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ABSTRACT

A method for the quantitative determination of zinc-65 in effluent is described. Zinc-65 is selectively extracted from a concentrate of effluent in HCl using Aliquat-336 in xylene. The extracted zinc-65 is determined by gamma spectrometry. Using an 8 in. x 4 in. NaI (Tl) crystal, concentrations as low as 0.07×10^{-12} Ci/ml can be determined, with ± 10 per cent statistical accuracy.

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CONTENTS

1. INTRODUCTION

A method is described for the determination of zinc-65 in effluent. Methods for the determination of a number of other nuclides in A.A.E.C. effluent have been reported (Lovell et al. 1961, Porritt 1967).

A direct measurement of ^{65}Zn by gamma ray spectrometry in the presence of ^{60}Co and ^{59}Fe is possible, but the method is imprecise and an initial chemical separation is necessary to obtain a reliable determination. A number of separation techniques are available, including precipitation, ion exchange (Dutton and Harvey 1967), dithizone extraction (Loveridge and Owens 1962), and solvent extraction with amines (Maeck et al. 1961).

Solvent extraction has the advantages of being rapid and selective. In the method recommended here, Aliquat-336 (a quaternary amine) in xylene is used to extract ^{65}Zn from a 1 M HCl solution containing ^{60}Co and ^{59}Fe. The extracted ^{65}Zn is then determined by gamma ray spectrometry.

2. EXPERIMENTAL

2.1 Reagents

Aliquat-336 (obtained from General Mills, Inc.) is a tricapryl methyl ammonium chloride $(R_1R_2R_3N\ CH_3)^+Cl^-$. Its molecular weight was determined by argentometric titration of the chloride in ethyl alcohol and found to be 489.

Reagent grade xylene, trichloroethylene and cyclohexane were used as diluents and solutions were stored in glass bottles.

Radioactive tracers ^{65}Zn (half-life 245 days), ^{59}Fe (half-life 45 days) and ^{60}Co (half-life 5.2 years) were supplied by Amersham, U.K. and standardised by the A.A.E.C. Radioisotope Standards Group. A zinc carrier solution containing 300 μg Zn/ml was used.

2.2 Apparatus

Distribution coefficients were determined with radioactive tracers using a well-type gamma scintillation counter. The counting arrangement consisted of a 0.75 x 1.5 in. thallium activated sodium iodide crystal coupled to an EMI 6097B photomultiplier tube in a 1.5 in. lead castle. Effluent samples labelled with ^{65}Zn were counted in a whole body monitor steel room using an 8 in. x 4 in. NaI (Tl) crystal.

2.3 Procedure

Distribution coefficients were obtained by shaking 5 ml each of the organic and aqueous phases in a 50-ml separatory funnel for 2 minutes at room temperature. After centrifuging, equal volumes of both phases were counted. Distribution coefficients were calculated from

$$D = \frac{\text{net counts/minute in organic phase}}{\text{net counts/minute in aqueous phase}}$$

The recovered zinc from effluent samples was evaporated on to a 0.0015 in. aluminium foil in an evaporating basin. The foil was completely dried and then folded into a 2 in. flattened square for subsequent evaluation by gamma counting.

3. RESULTS AND DISCUSSION

3.1 Effect of Diluent

Distribution coefficients were obtained for zinc from various concentrations of hydrochloric acid using Aliquat-336 in trichloroethylene, xylene and cyclohexane. Zinc-65 was used without the addition of carrier.

The results indicate that both the trichloroethylene and xylene gave similar distribution coefficients and good phase separation. However, with cyclohexane as the diluent and in the presence of acid concentrations greater than 4 M a third phase was obtained which was only apparent after centrifuging. This is probably due to the limited solubility of the amine in a non-polar solvent at higher acid concentrations. Distribution coefficients were not determined in these instances as activity balances were not obtained.

3.2 Rate of Zinc Extraction

The extraction of ^{65}Zn from 2 M HCl with 1 per cent Aliquat-336 in trichloroethylene was extremely rapid. After a contact time of 10 seconds more than 98 per cent was extracted, which is better than the extraction rate with tertiary amines (Mahlman et al. 1954). An extraction time of 2 minutes was chosen for all experiments for the determination of distribution coefficients.

3.3 Effect of Amine Concentration

A logarithmic plot of the distribution coefficient versus amine concentration shows an initial slope of approximately 2 at lower concentrations of amine, which is expected (Rydberg 1950) when the extracted ion is the divalent complex $ZnCl_4^{2-}$. At higher amine concentrations the slope decreases rapidly (Figure 1) presumably owing to association between amine molecules.

