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THE DETERMINATION OF STRONTIUM-90 IN ENVIRONMENTAL AND BIOLOGICAL MATERIALS USING DI-(2-ETHYLHEXYL) PHOSPHORIC ACID

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ABSTRACT

A method is described in which strontium-90 is determined by solvent extraction of the yttrium-90 daughter.

After a preliminary extraction of a hydrochloric acid solution of the sample by di-(2-ethylhexyl) phosphoric acid, yttrium-90 is allowed to return to equilibrium in the presence of yttrium carrier. A second extraction quantitatively separates the yttrium-90 which is subsequently stripped into concentrated hydrochloric acid. An extraction with Aliquat 336 is used to remove interfering radionuclides before the yttrium is finally precipitated and counted as the oxalate. Typical recovery is 85-90 per cent.

CONTENTS

1. INTRODUCTION

For a number of years strontium-90 in environmental and biological materials has been determined at the A.A.E.C. Research Establishment by an EDTA ion-exchange method (Davis 1962, Davis and Piper 1967).

This method has several disadvantages:

(a) The time involved in processing a sample through the ion-exchange column is excessive.

(b) Owing to the necessity for strict control of the EDTA:Ca molar ratio, analysis cannot be started until the calcium content is known.

(c) Interference from Fe, Al, and Zn entails an extraction modification. (Lahoud and Piper, 1967a, 1967b).

(d) Typical recovery is only 50-60 per cent.

(e) The need for a complex heating jacket for the ion-exchange column involves the reflux of CCl_4 with the attendant fume hazard.

A method was therefore sought which is rapid and specific and does not need complex apparatus.

In 1957 Peppard et al. at the Argonne National Laboratory demonstrated that di-(2-ethylhexyl) phosphoric acid (EHPA) could be used to extract the lanthanides and yttrium from aqueous mineral acid systems. They showed that the extraction varied in a systematic manner with atomic number; the heavier rare earth elements and yttrium were extracted much more efficiently than the lighter lanthanides. Davis and Arnold (1964) used EHPA to separate yttrium-90 in the presence of Ca, Ba, and Sr and proposed an extraction method for the determination of Sr-90 in food. Later they demonstrated that the method was specific for the removal of some of the radionuclides that might be found as contaminants from fall-out (Arnold and Davis 1965). Petrow (1965) in his method for the determination of Sr-90 in bone ash used Aliquat 336 to remove Zr, U, and Fe.

The modifications to the above methods that were necessary to enable routine determinations of Sr-90 in the many types of biological and environmental samples received at the A.A.E.C. Research Establishment, are incorporated in the procedure reported here. They include reduction of iron using $NH_2OH.HCl$ to prevent emulsion on extraction and the handling of larger sample volumes.

2. REAGENTS

(1) Standard Sr-90/Y-90 solution, approximately 250 d.p.m./ml, accurately standardised.

(2) Di-(2-ethylhexyl) phosphoric acid (EHPA), obtained from K and K Laboratories, Hollywood, U.S.A. : 20% solution, dilute 100 ml to 500 ml with n-heptane.

(3) Aliquat 336 (methyl tricapryl ammonium chloride) obtained from General Mills Inc., U.S.A.

30% solution; dilute 150 ml to 500 ml with toluene and wash with an equal volume of concentrated HCl; allow to settle overnight.

(4) Yttrium carrier solution, 2.0 mg Y^{3+}/ml, 1.2706 g 'Spec. Pure' Y_2O_3 dissolved in a slight excess of 5N HNO_3 and made to 500 ml with demineralised water.

(5) Strontium carrier solution, approximately 5 mg Sr^{2+}/ml; dissolve 5.0 g $SrCO_3$ in a slight excess of 5N HNO_3 and adjust volume to 500 ml with demineralised water.

(6) HNO_3, approximately 5N; dilute 165 ml concentrated HNO_3 to 500 ml with demineralised water.

(7) HCl, approximately 5N; dilute 500 ml concentrated HCl to 1 litre; HCl, approximately 0.5N; dilute 50 ml concentrated HCl to 1 litre.

