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DETERMINATION OF THALLIUM BY ACTIVATION ANALYSIS BASED ON THE REACTION $^{203}Tl(n, 2n)^{202}Tl$

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A B S T R A C T

Thermal neutron activation of thallium leads to 3.9-year ^{204}Tl and 4.3-min. ^{206}Tl isotopes which are not gamma emitters. However, a method of analysis based on the reaction ^{203}Tl(n,γ) ^{204}Tl has been developed by Delbecq et al., and used to detect thallium amounts with a sensistivity of 0.1 µg. In spite of this high sensitivity, this method has the disadvantage of measuring the beta activity and therefore is not very specific.

In the present note an activation analysis based on the reaction ^{203}Tl(n,2n)^{202}Tl is discussed. The product isotope ^{202}Tl has a convenient half-life of 12 days and is a gamma emitter, thereby makes the determination specific. On the other hand, owing to the rather high threshold (8-9 MeV) for this reaction the sensitivity is only about 20 µg of thallium for samples irradiated for 30 hours in the close-vicinity of the reactor fuel in a total flux of 10^{13} n/cm^2/sec.

I N T R O D U C T I O N

Most of the rat poisons used today contain thallium and are involved in many accidental and intentive cases, and a specific analytical method for thallium is of interest. A neutron activation technique based on the reaction ^{203}Tl(n,γ)^{204}Tl has been proposed by Delbecq et al.[1]. Although a high sensitivity is achieved, the method cannot be considered as specific unless a highly specific separation of thallium is applied, since ^{204}Tl is not a gamma emitter.

Therefore, the possibilities of an activation analysis based on ^{202}Tl which is a gamma emitter and has a convenient half-life of 12 days

were investigated. This isotope is obtained by (n,2n) reaction on ^{203}Tl. The cross section for this reaction is roughly 1 barn [2,3]. However, owing to the high threshold of 8-9 MeV for this reaction, the sensitivity achieved in 30-hour irradiation in the close-vicinity of the reactor fuel in a total flux of 10^{13} n/cm^2/sec. is only about 20 μg of thallium.

RESULTS AND DISCUSSION

Samples containing 3.9, 7.9, and 11.3 mg of thallium were sealed in quartz tubes and irradiated at the same time under the same conditions (position and flux). Gamma spectra of these samples were then recorded by using a well-type NaI(Tl) crystal (3" diameter x 3" deep) detector and a single-channel spectrometer (NMC, PHA-1B type). As seen in Fig. 1, all the spectra show peaks at 0.438, 0.52, and 0.088MeV. The first peak corresponds to ^{202}Tl decay, the second is a sum peak of the first plus the third one, the latter being due to ^{202}Hg K-X-rays [4]. It should be noted that the last peak is a compound one and contains also the characteristic K-X-rays of ^{204}Hg which is the decay product of ^{204}Tl formed according to the reaction $^{203}Tl(n,\gamma)^{204}Tl$. This is indicated in Fig. 2. It is seen that after the decay of 12-day ^{202}Tl a long-lived activity remains, which must belong to thallium, since the sample was vigorously purified by isopropylether extraction followed by TlI precipitation [5]. The fact that the measured activities are proportional to the amount of thallium in the irradiated sample is shown in Fig. 3.

A specific determination of thallium can be made by measuring the integral counts corresponding to the peak at 0.438 MeV of ^{202}Tl. These counts were collected between the marks 3.0-3.70 of the scanning potentiometer which correspond to the energies 0.40 and 0.56 MeV respectively. This range includes the photopeak of ^{202}Tl and the sum peak as well. The

shape of the two peaks depends on the nature of the sample. If the sample is metallic thallium then the sum peak is smaller owing to the self-absorption of the soft Hg-K-X-rays. On the other hand, the same peak is more intense if the sample is in solution (Fig. 4). In both cases, the integral counts measured in the above mentioned range remain constant and proportional to the amount of thallium present. A decay plot (Fig. 5) of the integral counts yields the correct half-life of 12 days, implying that the contribution to the sum peak from the long-lived thallium should be negligible.

S e n s i t i v i t y : The amount of thallium detectable by the ^{202}Tl-gammas recorded in the energy range 0.40 - 0.56 MeV when the net counts are comparable to the background, is about 20 µg.

A P P E N D I X

RADIOCHEMICAL SEPARATION OF THALLIUM

The procedure suggested by Bowen [5] is followed.