3.4 Stripping of Zinc

A solution of 5 per cent Aliquat-336 in trichloroethylene containing ^{65}Zn was stripped with various concentrations of nitric acid in the range 0.1 - 3.0 M. In every case the quantity of zinc released into the aqueous phase was greater than 99.9 per cent.

3.5 Separation of Zinc-65 from Fission Products

A dilute solution of freshly prepared fission products in 2 M HCl was labelled with ^{65}Zn and extracted with 5 per cent Aliquat-336 in xylene. The spectrum of the original mixture (Figure 2) indicated the presence mainly of ^{141}Ce, ^{103}Ru and $^{95}Zr/^{95}Nb$, together with ^{65}Zn. Figure 3 shows the removal of ^{65}Zn without any significant extraction of the fission products. The ^{65}Zn extracted was greater than 99 per cent (Figure 3).

Further experiments with a more concentrated fission product solution have shown that ^{141}Ce is not extracted by Aliquat-336 but approximately 1 per cent of $^{95}Zr/^{95}Nb$ and 4 per cent of ^{103}Ru are extracted. The low extraction of these nuclides does not interfere with the analysis of ^{65}Zn because their gamma ray energies are well below 1.1 MeV.

It was noted that in the presence of NaF (approximately 0.5 M) the extraction of $^{95}Zr/^{95}Nb$ is decreased (Figure 4). This is probably due to the formation of the highly stable fluoro-complex of the cations.

3.6 Extraction of Cobalt

Distribution coefficients were obtained for cobalt from various concentrations of hydrochloric acid using 1 per cent Aliquat-336 in trichloroethylene. Cobalt-60 tracer was used without the addition of carrier.

Cobalt extraction is negligible at low acid concentrations and increases with increasing acidity. At 6 M HCl the distribution coefficient is only 0.43 (Table 2).

A comparison with the distribution coefficients obtained for zinc (Table 1) shows that at 1 M HCl a decontamination factor of Zn/Co of approximately 2 x 10^5 is possible.

3.7 Extraction of Iron

Distribution coefficients were obtained for the extraction of both ferrous and ferric iron from HCl using 1 per cent Aliquat-336 in trichloroethylene.

Extraction of ferrous iron. Stock solutions of ^{59}Fe in 0.5 - 8.0 M HCl were reduced with ascorbic acid and extracted with 1 per cent Aliquat-336 in trichloroethylene. The higher distribution coefficients obtained with increasing acidity indicate that reduction is only complete at low acidities. Some Fe^{3+} remains at higher acidities and is extracted. The maximum acid concentration for complete reduction is approximately 2 M, as illustrated by the distribution coefficients for ferrous iron in Table 2.

Extraction of ferric iron. Stock solutions of ^{59}Fe in 0.5 - 8.0 M HCl were oxidised with H_2O_2 and extracted with 1 per cent Aliquat-336 in trichloroethylene.

The results indicate that at lower acid concentrations some iron is extracted and at high acidity (8 M HCl) the distribution coefficient is as high as 3×10^3.

This study of the extraction of iron by Aliquat-336 showed that in 1 M HCl in the presence of ascorbic acid a decontamination factor of Zn/Fe^{2+} of approximately 10^5 is possible (see Tables 1 and 2). A 1 per cent Aliquat-336 solution containing ferric iron is completely stripped of iron by washing twice with 1 M HCl containing ascorbic acid. This obviates the pre-reduction of the iron before extraction of ^{65}Zn from effluent with Aliquat-336.

3.8 Use of Xylene as a Diluent Instead of Trichloroethylene

It was observed that, using xylene as diluent instead of trichloroethylene, similar decontamination factors are obtained for Zn/Co and Zn/Fe^{2+} from 1 M HCl.

3.9 Separation of Zinc-65 from Effluent

Four litres of effluent containing a negligible quantity of β-γ activity were labelled with 2.8 nCi of ^{65}Zn, 61 nCi of ^{60}Co and 24 nCi of ^{59}Fe. These quantities represented one-tenth of the maximum permissible monthly discharge level (mpmd) for each nuclide.

In a gamma spectrum of the mixture, ^{65}Zn cannot be identified (Figure 5). However, extractions performed on 500-ml samples using the method given in Section 4 produced a good separation of ^{65}Zn, as evidenced by the spectrum of the recovered ^{65}Zn, shown in Figure 6. Two samples of pure ^{65}Zn equivalent to the quantity added to 500-ml effluent were used as standards to determine recovery data. The average recoveries of ^{65}Zn on four samples were 98.5, 99, 98.5 and 96 per cent.

