

## DETERMINATION OF ZINC-65 AND MANGANESE-54 IN SEA WATER

S. M. SHAH AND S. R. RAO

*Health Physics Division, Bhabha Atomic Research Centre, Bombay*

**E**FFLUENT from the reactors and fallout from the atomic explosion introduce several induced radio-isotopes, most of which have half lives of the order of minutes to a few hours.

In this paper a convenient method for the measurement of Zn-65 and Mn-54 after radiochemical separation from a wide variety of radio-isotopes from sea water is described in view of the comparatively long half lives of these induced radio-nuclides. For an appreciation of the overall contribution to the aquatic environment, results of biological organisms and sediments are also presented.

In principle, the method consists of coprecipitation of Zn and Mn from sea water with  $\text{Fe}(\text{OH})_3$ <sup>1</sup>. Iron is removed by extracting with methyl isobutyl ketone. Zinc is separated by using anion exchange column. Manganese is extracted with chloroform after complexing permanganate with tetraphenylarsonium chloride<sup>2,3</sup>.

**Reagents:** Analar grade reagents were used. The solutions were made with glass distilled water.

Ammonia solution ..	5%
Nitric acid ..	Concentrated
Sulphuric acid ..	do.
Hydrochloric acid ..	8 N
do. ..	0.5 N
do. ..	0.005 N
Ferric nitrate solution	Solution containing 40 mgm iron/ml
Tetraphenylarsonium chloride	3.5% solution in distilled water
Chloroform ..	..
Sodium bismuthate ..	..
Dowex 1 × 8 (50-100 mesh)	A strongly basic anion exchange resin is settled in 0.5 N HCl and the finest material is removed by repeated suspension and decantation. A slurry of the main portion of the resin is used to fill the column with glass wool plug at the base. The columns are conditioned with 0.5 N HCl before use

### PROCEDURE

#### A. Precipitation of Total Zinc and Manganese with ferric hydroxide

(1) To 200 litres of filtered (through Whatman No. 1 filter paper) sea water in polythene container, 100 ml of conc.  $\text{HNO}_3$  and 50 ml of ferric nitrate solution are added,

(2)  $\text{Fe}(\text{OH})_3$  is precipitated from sea water by gradual addition of 1,400 ml of 5%  $\text{NH}_3$  with constant stirring (pH—9).

(3) The solution is stirred for further 10 minutes and precipitates are allowed to settle overnight.

(4) The supernatant is siphoned off and the  $\text{Fe}(\text{OH})_3$  is separated from the slurry at the bottom.

(5) In order to remove Zn and Mn quantitatively steps 2, 3 and 4 are repeated twice after adding 200 ml of conc.  $\text{HNO}_3$  and 50 ml of  $\text{Fe}(\text{NO}_3)_3$  solution, to the ammoniacal supernate each time.

#### B. Purification of Ferric Hydroxide Precipitate

(1) The combined  $\text{Fe}(\text{OH})_3$  precipitates from the centrifuge tubes are dissolved in conc.  $\text{HNO}_3$  (100 ml total) and volume is made up to 1 litre.

(2) 25 ml of  $\text{H}_2\text{O}_2$  (30%, 100 volume) are added and the solution is boiled for 15 minutes.

(3) The insoluble impurity is centrifuged off and  $\text{Fe}(\text{OH})_3$  is precipitated from the supernatant by the gradual addition of 600 ml of 5%  $\text{NH}_3$  with constant stirring.

(4) The precipitates are centrifuged off and the precipitation of  $\text{Fe}(\text{OH})_3$  from the supernatant is repeated twice after addition of 1.5 ml of  $\text{Fe}(\text{NO}_3)_3$  solution and 4 ml of conc.  $\text{HNO}_3$  each time.

#### C. Removal of Iron

(1) Ferric hydroxide precipitates from centrifuge tubes are dissolved in 200 ml of 8 M HCl. On dissolution, the volume becomes approximately 400 ml. To this 100 ml of conc. HCl are added.

(2) The solution is extracted with 200 ml of methyl isobutyl ketone (MIBK) in a one litre capacity separating funnel.

(3) Step 2 is repeated twice with 200 ml of MIBK. At this stage of extraction often some emulsion is observed and it is broken down by centrifugation and the insoluble residue is discarded.

Aqueous layer contains Zn and Mn and traces of iron.

#### D. Separation of Zinc

(1) Hydrochloric acid is evaporated off and the organic matter in the residue is destroyed with 10 ml of conc.  $\text{HNO}_3$ .