Reagents :

HNO_3	70%
HCl	36% ; 18% ; 1.5%
$HClO_4$	70%
NH_4OH	60%
Ethyl alcohol	50%

Diisopropylether, equilibrated with 18% HCl

SO_2 generator

Aqueous solutions of :

$FeCl_3$	1% Fe

K_2CrO_4	10% ; 1%
KI	10%
Na_2SO_3	15%
$TlNO_3$	10 mg Tl/ml

standard : 10^{-5} g Tl as $TlNO_3$

Procedure :

1 - Dissolve the irradiated sample and/or standard in $HNO_3/HClO_4$ containing 2 ml of $TlNO_3$ (20 mg Tl) carrier solution. Evaporate to a small volume, add concentrated HCl and evaporate again. Add 10 ml of water, acidify with 18% HCl. Add 8 ml of Na_2SO_3 solution and boil. Add 2 ml of KI solution, cool the solution. Centrifuge, discard supernatant.

2 - Dissolve the TlI precipitate in HNO_3, evaporate to dryness. Take the residue with 18% HCl, add $KClO_3$ and heat. After adding holdback carriers if necessary, transfer the solution into a separatory funnel. Extract 3 times into isopropylether, wash the ether layers with 18% HCl.

3 - Evaporate the ether over 10 ml water, acidify with 18% HCl, reduce with 8 ml of Na_2SO_3 solution; boil. Add 2 ml of KI solution, cool, centrifuge, discard supernatant.

4 - Dissolve the TlI precipitate in HNO_3, evaporate to dryness. Take the residue with 1.5% HCl, add 0.5 ml of $FeCl_3$ solution. Reduce with SO_2, add an excess of ammonia. Filter through a filtering stick, discard precipitate.

5 - Acidify the filtrate with 18% HCl, reduce with 8 ml of Na_2SO_3 solution, add 2 ml of KI solution. Centrifuge, discard the supernatant and wash the precipitate with 1.5% HCl and KI solution.

6 - Dissolve the TlI precipitate in HNO_3, evaporate to dryness, take the residue with 1.5% HCl, reduce with Na_2SO_3, neutralize with ammonia.

Heat to 80°C, add 10 ml of 10% K_2CrO_4 solution; leave to stand for an hour. Centrifuge, discard supernatant. Wash the precipitate with 1% K_2CrO_4 solution, then with 50% ethyl alcohol. Transfer the Tl_2CrO_4 precipitate into a tared counting vessel.

7 - Dry the sample under infrared lamp, weigh for chemical yield calculation, and measure the radioactivity by collecting the integral counts corresponding to the peak at 0.438 MeV which is specific for ^{202}Tl.

ACKNOWLEDGMENT

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FIGURE CAPTIONS

Fig. 1. Gamma spectrum of thallium irradiated with fast-neutrons. The peak at 0.438 MeV corresponds to ^{202}Tl formed via (n,2n). reaction.

Fig. 2. Decay curve of thallium irradiated with fast-neutrons indicating the presence of a long-lived isotope (3.9-year ^{204}Tl) in addition to 12-day ^{202}Tl.

Fig. 3. Proportionality of the counts collected in the energy range 0.40 - 0.56 MeV including the 0.438 MeV ^{202}Tl photopeak and the sum peak of 0.52 MeV to the amount of thallium in the sample.

Fig. 4 a) The ^{202}Tl photopeak and the sum peak in the case of strongly self-absorbing sample (metallic).

b) The ^{202}Tl photopeak and the sum peak in the cases where self-absorption is negligible (solution).

Fig. 5. Decay curve for ^{202}Tl yielding a half-life of 12 days. The net integral counts on the ordinates are those collected in the energy range 0.40 - 0.56 MeV which covers the ^{202}Tl photopeak and the sum peak.