(8) Oxalic acid solution, 8%; dissolve 80 g A.R. Grade oxalic acid in about 400 ml demineralised water and dilute to 1 litre.

Oxalic acid solution, 0.1%; 12.5 ml of 8% solution made to 1 litre with demineralised water.

(9) Methyl red indicator solution, 0.1%; dissolve 0.1 g in a small amount of 10% NaOH and dilute to 100 ml with demineralised water.

(10) $NH_2OH.HCl$, 10% solution; dissolve 50 g in 250 ml demineralised water and dilute to 500 ml.

(11) NH_4OH, approximately 5N; dilute 150 ml concentrated NH_4OH to 500 ml with demineralised water.

3. SAMPLE PREPARATION

Generally the fresh, dry, and ash weights of all samples are recorded. To ensure efficient removal of carbon, ashing should be done at 700-800°C; however, samples received at the A.A.E.C. Research Establishment are also used for caesium-137 analysis and thus have to be ashed at 450°C to avoid loss of caesium.

The following procedures are used to obtain sufficient sample free from excessive carbon:

Fresh Milk: Evaporate to dryness at 110°C in an air oven, then ash at 450°C until free from excessive carbon. (Three gallons of milk gives about 100 g ash).

Powdered Milk: Weigh out 1 kg then ash.

Vegetation (grass, wood, leaves, seaweed, vegetables): Weigh the fresh samples, dry in an air oven at 110°C then ash. About 2 kg fresh weight should be sufficient.

Fish, Crabs, Oyster Flesh: Weigh the fresh samples, then ash. (About 2 kg fish, oyster flesh, and about 700 g crabs will give approximately 100 g ash).

Oyster Shell: Select an equal number of tops and bottoms, wash to remove any mud, moss or clinging shellfish and weigh approximately 250 g; dry in an air oven at 110°C, then ash.

Sand: Dry about 1 kg in an air oven at 110°C, sieve through a one-tenth inch mesh and discard the material retained by the sieve.

Soil: Dry about 1 kg in an air oven at 110°C then sieve through a quarter-inch mesh; discard the material retained by the sieve, and remove any organic material that passes through.

Rainwater: Add about 25 mg of strontium carrier, then evaporate to near dryness (about 5-10 litres is sufficient).

4. PROCEDURE

Part A

The amount of ashed or dried sample used for analysis is governed by the expected strontium-90 activity, and by the solubility of the sample on adjustment of pH after the leaching process. The following amounts have been found satisfactory:

Milk and Milk Powder: Weigh accurately 10-15 g ash into a 400 ml beaker; add 100 ml 5N HCl, cover and simmer for 30 minutes.

Vegetation: Weigh accurately 2-5 g ash into a 400 ml beaker; add 100 ml

5N HCl, cover and simmer for 30 minutes.

Fish, Crabs, Oyster Shell, Oyster Flesh: Weigh accurately 20-25 g ash into a 400 ml beaker; slowly add 100-150 ml 5N HCl, cover and simmer for 30 minutes.

Sand and Soil: Weigh accurately about 250 g dried sample into a 600 ml beaker; add 250 ml 5N HCl, bring to the boil with constant stirring; simmer for 30 minutes.

Rainwater: Take the total sample from the evaporation of 5-10 litres, transfer to a 400 ml beaker; add 100 ml 5N HCl, cover and simmer for 10 minutes.

Part B

(1) After leaching, filter the hot sample using a sintered glass filter, porosity 4. Wash the residue with 0.5N HCl, then with demineralised water.

(2) Transfer the filtrate and washings back to the beaker. Evaporate to approximately 200 ml if necessary, then cool to room temperature.

(3) Adjust the pH to about 1.0 with NH_4OH (using mechanical stirring).

(4) If a large amount of Fe^{3+} is present add 10% $NH_2OH.HCl$, while stirring at about 85°C, until the colour changes (use a fume hood). Cool to room temperature.