(2) Nitric acid is completely removed by heating and the nitrates in the residue are converted to chlorides by heating the residue with 10 ml of conc. HCl.

(3) The excess of HCl is removed by evaporation.

(4) The residue is taken up in 200 ml of 0.5 N HCl and passed through the anion exchange column of 30 cm length and 1 cm diameter at a flow rate of 0.5 ml per minute. Zinc is retained in the column and manganese comes in the effluent.

(5) Zinc from the column is eluted with 150 ml of 0.005 N HCl.

(6) The volume is concentrated to 20 ml and counted for Zn-65 in 512 channel analyser having 3" x 3" well type NaI(Tl activated) crystal.

#### E. Separation of Manganese

(1) 5 ml of conc.  $H_2SO_4$  are added to the effluent from the anion exchange column and the solution is evaporated to dryness to remove chlorides.

(2) The residue is taken up in distilled water containing 2 ml of conc.  $H_2SO_4$  and the volume is made up to 40 ml.

(3) Five drops of tetraphenylarsonium chloride solution are added and the mixture is extracted twice with 8 ml aliquots of  $CHCl_3$  in a separating funnel (100 ml capacity). This step removes interfering elements which would otherwise follow Mn extraction.

(4) Following this process, the aqueous layer containing Mn is evaporated to fumes of  $H_2SO_4$  to remove the traces of chloride ion and complexing agent.

(5) The residue from step 4 is diluted to 40 ml and transferred to a beaker.

(6) Manganese is oxidised to permanganate by stirring with 2 gm of sodium bismuthate. The solution is gently warmed for 15 minutes on a hot plate and the suspension is centrifuged off. (Chloride and tetraphenylarsonium chloride are completely removed in step 4 to avoid at this stage the trapping of the tetraphenylarsonium permanganate complex in the sodium bismuthate sludge and the reduction of permanganate by chloride.)

(7) The supernatant liquid is transferred to a separating funnel and five drops of tetraphenylarsonium chloride are added to the contents of the separating funnel and mixed well.

(8) The tetraphenylarsonium permanganate complex is then extracted twice by shaking with 8 ml aliquots of chloroform.

(9) Steps 7 and 8 are repeated till no permanganate colour is visible in the aqueous layer.

(10) In order to recover any Mn trapped in the sodium bismuthate sludge and Mn reduced by  $CHCl_3$  and remained in the aqueous layer, sodium bismuthate sludge is washed with water. The

washings are added to the aqueous layer of separating funnel and the aqueous layer is evaporated to fumes of  $H_2SO_4$ . The residue is diluted to 40 ml. Manganese is oxidised to permanganate by sodium bismuthate and extracted in  $CHCl_3$  after complexing with tetraphenylarsonium chloride.

(11) Step 10 is repeated till no permanganate colour is visible on oxidation with sodium bismuthate.

(12) The combined  $CHCl_3$  extracts are added to 200 ml of 4 N HCl in a beaker and heated gently till all  $CHCl_3$  is evaporated.

(13) Hydrochloric acid is concentrated to 20 ml and counted for Mn-54 in 512 channel analyser.

Four recovery experiments were carried out by adding known amounts of Zn-65 and Mn-54 tracers to 200 litres of filtered sea water.

To verify the radiochemical separation of Zn-65 and Mn-54 from other radionuclides with which they are likely to be associated, a mixture of Zn-65, Mn-54, and fission products (15 days old) was added to sea water and the radiochemical separation was carried out by the above procedure.

The chemical recoveries of the method for the total Zn and Mn (organic and inorganic) were verified by direct estimation of Zn and Mn in four litres of sea water after destruction of organic matter (by complete evaporation and heating) and comparing these values with Zn and Mn in about 200 litres of sea water determined by the present method. In order to reduce the blank of the reagent for Zn, HCl was purified by passing through the anion exchange column, iron was purified by MIBK extraction,  $HNO_3$  was purified by distillation and ammonia was purified by bubbling ammonia gas into glass distilled water.

#### DISCUSSION

Table I represents the stagewise recovery values of Zn-65 and Mn-54 in the four experiments carried out by adding known amounts of Zn-65 and Mn-54 to 200 litres of sea water. The final recovery values of Zn-65 varied from 74 to 84%, while those of Mn-54 from 69 to 74%.

Figure 1 represents the gamma spectrum of a mixture of fission product, Zn-65 and Mn-54 added to the sea water. Figures 2 and 3 represent the gamma spectra of Mn-54 and Zn-65 tracers used. Figures 4 and 5 give the gamma spectra of Mn-54 and Zn-65 after separation. From these figures it is seen that radiochemical separation of Zn-65 and Mn-54 from other fission products is complete.