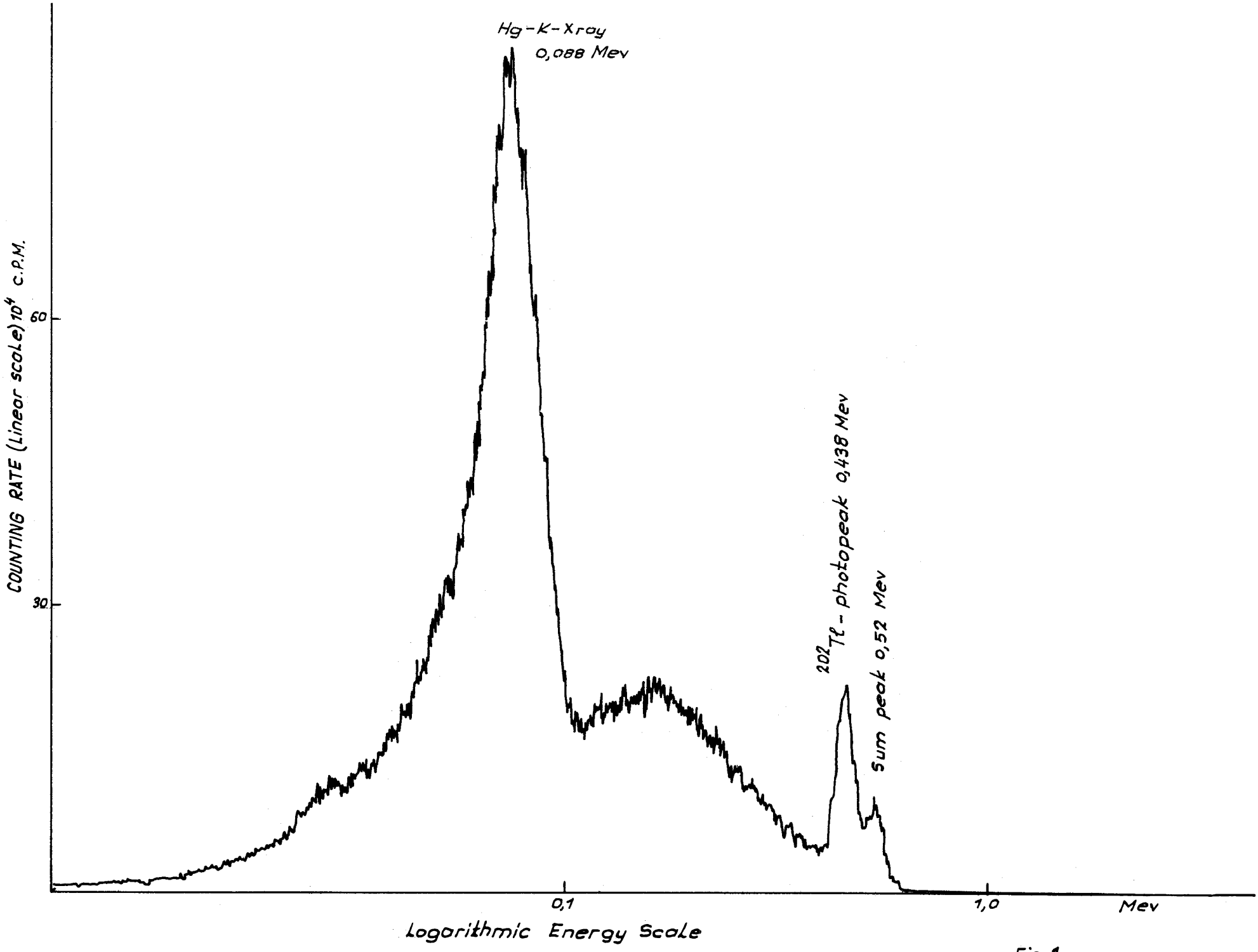

Hg-K-Xray
0,088 Mev
^{202}Tl - photopeak 0,438 Mev
Sum peak 0,52 Mev
COUNTING RATE (Linear scale) 10^4 C.P.M.
60
30
0,1
1,0
Mev
Logarithmic Energy Scale