4. RECOMMENDED PROCEDURES

(i) To 500 ml (or more) effluent solution add 5 ml of Zn carrier (1.5 mg Zn) and 2 ml H_2O_2 (see Note A). Evaporate in a beaker and finally to dryness in a platinum dish under an infra-red lamp.

(ii) Stir the residue with 5 ml of 2 M HCl and heat to dissolve. Transfer the solution to a 50-ml separatory funnel with washing until the final volume is approximately 10 ml.

(iii) Add 10 ml of 1 per cent Aliquat-336 in xylene and shake for 2 minutes. Centrifuge to clarify.

(iv) Run off the aqueous phase into another separatory funnel and extract again with a further 10 ml of 1 per cent Aliquat-336. Centrifuge and discard the aqueous phase, or retain it if ^{60}Co analysis is desired. Combine organic phases and wash three times with an equal volume of 1 M HCl containing a little (approximately 0.2 g) ascorbic acid.

(v) Strip the organic phase three times with 5-ml portions of 3 M HNO_3. Combine strip solutions, evaporate almost to dryness, cool, and make alkaline with dilute NH_4OH. Transfer with washing to a small evaporating basin which has been lined carefully with a double layer of 0.0015 in. aluminium foil (see Note B).

(vi) Evaporate solution in aluminium foil under infra-red lamps until completely dry. Fold the foil into a 2 in. flattened square and count for 100 minutes. Evaporate a standard ^{65}Zn solution on aluminium foil and count for a similar time to obtain a quantitative determination of ^{65}Zn in the sample.

Notes: (A) Heating with H_2O_2 clarifies turbid effluent solutions.

(B) Extra tenacity is achieved by spraying the foil with Krylon spray.

5. CONCLUSION

The method described is rapid and simple. If an 8 in. x 4 in. NaI (Tl) crystal is used the detection limit is 0.07 x 10^{-12} Ci of ^{65}Zn per ml of effluent, with a statistical accuracy of ± 10 per cent.

6. ACKNOWLEDGEMENT

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7. REFERENCES

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TABLE 1

EFFECT OF DILUENT ON THE EXTRACTION OF ZINC-65 WITH 1% ALIQUAT-336

Concentration of HCl ($\underline{M}$)	Distribution Coefficient		
	Trichloroethylene	Xylene	Cyclohexane
0	< 0.01	< 0.01	-
0.5	29	25	6
1.0	77	68	24
1.5	112	91	42
2.0	127	119	56
2.5	126	81	42
4.0	74	59	ND
6.0	24	17	ND
8.0	-	4	ND

ND not determined due to third phase

TABLE 2

EFFECT OF ACID CONCENTRATION ON THE DISTRIBUTION COEFFICIENTS OF COBALT AND IRON WITH 1% ALIQUAT-336 IN TRICHLOROETHYLENE

Concentration of HCl ($\underline{M}$)	Distribution Coefficient of Cation		
	Cobalt	Ferrous	Ferric
0.5	1.1×10^{-4}	4.7×10^{-4}	0.1
1.0	3.9×10^{-4}	8.4×10^{-4}	0.5
1.5	1.2×10^{-3}	-	-
2.0	2.6×10^{-3}	9.0×10^{-3}	12
3.0	1.0×10^{-2}	0.21*	67
4.0	5.0×10^{-2}	1.7*	317
5.0	-	10.9*	493
6.0	0.43	168*	1,547
8.0	-	1,533*	3,113