Tables II and III give the chemical recovery of total Zn and Mn in 200 litres of sea water by the



present procedure. From this it is seen that the present procedure determines Zn-65 and Mn-54 present in the organic form also.

below detectable level. However, marine sediments were found to contain Zn-65. Ganapathy *et al.*<sup>4</sup> have also pointed out the high sorption capacity of sediment for Zn.

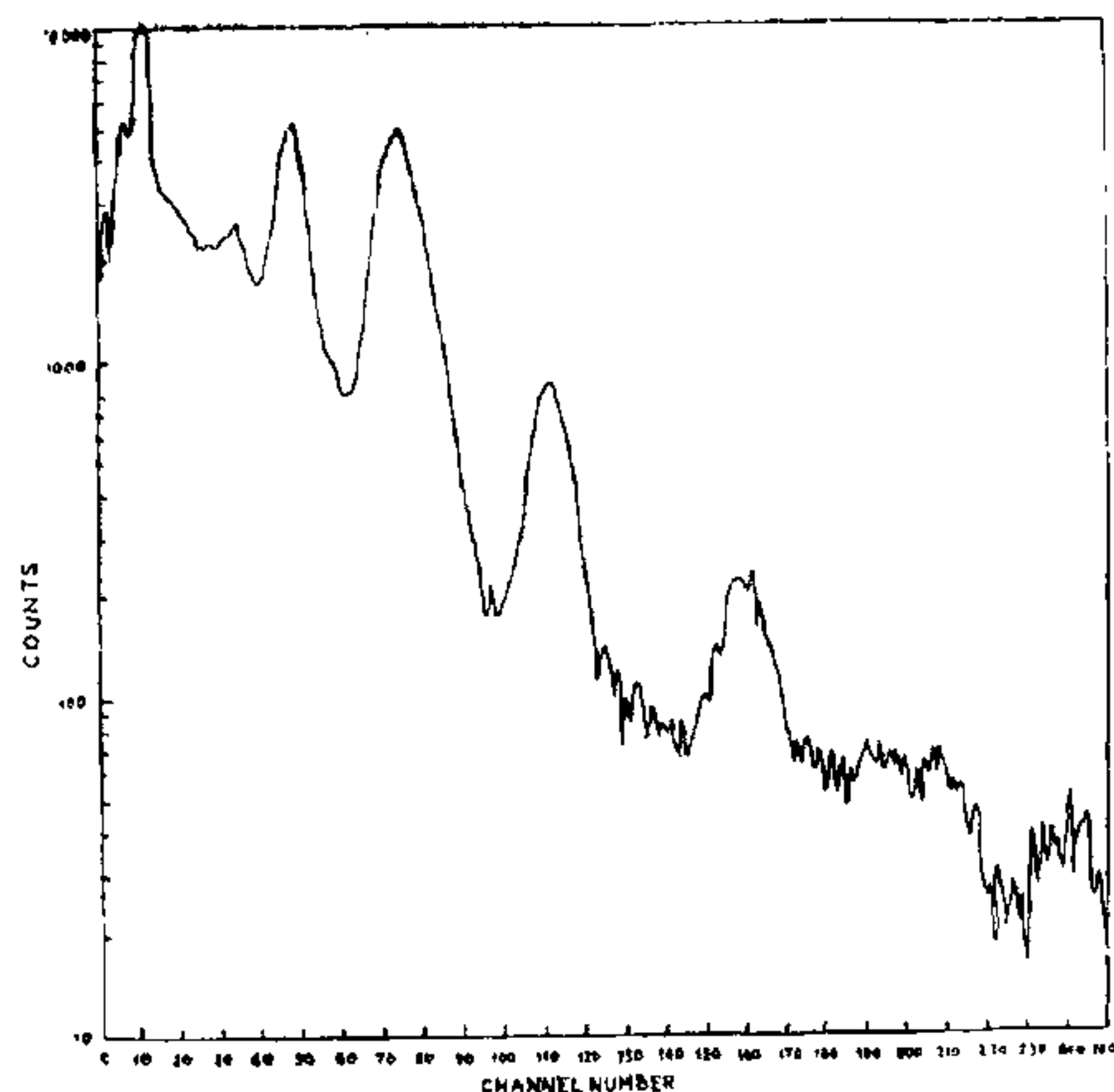


FIG. 1. Gamma spectrum of the mixture of fission product, manganese-54 and zinc-65.

