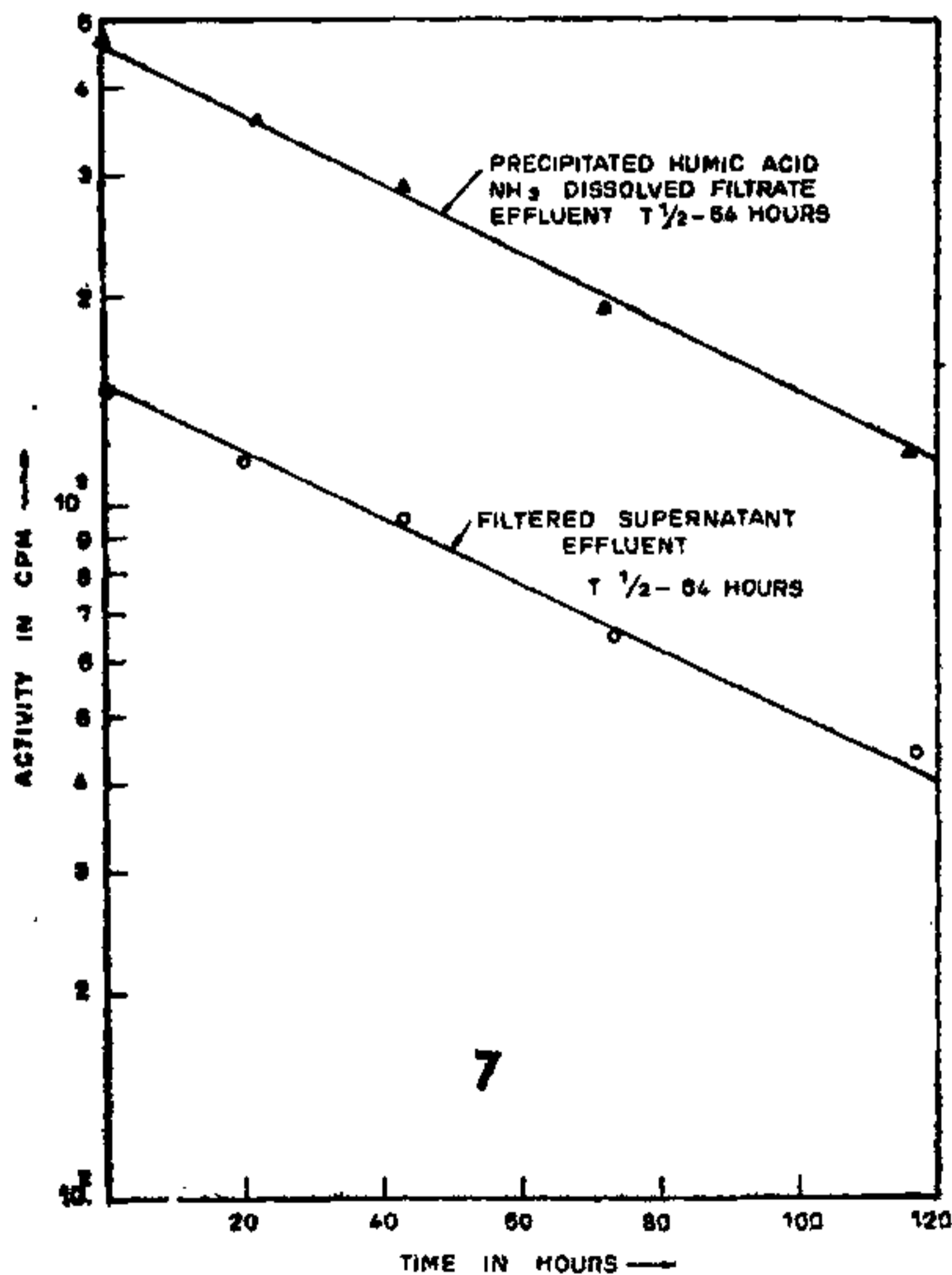
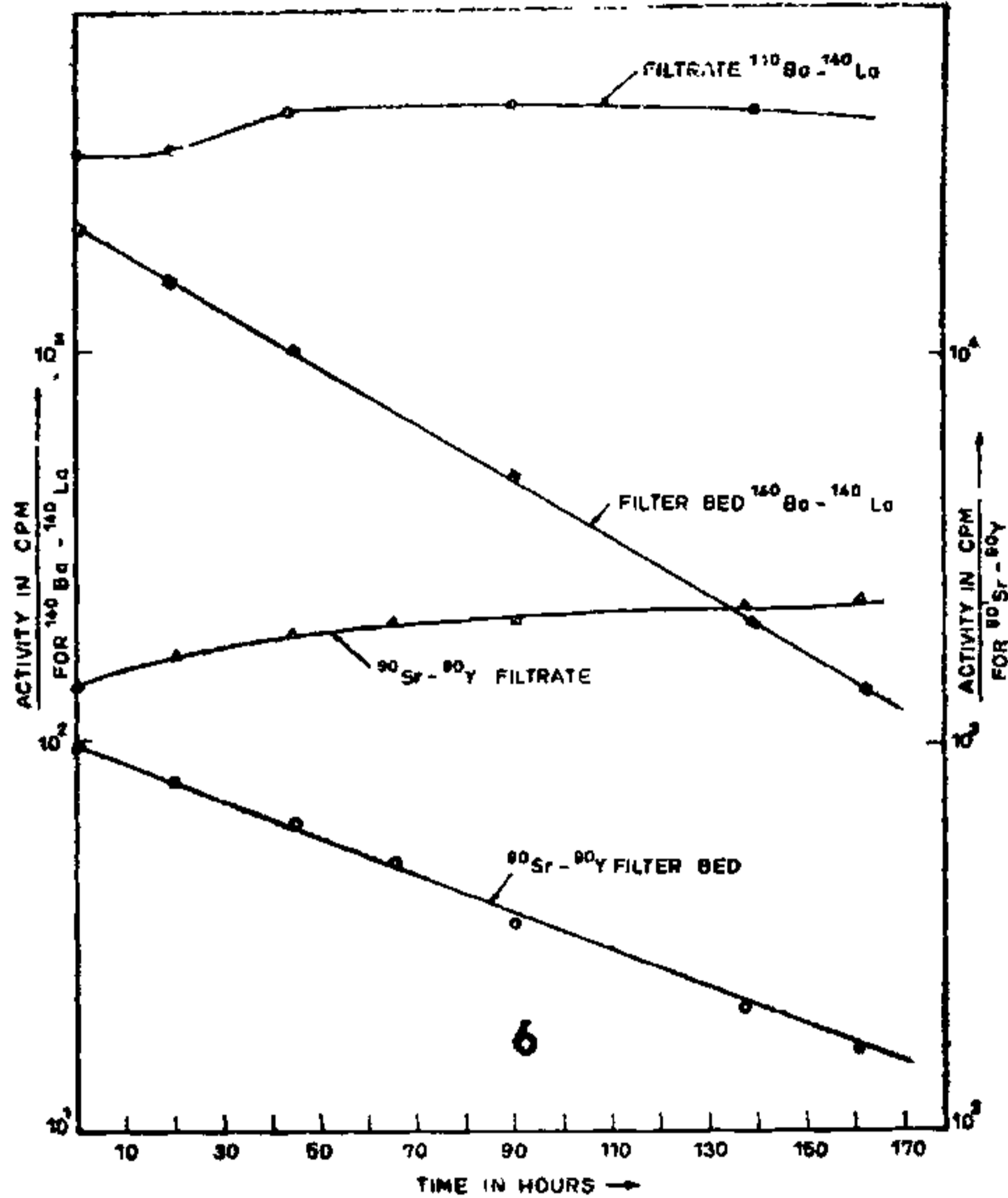
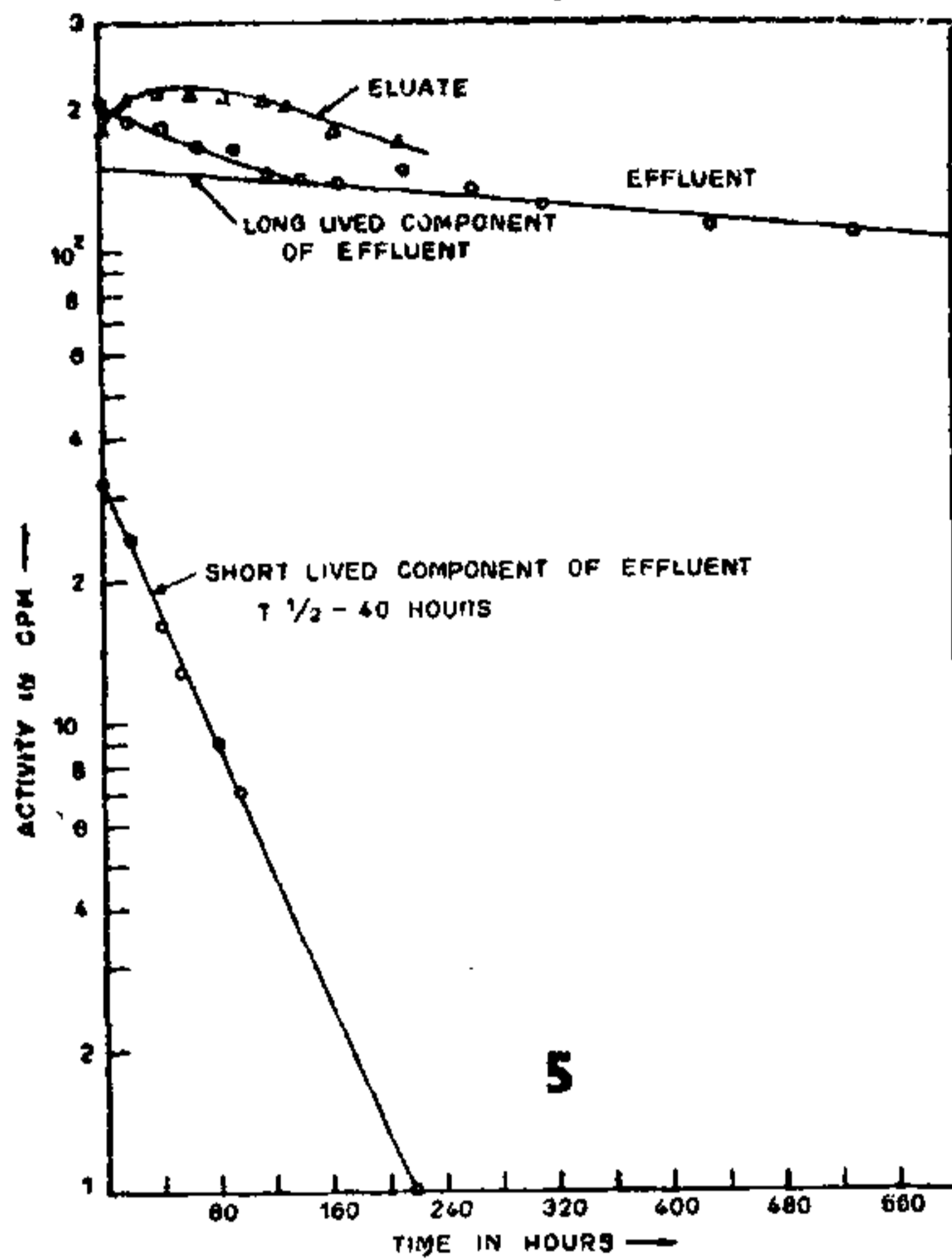
FIGS. 1-4. Fig. 1. Interaction of humic acid with $^{90}\text{Sr}-^{90}\text{Y}$ (Ammoniacal medium). Fig. 2.* Interaction of humic acid with $^{140}\text{Ba}-^{140}\text{La}$ (Ammoniacal medium). Fig. 3. Interaction of humic acid with $^{228}\text{Ra}-^{228}\text{Ac}$ (Ammoniacal medium). Fig. 4. Interaction of fulvic acid with $^{90}\text{Sr}-^{90}\text{Y}$ (Ammoniacal medium).