(5) Prepare a standard by measuring accurately about 15 pCi strontium-90/yttrium-90 solution into a 400 ml beaker. Add about 250 ml demineralised water and adjust the pH to 1.0. At the same time prepare a blank by using the same amounts of reagents as have been used for the sample; adjust the pH to 1.0.

(6) Check that the pH of all solutions after cooling is 1.0 and ensure that there is no precipitate present. (A dilution of the solution to a maximum of 400 ml is permissible).

(7) Transfer the solution to a 500 ml separating funnel. Add 50 ml of 20% EHPA and shake for one minute.

(8) Allow the phases to separate, then run the aqueous solution into a bottle containing 10.0 mg of yttrium carrier.

(9) Discard the organic layer and set the aqueous solution (with carrier) aside for 16 days.

Part C

(1) After the ingrowth period, check that the pH is 1.0. Transfer the solution to a 500 ml separating funnel.

(2) Add 50 ml of 20% EHPA, and shake for one minute, allow the phases to separate, then run the aqueous solution back into the bottle. (Retain until analysis is completed in case of accident).

(3) Record the time of separation for calculation of yttrium-90 decay.

(4) Wash the organic phase with 20 ml 0.5N HCl by shaking for one minute. Allow the phases to separate, then discard the wash solution. Repeat.

(5) Back extract the yttrium from the organic phase by shaking with 15 ml concentrated HCl for one minute. Allow the phases to separate, then transfer the HCl to a 250 ml separating funnel. Repeat.

(6) Discard the organic layer, then add 50 ml 30% Aliquat 336 to the HCl extracts. Shake for one minute, then allow the phases to separate.

(7) Run the HCl into a 100 ml beaker and discard the organic layer.

(8) Evaporate the HCl to dryness, then place the beaker in a muffle furnace. Heat to about 650°C until all the organic residue is destroyed.

(9) Cool. Add 10 ml of 0.5N HCl and warm until the yttrium is in solution. If any organic residue is still present, filter through a Whatman No. 541 filter paper.

(10) Add one drop of methyl red indicator solution, then add 5N NH_4OH dropwise until the colour changes. Add 2 drops 5N HCl.

(11) Heat to about 80-90°C. Add 20 ml of 8% oxalic acid solution. Cover with a watch glass and maintain at 80-90°C for about 30 minutes. Cool to room temperature.

(12) Place a one inch diameter Whatman No.5 filter paper on the special filter stick (H.A.S.L. manual 1959); wash with demineralised water using vacuum filtration.

(13) Filter the solution. Wash with 0.1% oxalic acid solution, then with methanol.

(14) Transfer the filter paper to the special mount (Figure 1) and dry under an infra-red lamp.

(15) Transfer the mounted filter paper to the low-background β counter

and count for at least six separate hours over a period of at least 65 hours. Note the time of the mid-point of each count.

(16) Weigh a porcelain crucible to constant weight after ignition at 800°C.

(17) Transfer the filter paper with precipitate from the mount to the crucible and ignite at 800°C for one hour.

(18) Cool, and weigh to constant weight.

(19) Calculate yttrium recovery. (mg Y_2O_3 x 0.787 = mg Y).

(20) Using the decay tables for yttrium-90 (Table 1) calculate the count rate at zero time (time of separation).

Calculations

$$\text{pCi Sr-90/g Ca} = \frac{C_o}{2.22} \times \frac{100}{E} \times \frac{100}{Y} \times \frac{100}{Ca} \times \frac{1}{ash}$$

C_o : Count rate in counts per minute at zero time, obtained by multiplying the actual count (corrected for background) by a decay factor, depending on the time elapsed between separation and count.

E : Per cent efficiency of counter (obtained from standard).

Y : Per cent yttrium recovery.

Ca : Per cent calcium in ashed or dried sample.

Ash : Weight in grams of ashed or dried sample.

Note: In sand samples, results are calculated as pCi/100 g and in rain-water pCi/l.