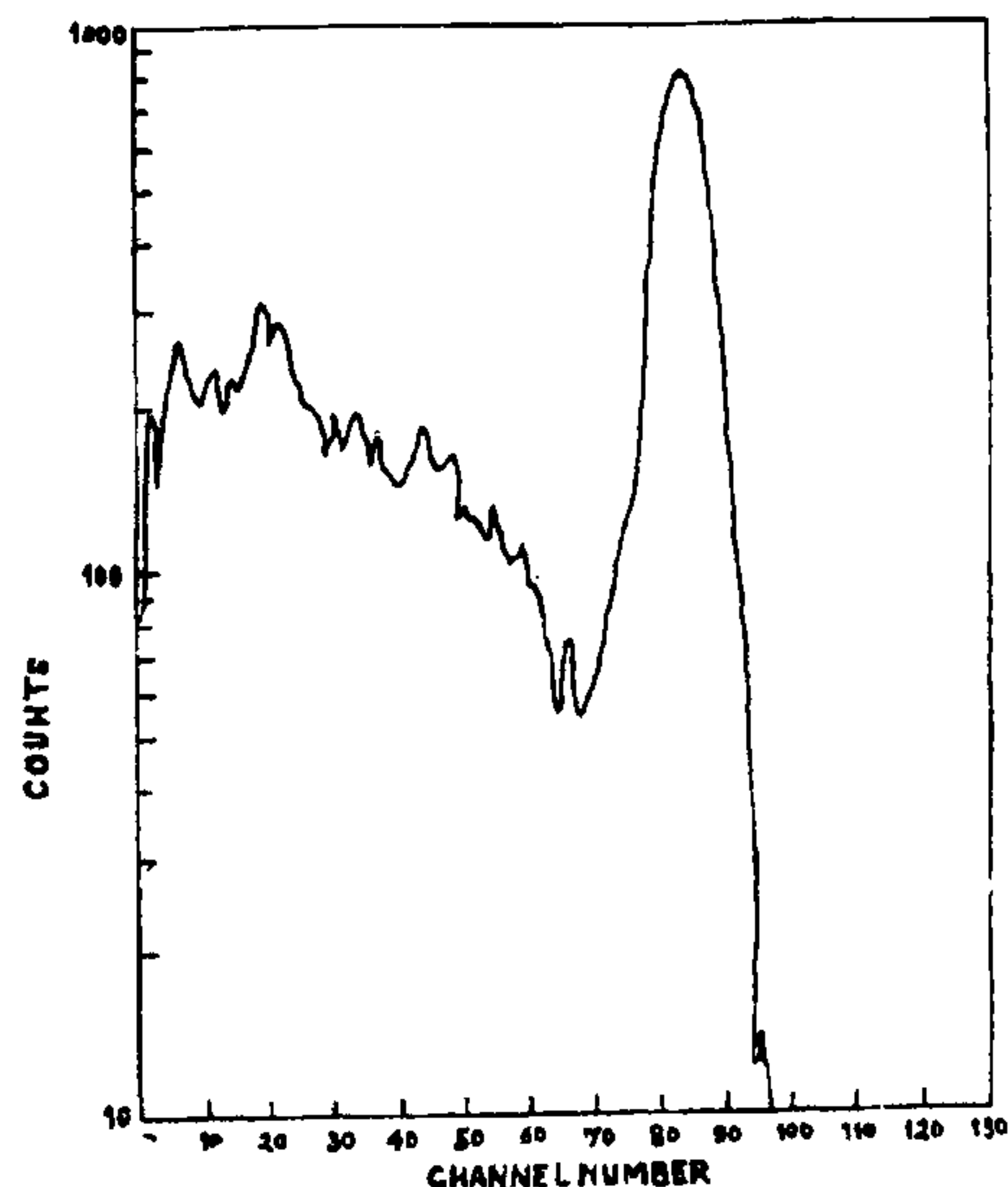


FIG. 2. Gamma spectrum of manganese-54 component.