Fig:1

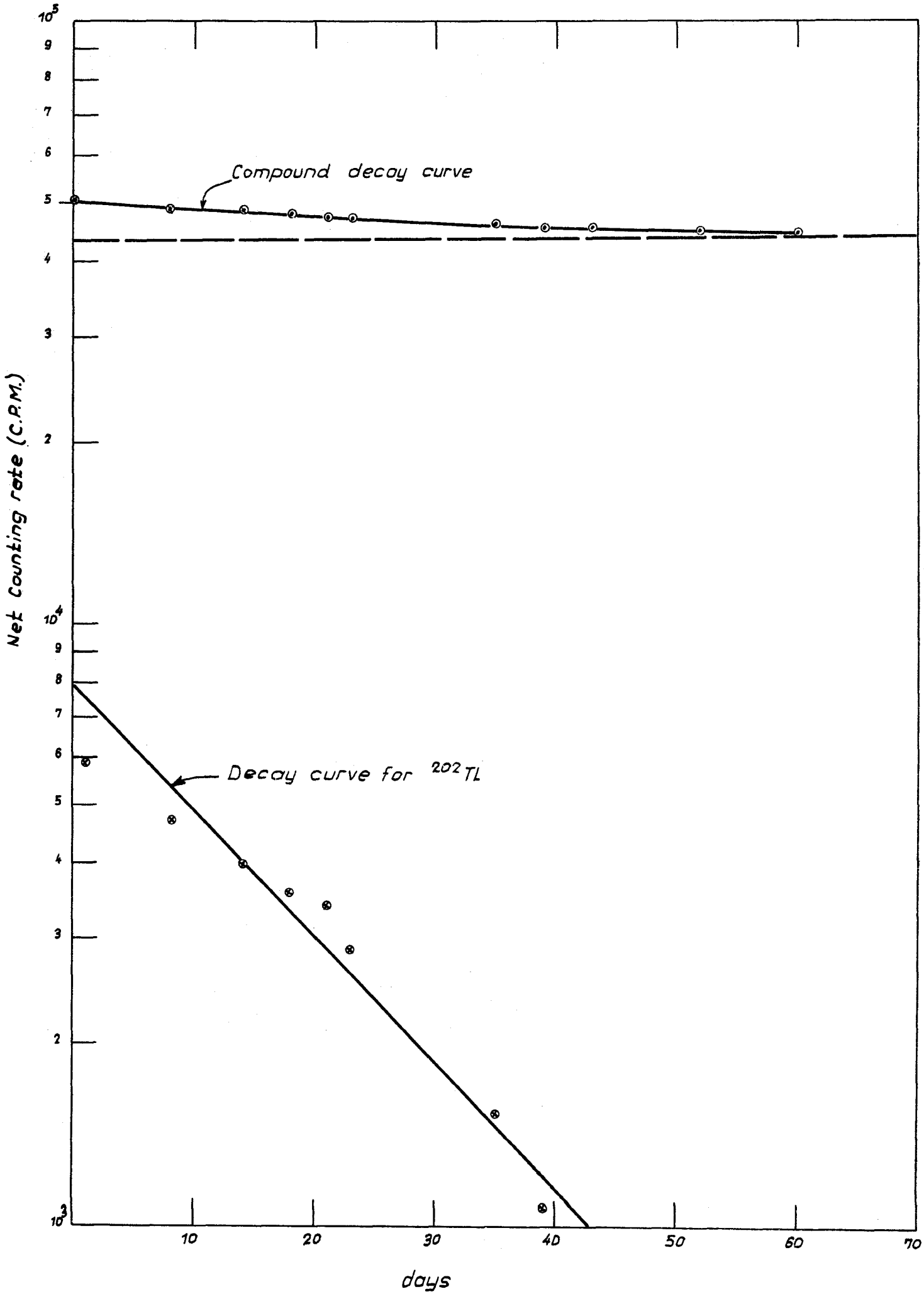

Net counting rate (C.P.M.)
10^5
9
8
7
6
5
4
3
2
10^4
9
8
7
6
5
4
3
2
10^3
Compound decay curve
Decay curve for ^{202}Tl
10
20
30
40
50
60
70
days