5. DISCUSSION

Initial studies showed that a preliminary extraction with EHPA was essential to remove any chemical yttrium and yttrium nuclides that could be co-extracted with the Y-90. Any other nuclides present that co-extract would also be removed from the solution and thus the second extraction after in-growth of Y-90 would be relatively free from interference.

With samples of milk, oysters, and fish, precipitation occurred on adjustment of pH after the leaching process. Investigation of the extraction of yttrium from increased volume of solution showed no loss of extraction efficiency using standard yttrium solution up to at least 400 ml. Accordingly, on increasing sample volumes before pH adjustment no precipitation was evident using sample quantities specified in the procedure, and comparisons with results obtained by the EDTA ion-exchange method showed good agreement (Table 2).

Large quantities of Fe^{3+} (greater than 1 g) in soil and sand samples gave emulsions on extraction with EHPA. It was considered impractical to limit the quantity of sample, so preliminary investigations were undertaken to improve extraction by reduction of the Fe^{3+}. The use of $SnCl_2$ proved effective but an emulsion was still produced on extraction. The addition of $NH_2OH.HCl$ on the other hand gave reduction without emulsion. In the presence of Cr^{6+}, reduction is obscured by co-reduction of the Cr^{6+}, but the addition of up to 10 g of $NH_2OH.HCl$ in excess was found to have no effect on extraction efficiency (Table 3). A comparison with results obtained by the EDTA ion-exchange method showed good agreement (Table 2).

Extraction of yttrium from 400 ml standard solution at varying pH showed good recovery in the range 0.4 to at least 2.0 (Figure 2). Investigation of carrier recovery at each of the steps of the procedure showed that 100 per cent recovery is possible (Table 4); about 86 per cent was removed from the EHPA in the first HCl strip and the remainder in the second. A third HCl strip showed no evidence of yttrium.

Recovery of yttrium-90 from a solution containing 20 g Ca, Ba, and 50 mg Sr, Zr, La, and Sc showed the specificity of the method for yttrium (Table 5). Extraction of yttrium using varying concentrations of EHPA in n-heptane showed that recovery dropped if the concentration of EHPA was less than 5% (Figure 3).

Aliquat 336 proved effective in removing iron from the strip solution. Examination of the decay curves of many samples verified radiochemical purity of the final yttrium-90 sources.

Blanks on the reagents showed no increased counts over the counter background. EHPA obtained from K and K Laboratories, Hollywood, U.S.A., needed no purification. Decontamination factors determined by Petrow, and Arnold and Davis, show that the method is applicable in the presence of a wide range of radionuclides (Table 6).

6. REFERENCES

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TABLE 1

YTTRIUM-90 DECAY FACTORS - 1 TO 100 HOURS (0.5 HOUR STEPS)

($t_{\frac{1}{2}}$ OF Y-90 TAKEN AS 64.4 HOURS)