Eight sea water samples, six biological samples of prawns and Bombay duck and four N/20 HCl leaches of sediment samples have been analysed for Zn, Mn, Zn-65 and Mn-54. The values are given in Tables IV, V and VI. In sea water and biological samples Zn-65 and Mn-54 are found

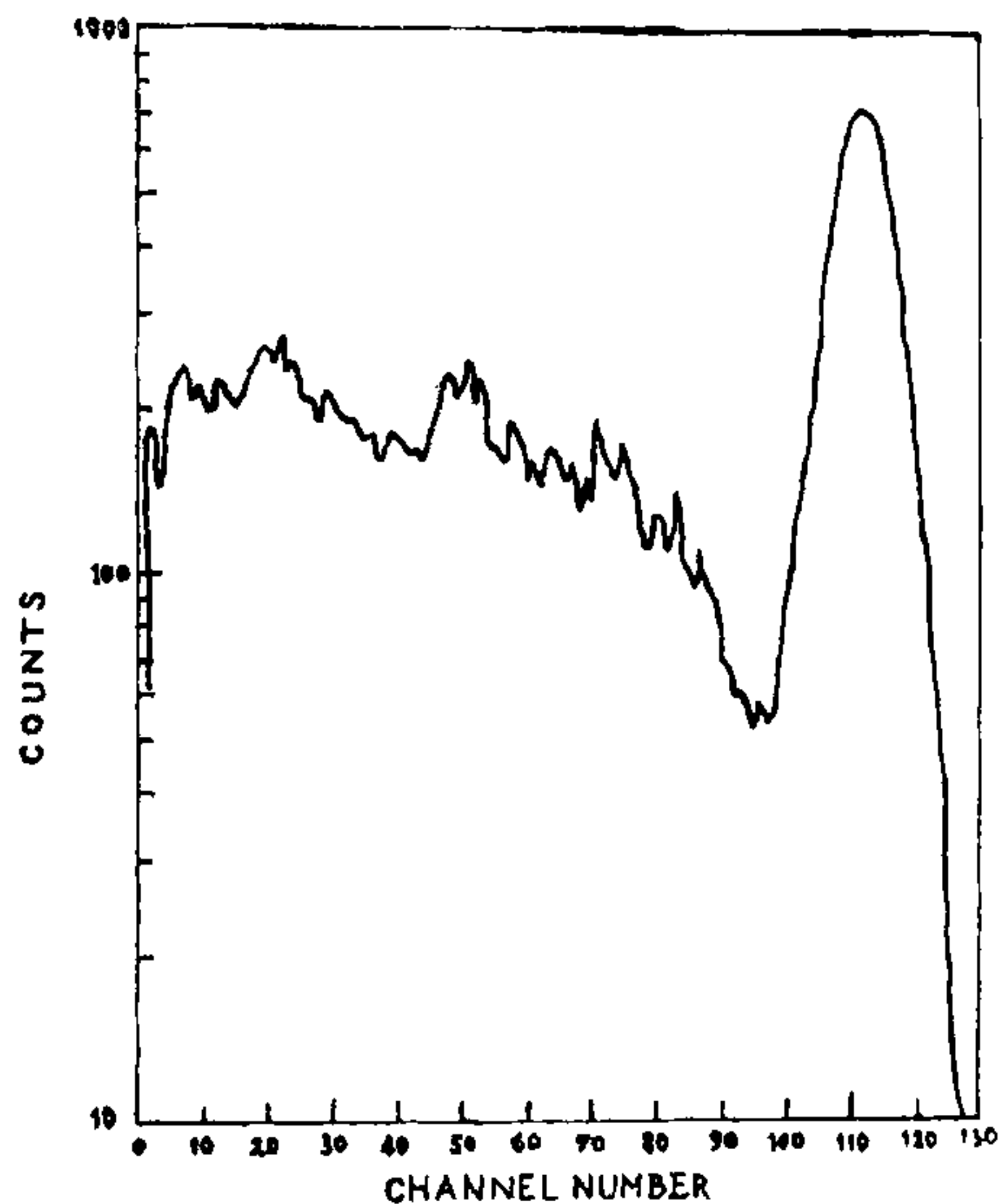


FIG. 3. Gamma spectrum of zinc-65 component.