Fig: 2

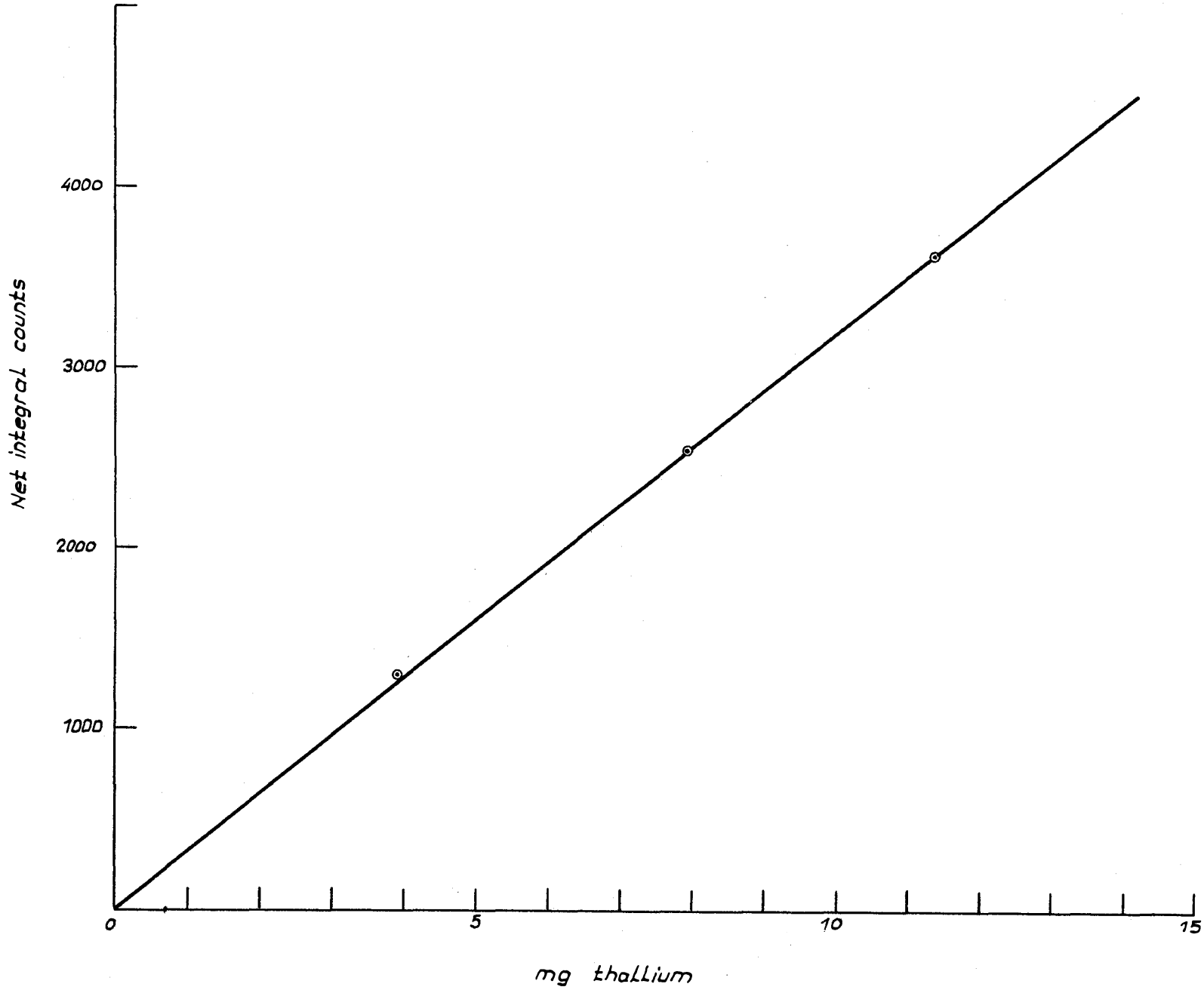