Time	Factor	Time	Factor	Time	Factor	Time	Factor	Time	Factor
1.0	1.011	25.5	1.316	50.0	1.713	74.5	2.229	99.0	2.903
1.5	1.016	26.0	1.323	50.5	1.722	75.0	2.242	99.5	2.917
2.0	1.022	26.5	1.330	51.0	1.732	75.5	2.253	100	2.934
2.5	1.028	27.0	1.338	51.5	1.741	76.0	2.266		
3.0	1.033	27.5	1.345	52.0	1.750	76.5	2.278		
3.5	1.039	28.0	1.352	52.5	1.760	77.0	2.291		
4.0	1.044	28.5	1.359	53.0	1.769	77.5	2.302		
4.5	1.050	29.0	1.367	53.5	1.778	78.0	2.315		
5.0	1.055	29.5	1.374	54.0	1.788	78.5	2.328		
5.5	1.061	30.0	1.381	54.5	1.798	79.0	2.341		
6.0	1.067	30.5	1.389	55.0	1.807	79.5	2.352		
6.5	1.073	31.0	1.396	55.5	1.818	80.0	2.364		
7.0	1.078	31.5	1.404	56.0	1.827	80.5	2.378		
7.5	1.084	32.0	1.411	56.5	1.837	81.0	2.392		
8.0	1.090	32.5	1.419	57.0	1.847	81.5	2.405		
8.5	1.096	33.0	1.427	57.5	1.857	82.0	2.416		
9.0	1.102	33.5	1.434	58.0	1.866	82.5	2.430		
9.5	1.108	34.0	1.442	58.5	1.877	83.0	2.443		
10.0	1.114	34.5	1.450	59.0	1.887	83.5	2.457		
10.5	1.119	35.0	1.457	59.5	1.897	84.0	2.469		
11.0	1.126	35.5	1.465	60.0	1.907	84.5	2.482		
11.5	1.132	36.0	1.473	60.5	1.918	85.0	2.497		
12.0	1.138	36.5	1.481	61.0	1.928	85.5	2.510		
12.5	1.144	37.0	1.489	61.5	1.938	86.0	2.523		
13.0	1.150	37.5	1.497	62.0	1.949	86.5	2.536		
13.5	1.156	38.0	1.505	62.5	1.959	87.0	2.551		
14.0	1.162	38.5	1.513	63.0	1.970	87.5	2.565		
14.5	1.169	39.0	1.522	63.5	1.981	88.0	2.578		
15.0	1.175	39.5	1.530	64.0	1.991	88.5	2.592		
15.5	1.181	40.0	1.538	64.5	2.002	89.0	2.606		
16.0	1.188	40.5	1.546	65.0	2.013	89.5	2.620		
16.5	1.194	41.0	1.554	65.5	2.023	90.0	2.635		
17.0	1.200	41.5	1.563	66.0	2.034	90.5	2.648		
17.5	1.207	42.0	1.571	66.5	2.046	91.0	2.663		
18.0	1.213	42.5	1.580	67.0	2.057	91.5	2.677		
18.5	1.220	43.0	1.589	67.5	2.067	92 0	2.693		
19.0	1.227	43.5	1.597	68.0	2.079	92.5	2.705		
19.5	1.233	44.0	1.605	68.5	2.090	93.0	2.720		
20.0	1.240	44.5	1.614	69.0	2.101	93.5	2.736		
20.5	1.247	45.0	1.623	69.5	2.113	94.0	2.751		
21.0	1.254	45.5	1.632	70.0	2.124	94.5	2.765		
21.5	1.260	46.0	1.641	70.5	2.136	95.0	2.780		
22.0	1.267	46.5	1.649	71.0	2.147	95.5	2.796		
22.5	1.275	47.0	1.659	71.5	2.159	96.0	2.810		
23.0	1.280	47.5	1.667	72.0	2.170	96.5	2.824		
23.5	1.287	48.0	1.676	72.5	2.182	97.0	2.840		
24.0	1.295	48.5	1.686	73.0	2.194	97.5	2.856		
24.5	1.302	49.0	1.694	73.5	2.206	98.0	2.872		
25.0	1.309	49.5	1.703	74.0	2.218	98.5	2.887		

TABLE 2

COMPARISON BETWEEN EHPA AND EDTA ION-EXCHANGE METHODS

Sample	Ash Used grams	Number of Determinations	EHPA Method	EDTA Ion-Exchange Method
			pCi/g Ca	
Milk	15	2	3.5 ± 0.2	3.8
		2	5.5 ± 0.1	5.5
		2	2.7 ± 0.1	2.9
Grass	2.0	2	82.0 ± 2.0	80.0
		2	112	121
		2	242 ± 14	264
Fish	20	1	0.75	0.81
		1	0.92	< 0.90
		1	0.58	0.42
Oyster flesh	20	1	< 0.1	Not detectable
		1	< 1.0	< 1.3
		1	< 0.9	< 1.5
Oyster shell	20	1	< 0.1	< 0.6
		1	< 0.1	< 0.6
		1	< 0.1	< 0.3
Soil*	250	2	75.0 ± 2.0	87.0
		3	38.0 ± 3.2	36.3
		2	168 ± 6	200
I.A.E.A. food diet sample	4.0	4	34.5 ± 2.0	39.4 ± 5.2 (Average of 6)
			pCi/100 g	
Sand*	250	1	1.0	0.80
		1	0.80	0.80
	100	1	Not detectable	0.14