* reduction incomplete at higher acid concentrations

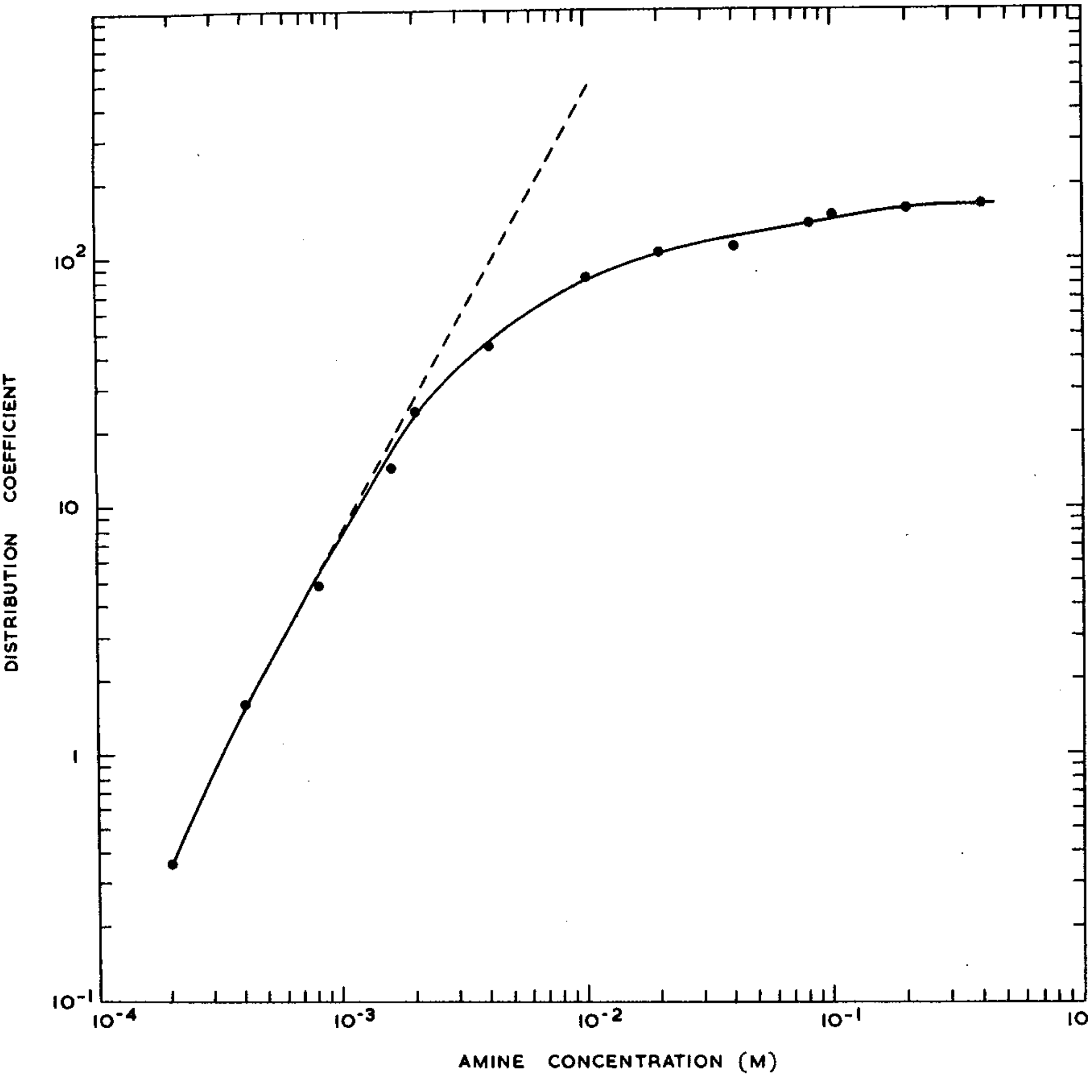

FIGURE 1. EFFECT OF AMINE CONCENTRATION ON THE EXTRACTION OF ZINC