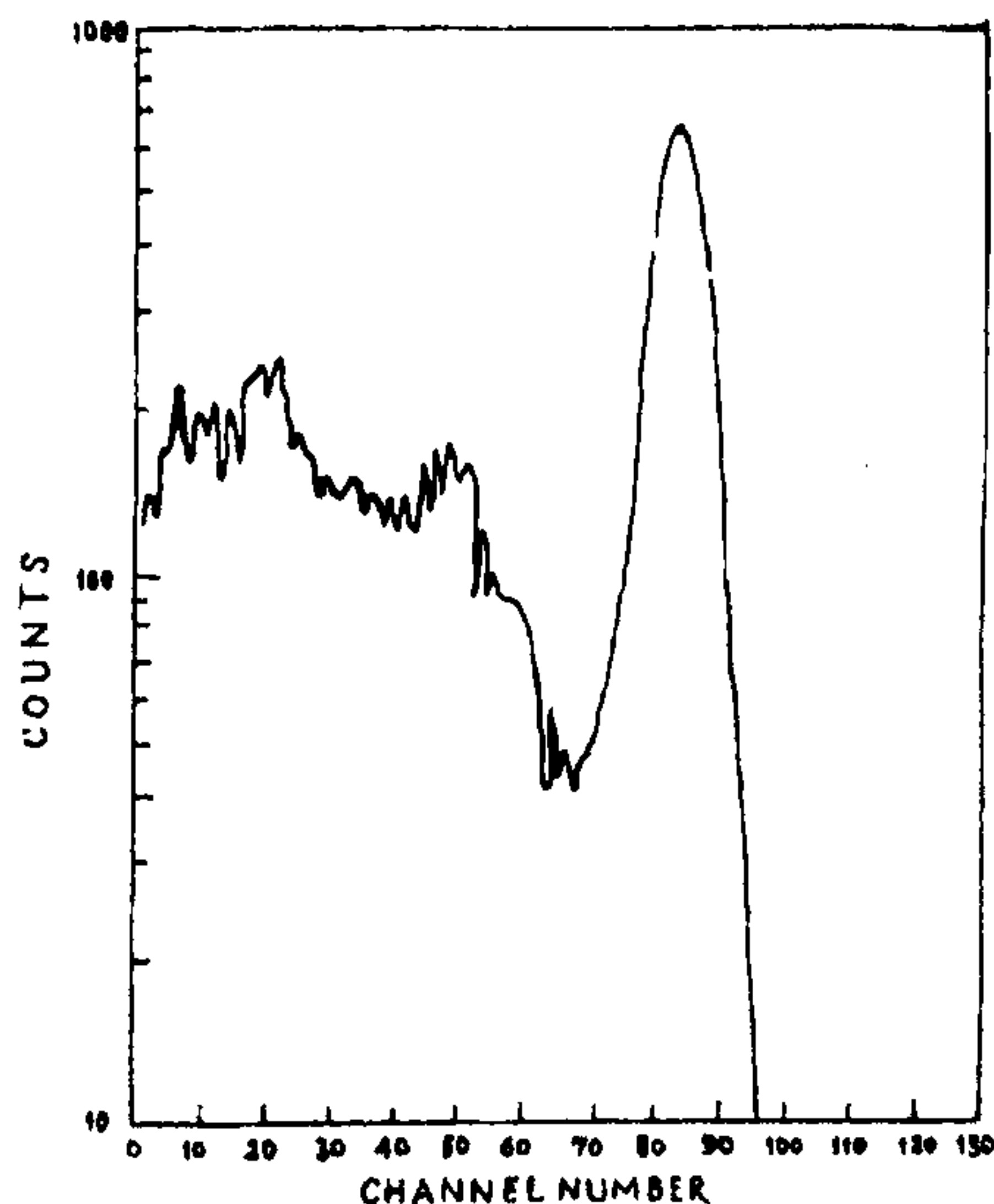


FIG. 4. Gamma spectrum of manganese-54 after separation.