* $NH_2OH.HCl$ added

TABLE 3

EFFECT ON $NH_2OH.HCl$ ON EXTRACTION EFFICIENCY FOR YTTRIUM-90

Sample	$NH_2OH.HCl$ Used grams	EHPA	EDTA Ion-Exchange
		pCi Sr-90/g Ca	
150 g soil	2	34.6	36.3
	5	39.6	
	7.5	34.7	
	15	37.2	

TABLE 4

YTTRIUM RECOVERY FROM STANDARD YTTRIUM SOLUTION

Stage	Per cent Yttrium Detected	
	Run A	Run B
Aqueous after EHPA extraction	nil	nil
HCl washes	nil	nil
1st HCl strip	86.6	86.6
2nd HCl strip	15.7	11.0
3rd HCl strip	nil	nil
Strip solution after Aliquat 336 extraction	99.9	93.7

TABLE 5

EXTRACTION OF YTTRIUM-90 FROM STANDARD STRONTIUM-90/YTTRIUM-90 SOLUTION

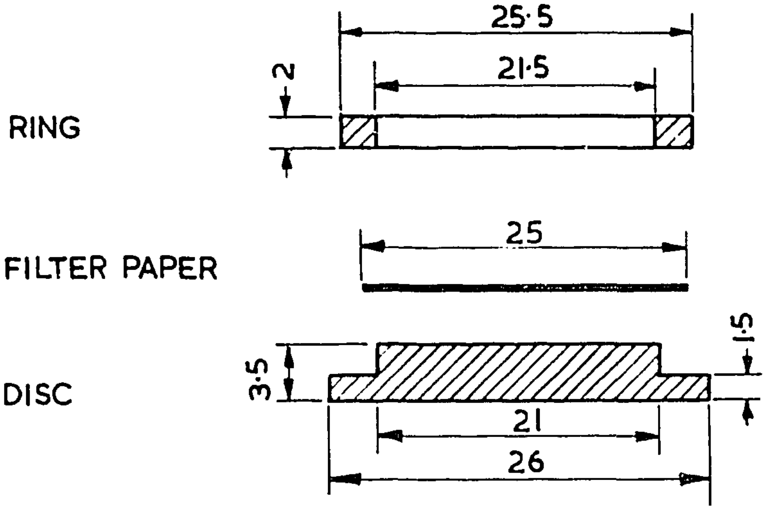
Sample	pH	Yttrium-90* counts/min
Standard Sr-90/Y-90 solution 27.9 d.p.m.	0.4	16.3
		15.0
	1.0	16.3
		16.6
	2.0	16.8
		16.4
Standard Sr-90/Y-90 solution 27.9 d.p.m. containing 20 g Ca, Ba 50 mg Sr, La, Sc, Zr	1.0	16.2
		16.6

* Corrected for yttrium recovery

TABLE 6

DECONTAMINATION FACTORS FOR YTTRIUM-90 EXTRACTION USING EHPA

	Petrow (1965)	Arnold and Davis (1965)
Ac-228	$> 10^3$	
Ba-140/La-140		$> 10^3$
Ca-45		$> 10^3$
Ce-144/Pr-144	$> 10^3$	$> 10^3$
Co-60	$> 10^3$	
Cr-51		$> 10^3$
Cs-137	$> 10^3$	$> 10^3$
Fe-55	$> 10^3$	
Fe-59		$> 10^3$
Mn-54	$> 10^3$	
Mo-99		$> 10^3$
Nd-147/Pm-147		$> 10^3$
Pm-147	20	
Ra-224	$> 10^3$	
Ru-106/Rh-106	$> 10^3$	$> 10^3$
Sr-90	$> 10^3$	
Th-228	200	
U	$> 10^3$	
Zn-65	$> 10^3$	$> 10^3$
Zr-95/Nb-95	$> 10^3$	$> 10^3$