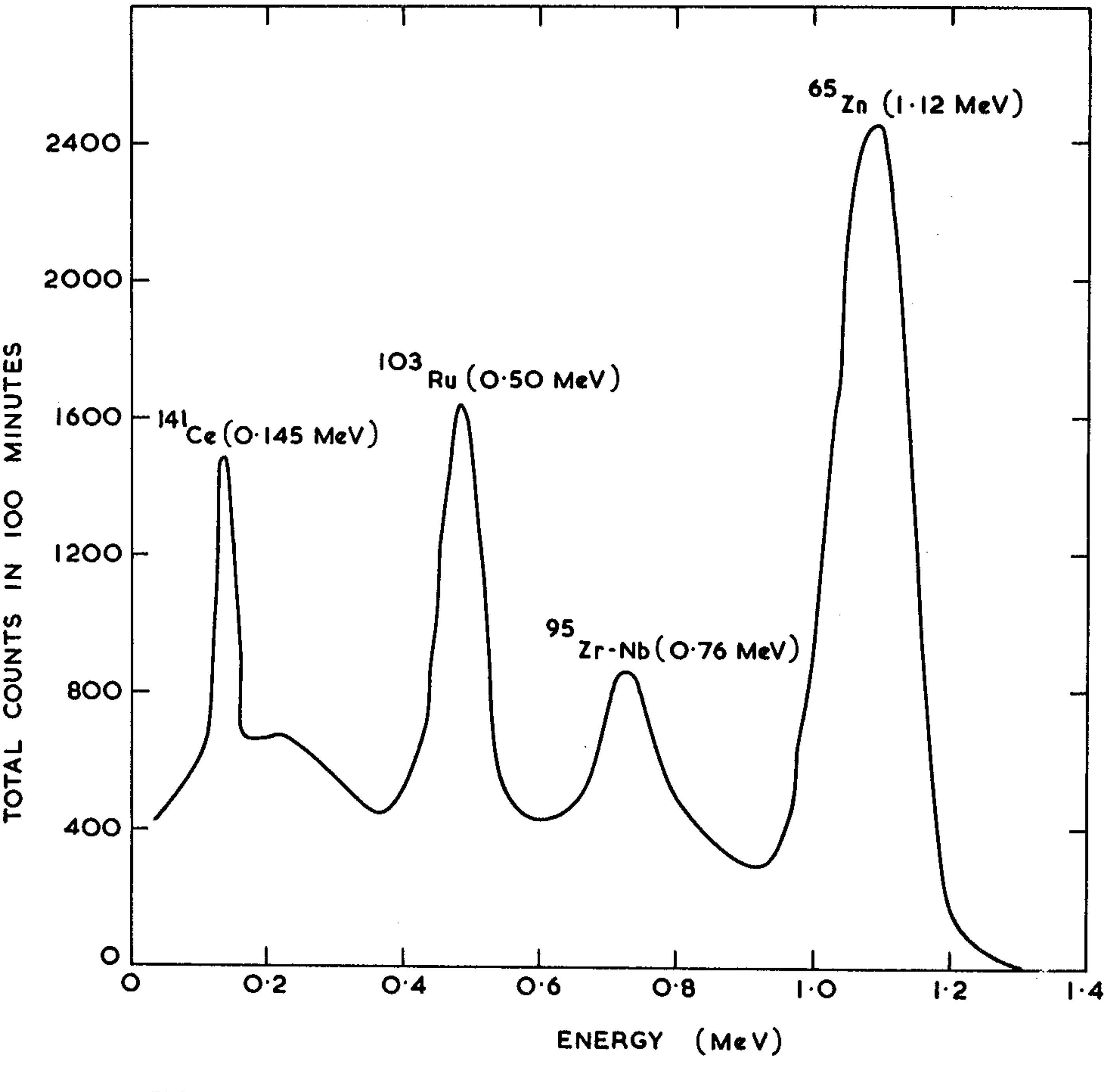

FIGURE 2. GAMMA SPECTRUM OF ZINC-65 AND FISSION PRODUCTS

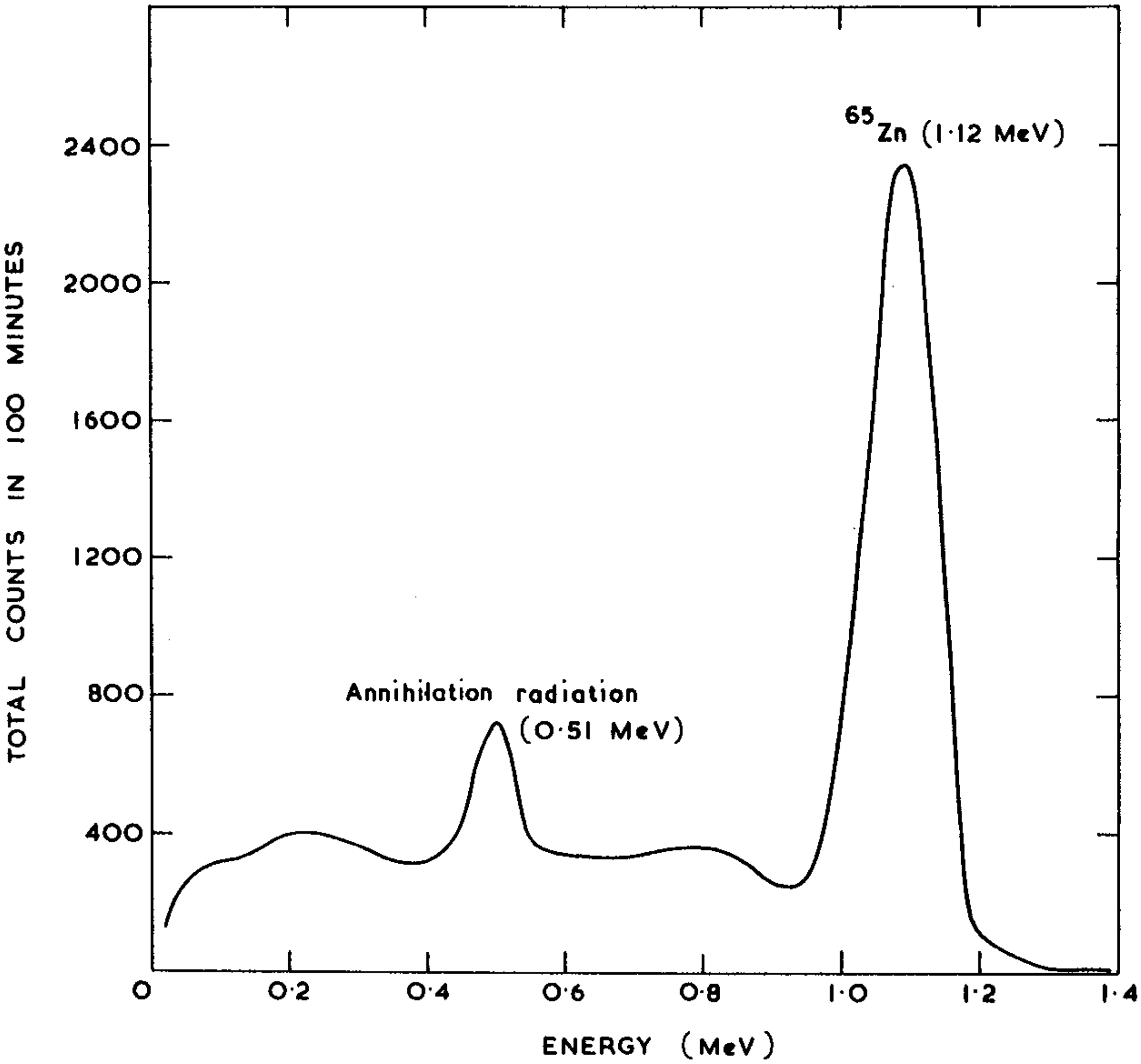