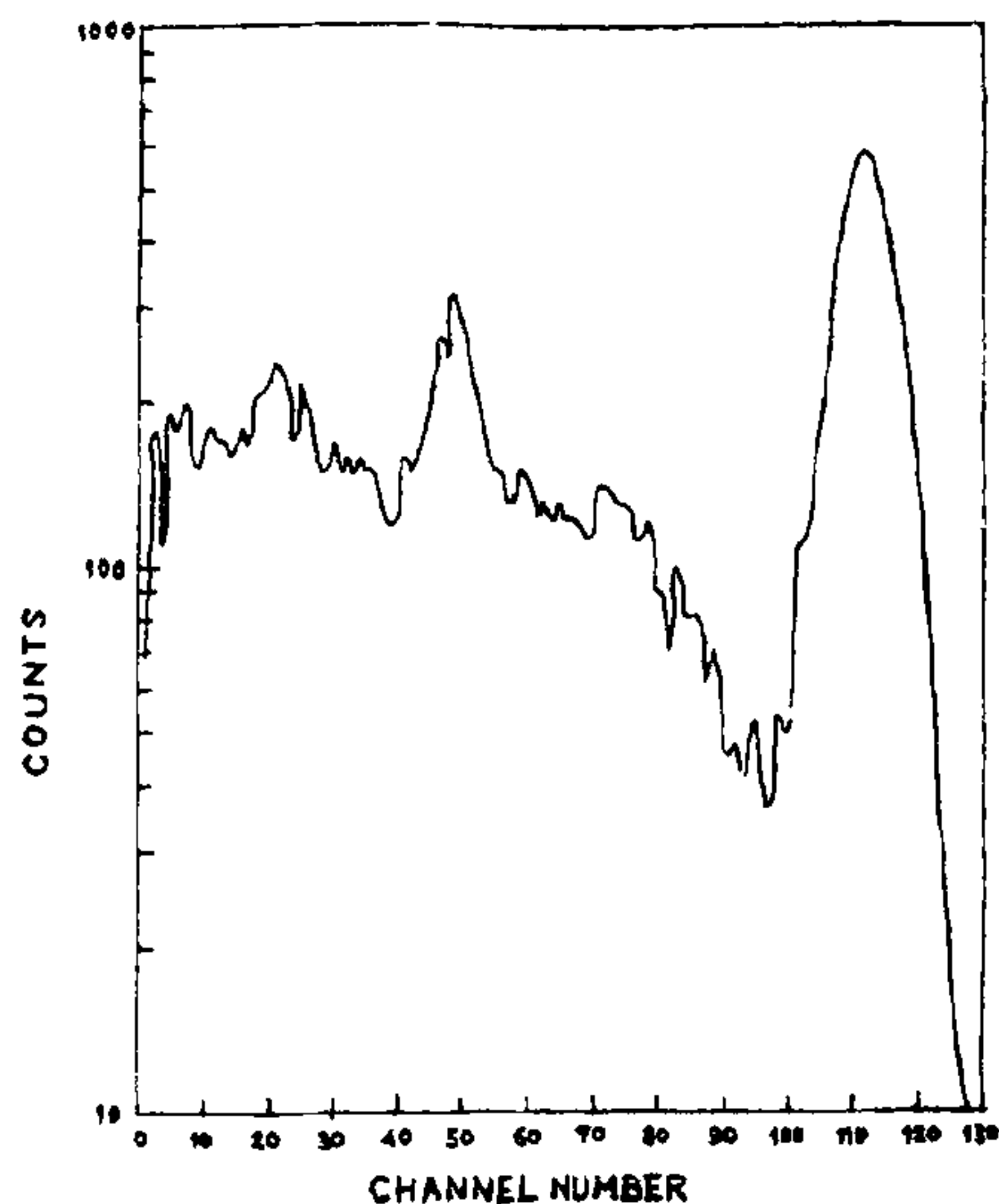


FIG. 5. Gamma spectrum of zinc-65 after separation.

TABLE I

Recovery values of Zn-65 and Mn-54 tracers at the various stages of the method

Stage of the method	Radio-nuclide	Percentage recovery			
		Expt. 1	Expt. 2	Expt. 3	Expt. 4
Precipitation of Zn and Mn with Fe (OH) <sub>3</sub>	Zn-65	100	100	96	94
	Mn-54	87	96	88	91
Purification of Fe (OH) <sub>3</sub> precipitates	Zn-65	84	90	90	82
	Mn-54	79	82	84	83
MIBK extraction	Zn-65	78	86	87	79
	Mn-54	76	79	80	78
Ion exchange separation	Zn-65	74	84	80	75
Extraction of Mn with tetraphenylarsodium chloride	Mn-54	70	74	73	69

TABLE II

Chemical recovery values of total Zn from sea water

Sample No.	Volume	Zn recovered	Direct estimation of Zn in 4 litres of the sample after destruction of organic matter	% recovery
1	185 litres	1587 µg	44 µg	78
2	195 "	1738 µg	44 µg	81

TABLE III

Chemical recovery values of total Mn from sea water

Sample No.	Volume	Mn recovered	Direct estimation of Mn in 4 litres of the sample after destruction of organic matter	% recovery
1	185 litres	1200 µg	32.56 µg	80
2	195 "	840 µg	20.88 µg	82

TABLE IV

Zn, Mn, Zn-65 and Mn-54 contents of sea water samples

Sample No.	Zn µg/ml × 10 <sup>3</sup>	Mn µg/ml × 10 <sup>3</sup>	Zn-65 µµci/200 L	Mn-54 µµci/200 L
1	8.4	4.2	B.D.L.	B.D.L.*
2	8.9	4.1	B.D.L.	B.D.L.
3	8.2	5.1	B.D.L.	B.D.L.
4	8.7	6.4	B.D.L.	B.D.L.
5	7.4	4.3	B.D.L.	B.D.L.
6	8.3	4.8	B.D.L.	B.D.L.
7	7.1	4.1	B.D.L.	B.D.L.
8	6.9	4.7	B.D.L.	B.D.L.