MATERIAL: STAINLESS STEEL DIMENSIONS IN mm

FIGURE 1. MOUNTING DISC FOR YTTRIUM PRECIPITATE

P1067

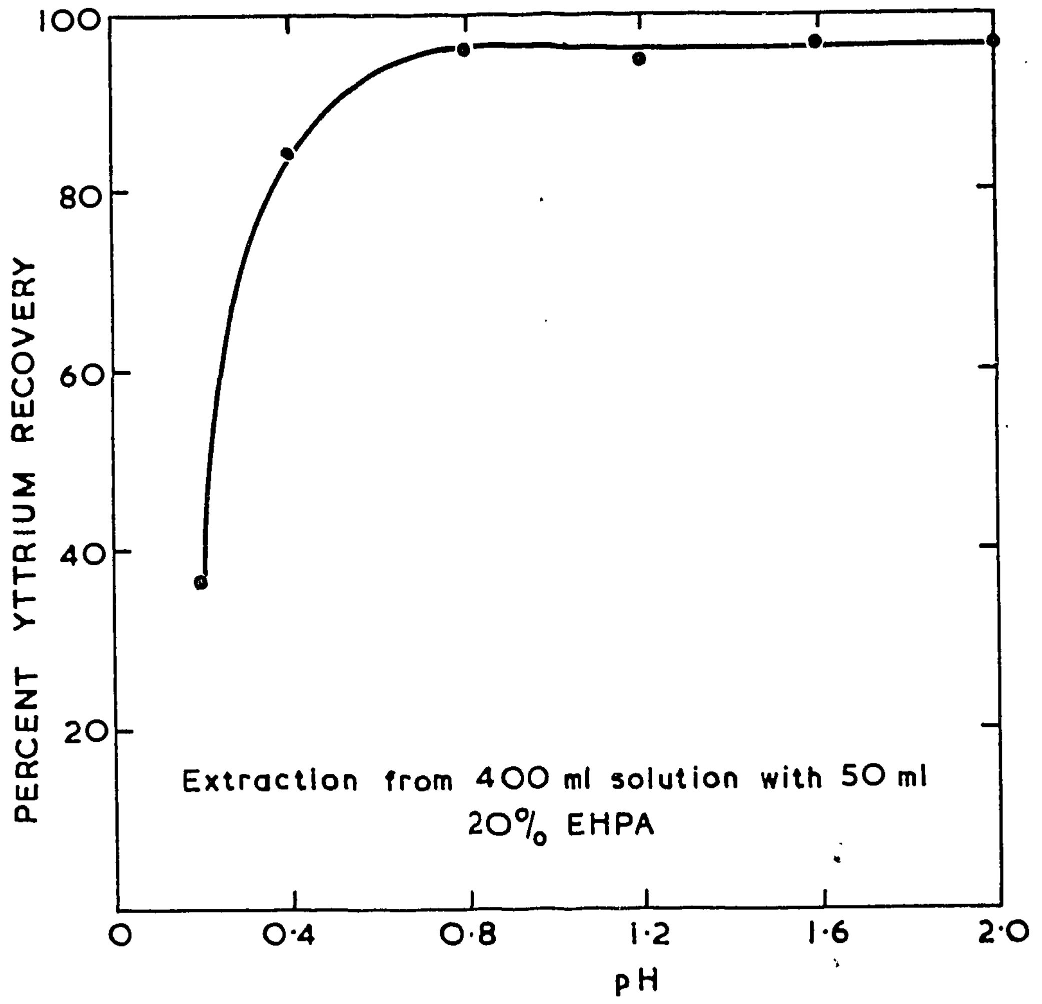