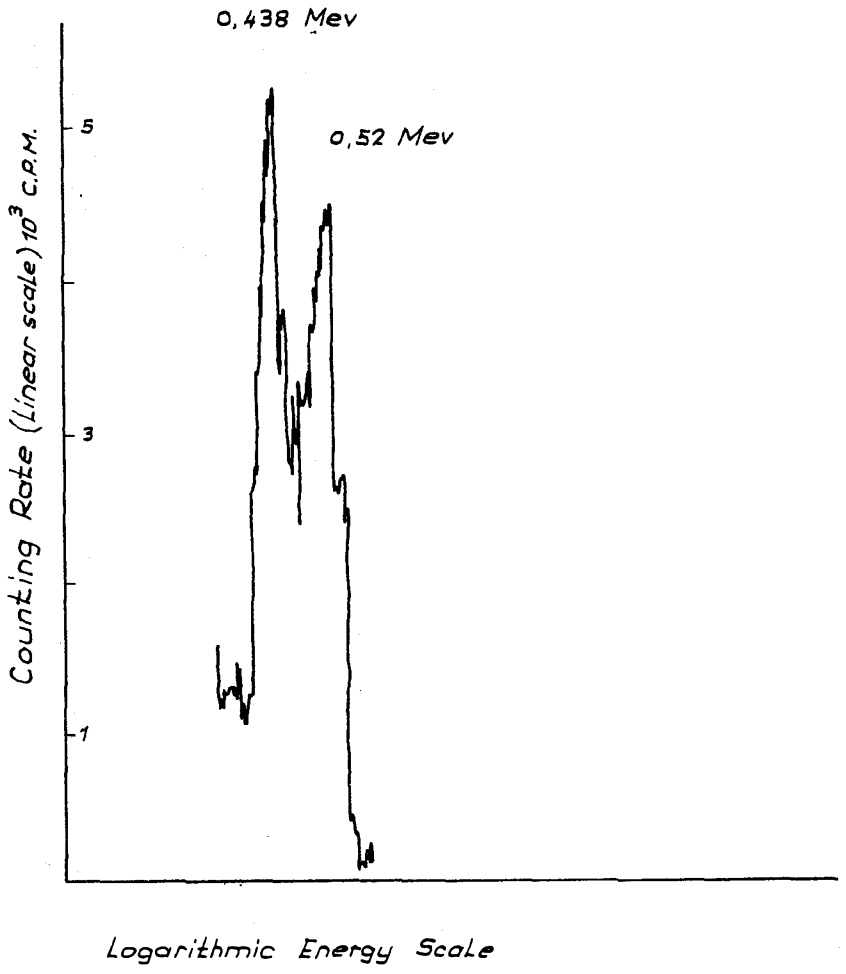
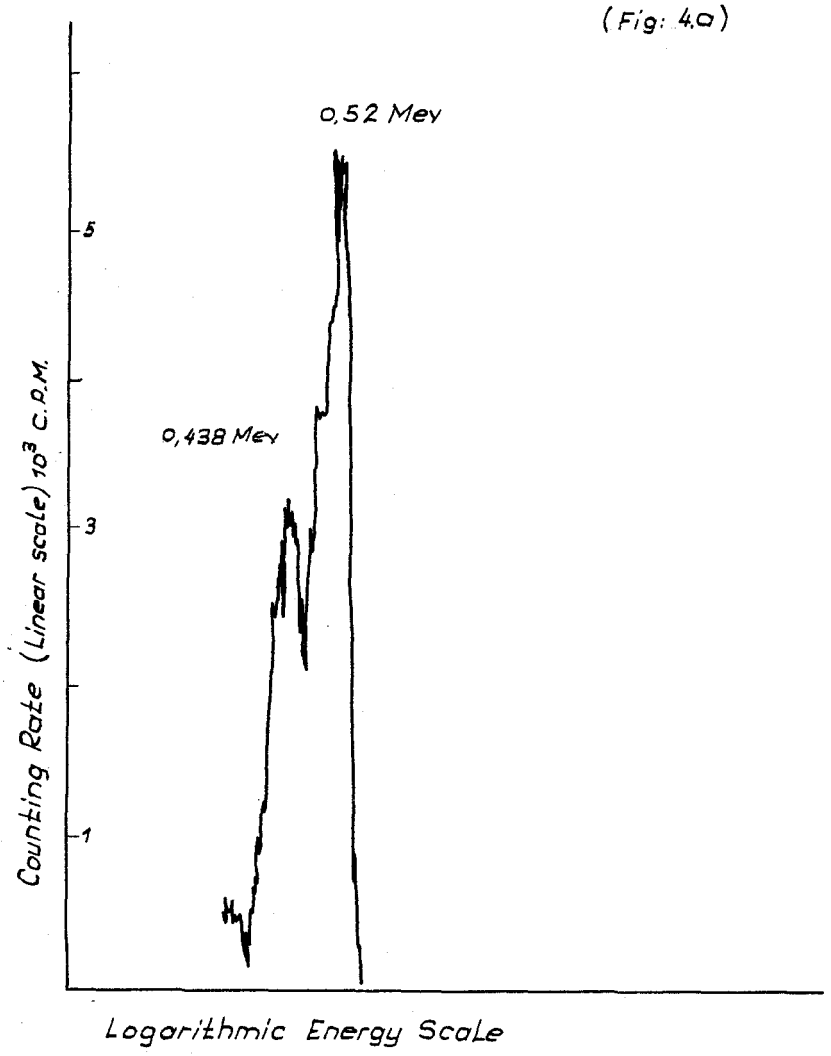