* Prepared from fission products having a trace of long-lived component as a contaminant. The decay curve for the short-lived component has been obtained after subtracting from the total counts of the effluent the corresponding extrapolated counts of the long-lived component.

The following solutions :

Blank : 90 ml. filtered sea-water + 5 ml. filtered double concentrated sea-water + 5 ml. double-distilled water + ^{90}Sr - ^{90}Y or ^{140}Ba - ^{140}La and

Sample : 90 ml. filtered sea-water + 5 ml. filtered double-concentrated sea-water + 5 ml. humic acid + ^{90}Sr - ^{90}Y or ^{140}Ba - ^{140}La were kept for a week with intermittent shaking. Two ml. of well-mixed aliquots



FIGS. 5-8. Fig. 5 * Interaction of fulvic acid with ^{140}Ba - ^{140}La (Ammoniacal medium). Fig. 6. Interaction of humic acid with ^{140}Ba - ^{140}La and ^{90}Sr - ^{90}Y (Sea-water medium). Fig. 7. Interaction of humic acid with ^{90}Sr - ^{90}Y (Sea-water medium). Fig. 8. Interaction of humic acid with ^{228}Ra - ^{228}Ac (Sea-water medium).

* See the comments in Fig. 2.

of each were filtered, the filter-beds and the filtrates were counted for beta activity—the decay and build-up were followed. The filter-bed activity of the control was subtracted from that of the sample filter-bed and the resulting values are plotted in Fig. 6.

Discussion.—Figure 6 shows that activities retained on the filter-beds decayed with the half-lives of ^{90}Y and ^{140}La . The sample filtrate activity showed build-up, reaching saturation activities at the expected rates. The decay curves for ^{90}Y and ^{140}La also show the radiochemical purity of the picked up Y and La.

Experiment.—To re-examine the state of combination of the elements in the precipitated humic acid, the precipitates obtained in another set of experiments in sea-water medium with ^{90}Sr - ^{90}Y and ^{228}Ra - ^{228}Ac were centrifuged, the supernatant and the residue separated.

The residue was dissolved in 2 ml. of ammonia (6N), diluted to 5 ml. with distilled water, centrifuged and filtered. One ml. filtrate was counted and another 1 ml. aliquot was passed through a cation column conditioned to NH_4^+ form as before and the effluents and washings were counted. The column was eluted with 4 M HNO_3 -eluate, evaporated and counted. Results are given in Table IV and Figs. 7 and 8.

Discussion.—It is to be observed that the activity picked up by the precipitated humic acid decays with the half-lives of rare earths. The same decay characteristic is observed with the effluents and washings confirming the earlier observations (with solubilized fraction) with the trivalent elements associated with humic acid as non-cationic complexes. The eluates gave very few counts with a tendency to build up at the rate of corresponding alkaline earth. This is ascribed only to the alkaline earth contamination remaining with the residue on centrifugation rather than any definite pick-up by the precipitate. We may conclude then that the complexed ^{90}Y and ^{228}Ac are in similar states of combination both in the solubilized and the precipitated state of humic acid.

Experiment.—It has been observed earlier² that there is always a dissolved fraction of humic acid present in the sea-water filtrate. Eighty-five per cent of the dissolved fraction was found to be precipitable in the acid and

this has the same characteristic UV absorption spectrum of the original humic acid. The balance 15% that does not precipitate out has an absorption spectrum similar to fulvic acid. It has been observed that the solubility of the separated humic acid in sea-water ranges from 75 to 100 μg . per ml. And in earlier experiments it was observed that Fe was significantly solubilized by this dissolved fraction.² To examine the possible similarity of interaction with Y and Ac, the filtered supernatants (in sea-water) were passed through cation columns conditioned to Na^+ form by 3.5% NaCl. The effluents and washings were counted and followed for decay. Results are presented in Figs. 7 and 8.

TABLE IV

Interaction of humic acid with alkaline earth and rare earth elements (sea-water medium)

	Activity in cpm per ml.					
	$^{90}\text{Sr} - ^{90}\text{Y}$			$^{228}\text{Ra} - ^{228}\text{Ac}$		
	Blank	Humic acid	Ppted HA in NH_3^\dagger	Blank	Humic acid	Ppted HA in NH_3^\dagger
Added ..	19047	19047	..	929	929	..
Filtrate ..	15100	9591	..	526	197	..
Influent ..	15100	9591	5620	526	197	270
*Effluent and washings	216	1464	4707	Nil	70	221
*Eluate	755	24	13

* See Figs. 7 and 8 for decay, † This is humic acid that precipitated in sea-water picking up the elements and was dissolved in NH_3 and filtered.

Discussion.—It is to be observed that ^{90}Y and ^{228}Ac pass through the column whereas the same activities of the blank solutions were quantitatively retained. The state of combination of the rare earth elements with humic and fulvic acids in dissolved state—in the ammoniacal medium or in the sea-water medium—and also in the precipitated state are the same, viz., the non-cationic complex. The same statement would apply to trivalent elements such as Fe, Al, etc.

1. Koshy, E., Desai, M. V. M. and Ganguly, A. K., *Curr. Sci.*, 1969, 38, 582.
2. — and Ganguly, A. K., *BARC-403*, 1969.
3. Pillai *et al.*, 1970 (Unpublished work).
4. Desai, M. V. M. and Ganguly, A. K., 1970 (Under publication).