\* Below detection limit.

TABLE V

Zn, Mn, Zn-65 and Mn-54 contents of biological samples

Sample No.	Species	Zn µg/g (wet wt.)	Mn µg/g (wet wt.)	Zn-65 µµci/g	Mn-54 µµci/g
1	Prawns	3.2	0.52	B.D.L.	B.D.L.
2	"	5.2	0.44	B.D.L.	B.D.L.
3	"	2.1	0.65	B.D.L.	B.D.L.
4	Bombay duck	1.5	0.47	B.D.L.	B.D.L.
5	"	1.7	0.52	B.D.L.	B.D.L.
6	"	1.7	0.38	B.D.L.	B.D.L.

TABLE VI

Zn, Mn, Zn-65 and Mn-54 contents of sediment (N/20 HCl leach)

Sample No.	Zn µg/g dry wt	Mn µg/g dry wt	Zn-65 µµci/500 g dry wt.	Mn-54 µµci/500 g dry wt.
1	82	568	0.5	B.D.L.
2	95	600	0.4	B.D.L.
3	78	628	0.3	B.D.L.
4	93	600	0.5	B.D.L.

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## ELIMINATION OF STATIC RISKS IN EXPLOSIVES FACTORIES

P. V. SATYAVRATAN

*Electronics Division, Indian Detonators Ltd., Hyderabad*

AND

KIRTI

*Scientific Officer, Isotope Division, Bhabha Atomic Research Centre, Bombay*

**M**OST explosives are liable to collect static electricity, particularly when handled in quantity, the degree of the charge depending on the explosive. Thus, Lead Styphnate is known to be more prone to static charges than other explosives. Every explosive has a limit of electric charge above which it is liable to go off. It, therefore, follows that potentially in the handling of explosives there is always a risk of static charge accumulating to this dangerous level unless positive steps are taken to dissipate such charge or prevent its accumulation.

It has been known that in the Ordnance Filling Factories during the dry months of February, March and November, when humidity is very low a number of accidents occur in the handling of initiating composition particularly those containing Lead Styphnate. The prevention of such accidents has always been a problem. It is also known that if the prevailing humidity in the vicinity of the explosive is 70% or above, the chances of accumulation of static electricity is very much lessened. However, certain operations do not allow maintenance of this RH continuously as at this high humidity the other components or the performance of the explosive is affected by the moisture.

At the Indian Detonators Limited, Hyderabad, where large quantities of Lead Azide, Lead Styphnate and P.E.T.N. (Pentaerythritol Tetranitrate) are handled, we are aware of these risks and have prescribed certain precautions to prevent accumulation of static charges. But in the months of April and May and also in the winter months the humidity at Hyderabad goes down to 20% and in these circumstances the risks become aggravated. We have had a few accidents in our shops, some of which could be attributed only to

static electricity. We, therefore, took up this problem of elimination/prevention of static electricity in a very systematic manner.

Our main problem was the handling of dry Pentaerythritol Tetranitrate (P.E.T.N.). Dry P.E.T.N. during its handling can accumulate heavy static charges. At Hyderabad we are not only drying P.E.T.N. in batches of 1.2 Tonnes but also sieve this quantity through an 18 mesh B.S.S. sieve to remove agglomerates before use in filling. The sieving is done on a wooden frame mounted on an Aluminium bin. This sieved material is transported in Aluminium milk cans to the various sections. Considerable static charge accumulates both during sieving and during scooping of the sieved material into the Aluminium cans. A system of earthing of all containers has been in vogue and this was all the precautions offered.

Static charges also can be caused by the individuals handling explosives by their movements and especially if they are insulated by Rubber/P.V.C. shoes. We have, therefore, insisted that all our workmen handling explosives should be barefooted. It is said that certain individuals are more prone to the accumulation of static charges than others but we have not established this fact.

Measurement of these charges poses a problem. Normal electronic instruments which involve the use of probes are not applicable from safety considerations as there is a danger of sparking and explosion. We have now procured a static meter from Messrs. 3 M Company, 3 M Centre, St. Paul, Minnesota 55101. This is a gun type static meter and works on the following principle. The charge on the surface being measured is induced on to an internal element on the meter. This is detected by using a nuclear source and high resistance