Fig: 3


0,438 Mev
0,52 Mev
5
3
1
Counting Rate (Linear scale) 10^3 c.p.m.
Logarithmic Energy Scale

(Fig: 4.a)


0,52 Mev
0,438 Mev
5
3
1
Counting Rate (Linear scale) 10^3 c.p.m.
Logarithmic Energy Scale

(Fig: 4.b)

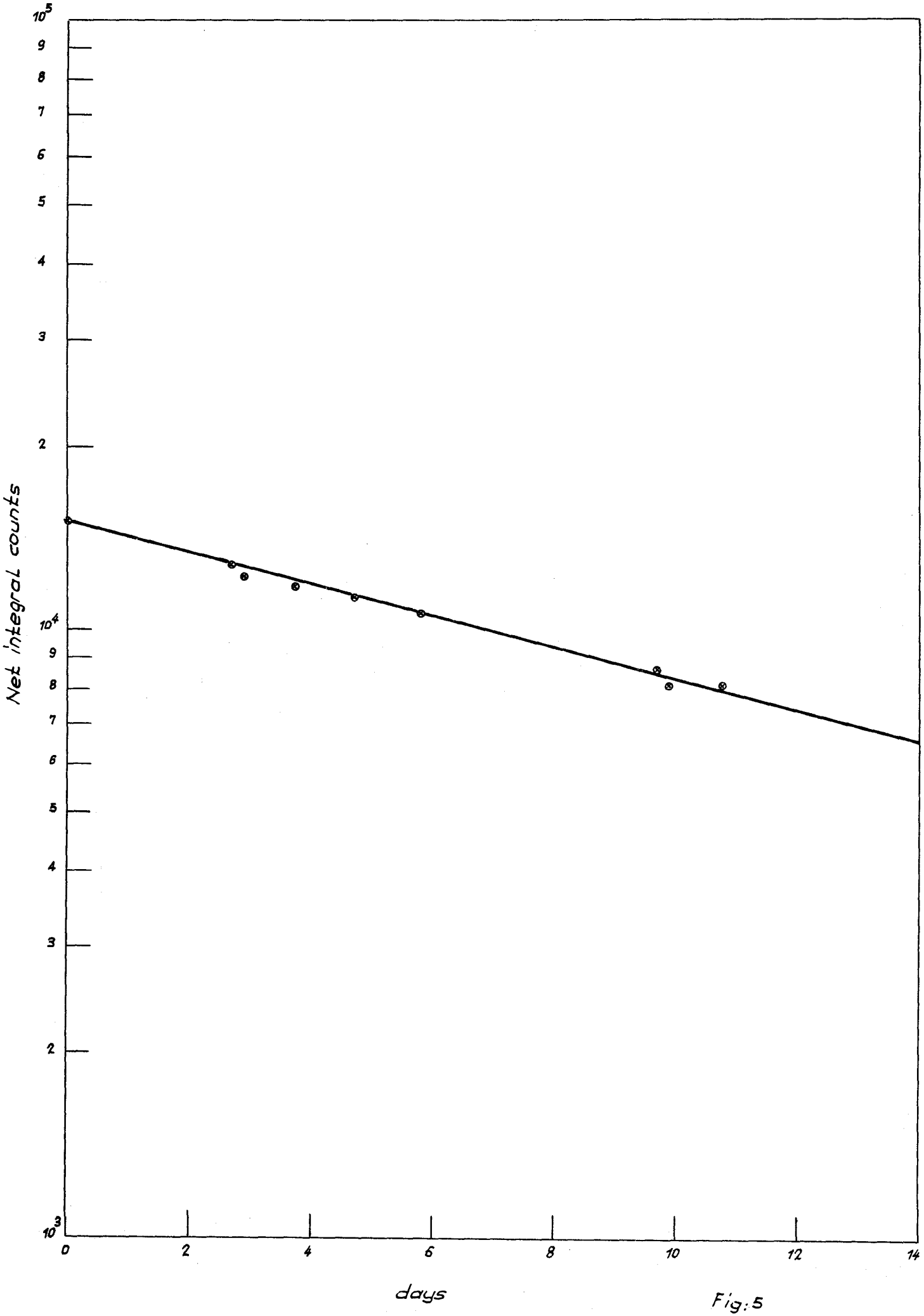

Net integral counts
10^5
9
8
7
6
5
4
3
2
10^4
9
8
7
6
5
4
3
2
10^3
0
2
4
6
8
10
12
14
days

Fig: 5