FIGURE 2. EFFECT OF pH ON YTTRIUM RECOVERY

P1253

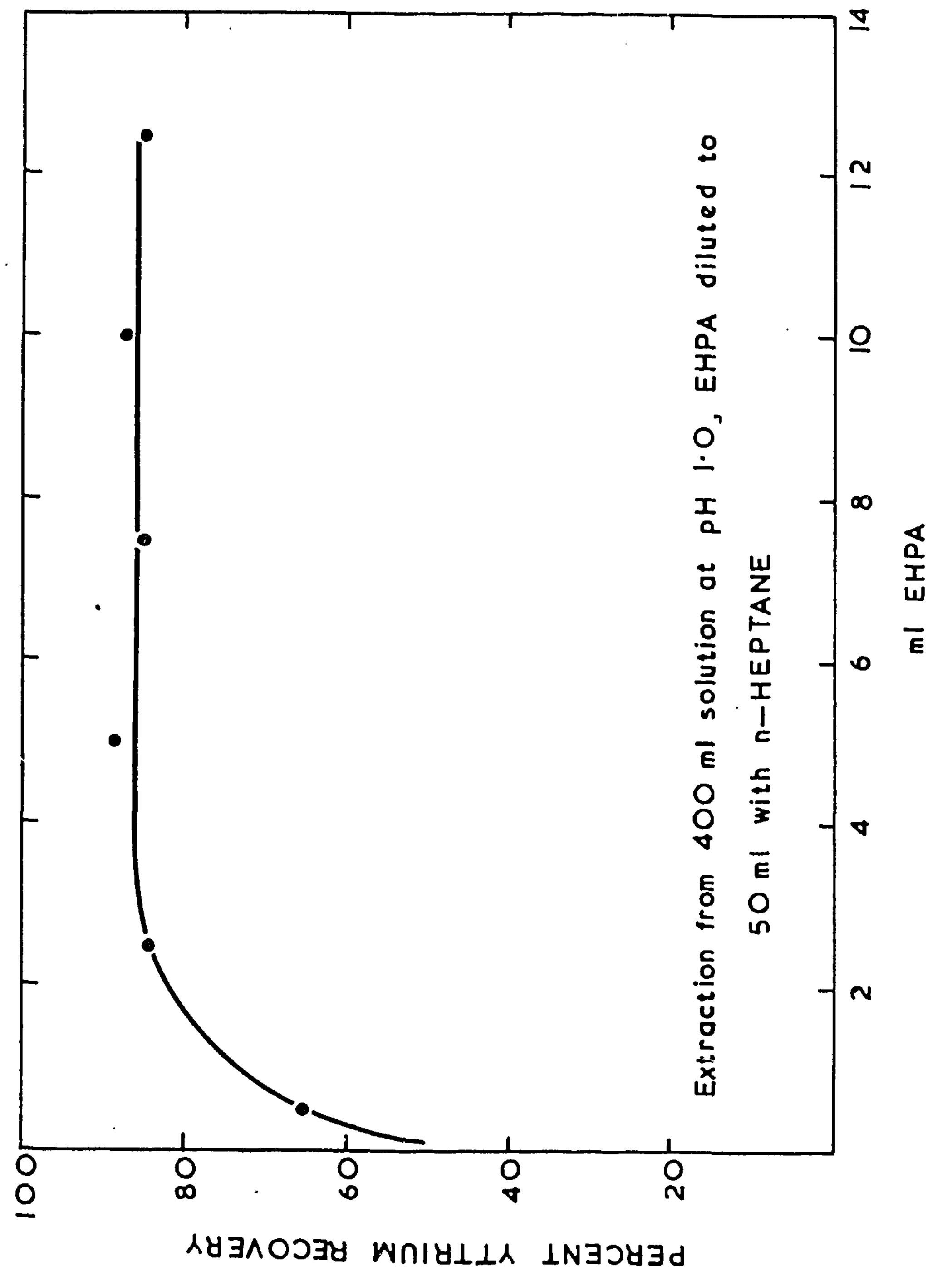


FIGURE 3. EFFECT OF EHPA ON YTTRIUM RECOVERY

P1253