FIGURE 3. GAMMA SPECTRUM OF ZINC-65 SEPARATED FROM FISSION PRODUCTS

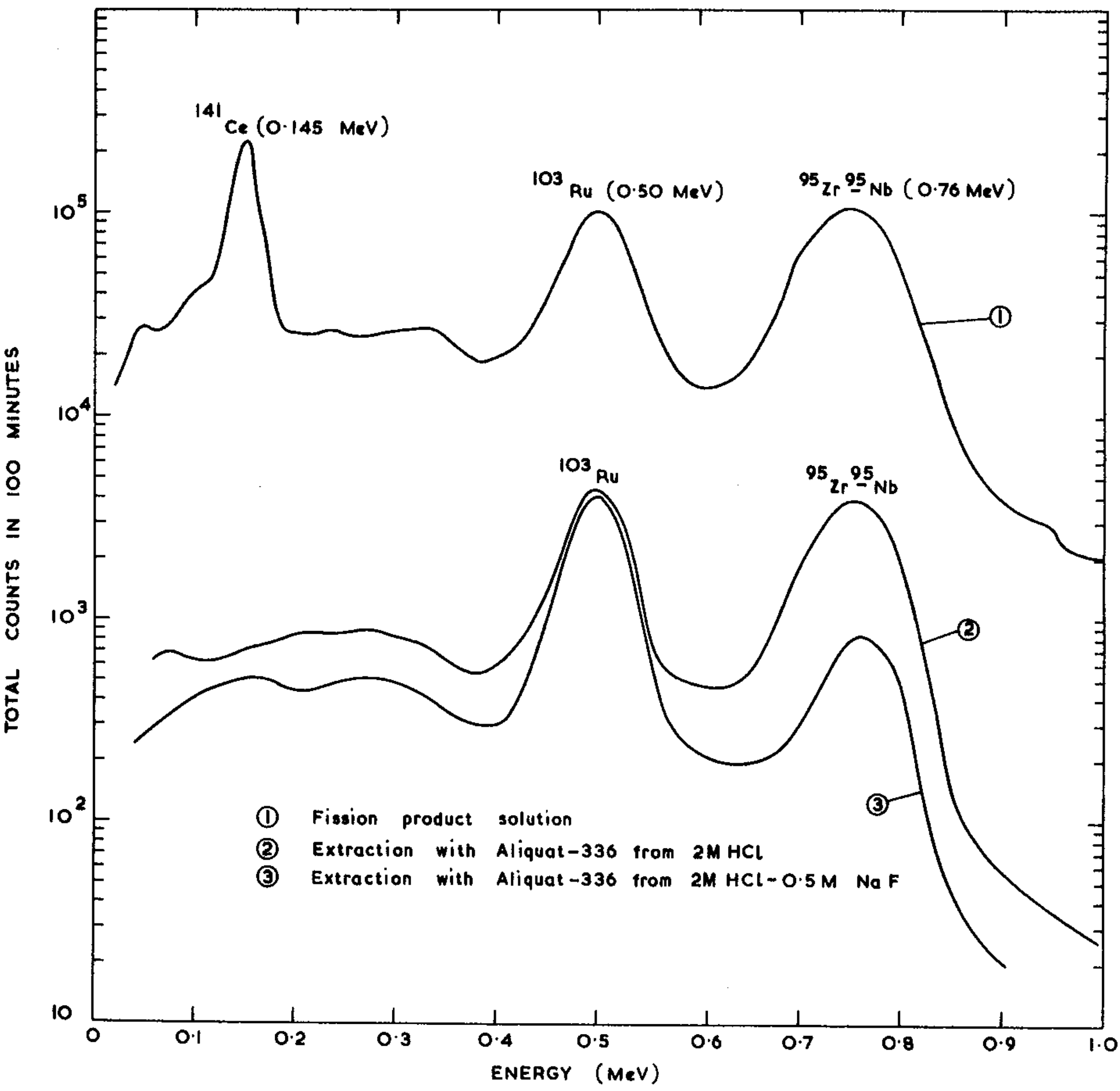

FIGURE 4. GAMMA SPECTRUM OF FISSION PRODUCT SOLUTION AND EXTRACTS

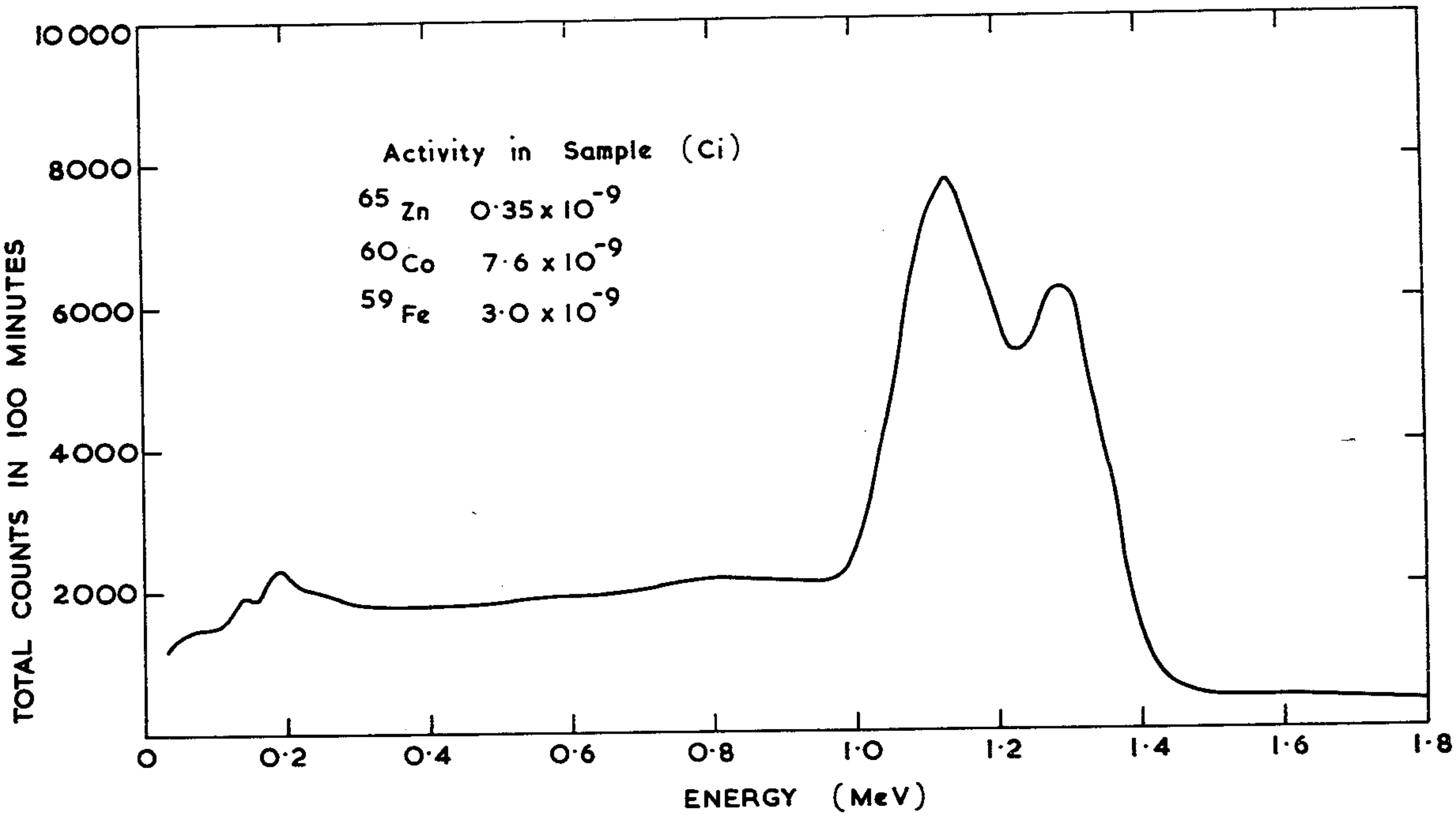

FIGURE 5. GAMMA SPECTRUM OF EFFLUENT CONTAINING mpmd/10 CONCENTRATIONS OF COBALT-60, IRON-59 AND ZINC-65

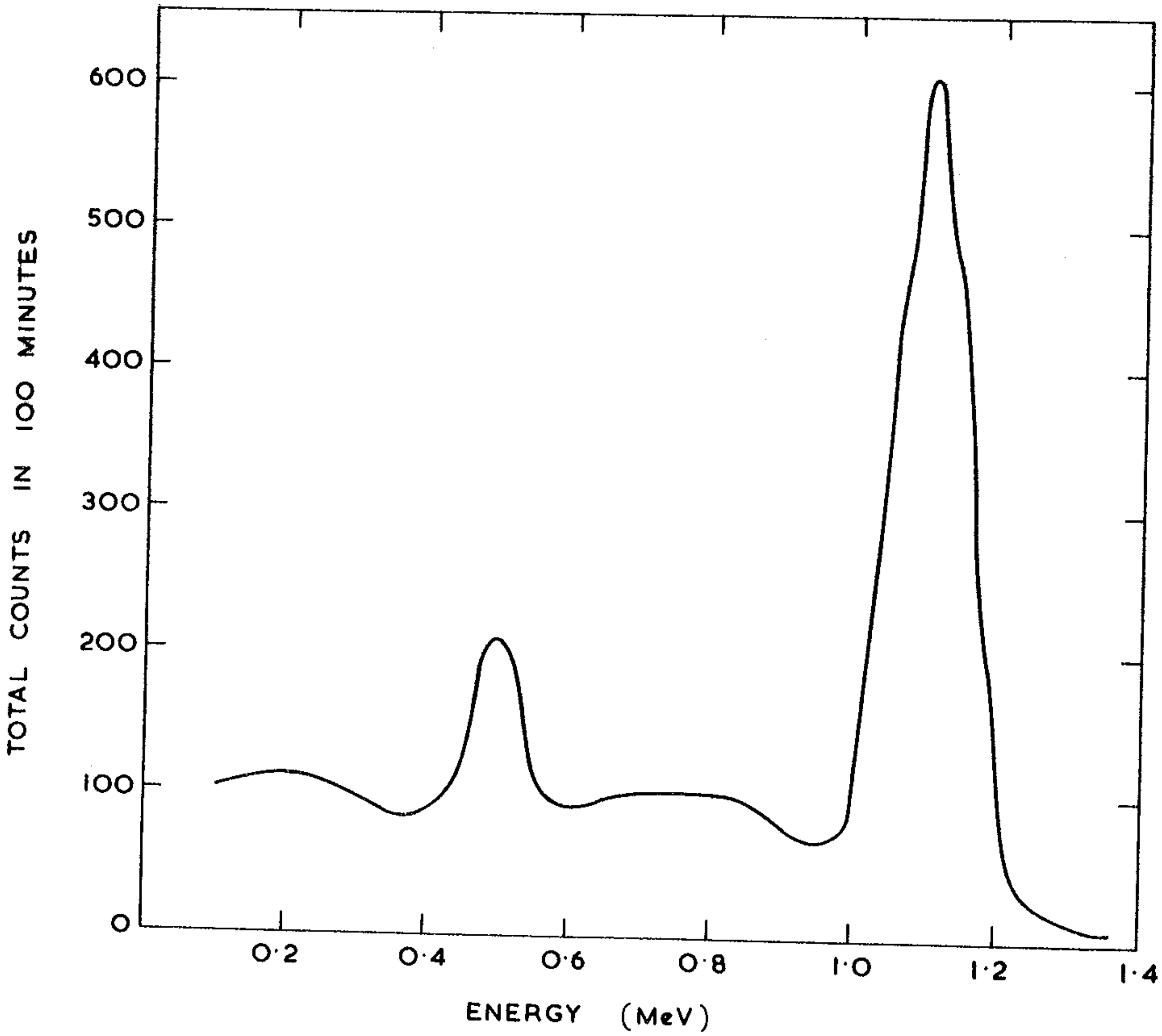

FIGURE 6. GAMMA SPECTRUM OF ZINC-65 EXTRACTED FROM A MIXTURE OF COBALT-60 AND IRON-59