Chapter III

EXPERIMENTAL

3.1 Source of Neutrons

All irradiations were performed in the Thai Research Reactor-I (TRR-I). The approximate thermal neutron flux in the reactor core is about 6×10^{12} n/cm^2- sec. The flux in the pneumatic tube is lower.

3.2 Measurement of Induced Radioactivity

A 26 cm^3 Ge (Li) detector, a true right circular cylinder coaxial detector from ORTEC, was used for gamma radiation measurements. The output signals from the detector were passed through a preamplifier (ORTEC Model 118 A), linear amplifier (ORTEC Model 716 A), biased amplifier (ORTEC Model 459) to a 1024-channel (Nuclear Data Model 2200) pulse height analyzer. The data obtained were automatically printed and plotted. The FWHM of the ^{60}Co 1332 keV gamma ray photopeak was 2.2 keV. Fig. 3-1 shows the multichannel analyzer and the printer, whereas Fig. 3-2 shows the detector with the shielding and cooling systems.

The photopeak efficiencies of the detector were experimentally determined by counting standards from the Radiochemical Centre Amersham, England (Set No. 401, Activity reference time 1200 GMT on October 1, 1974). The results are given in Table 3-1 and the efficiency curve is plotted in Fig. 3-3
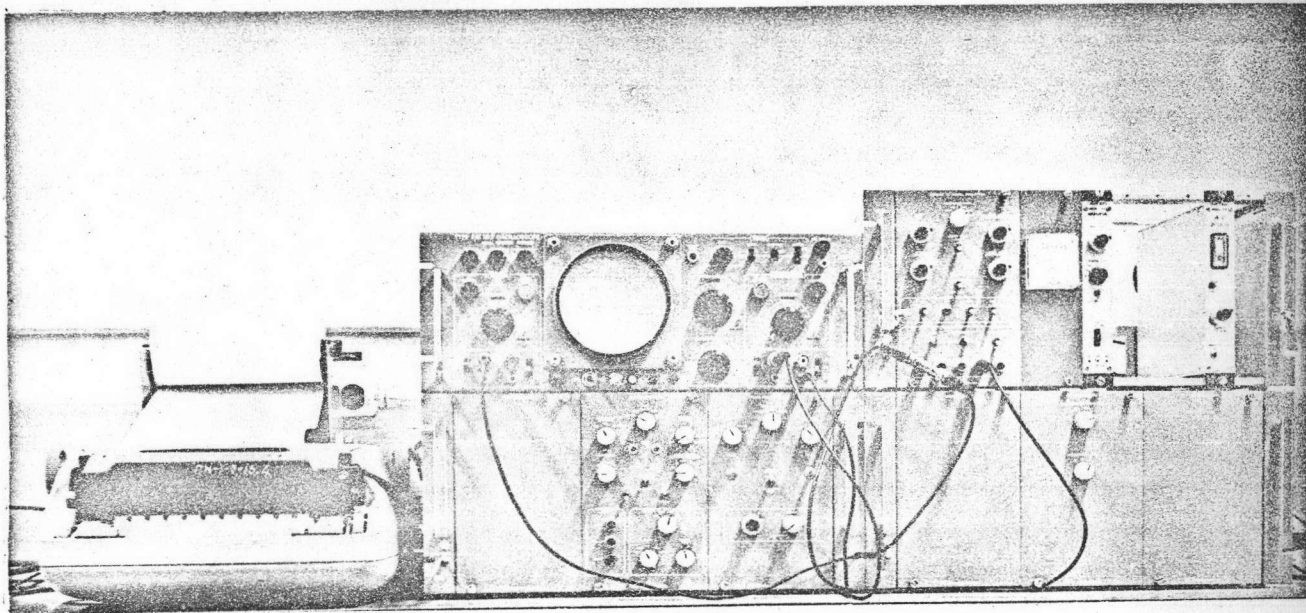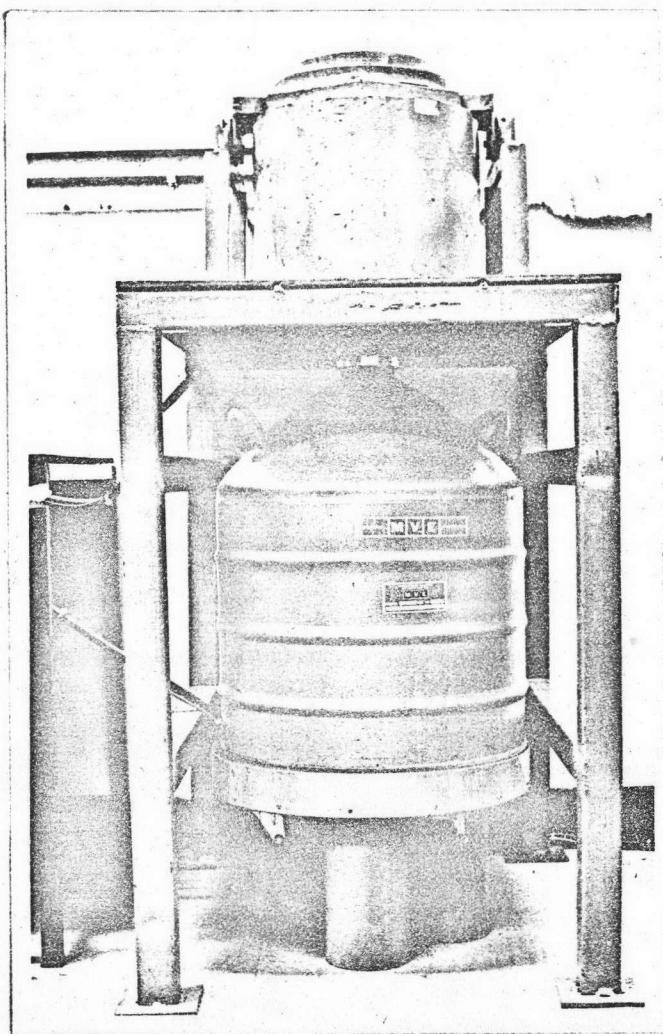
Fig. 3-1 The multichannel analyzer
and the printer

Fig. 3-2 The Ge(Li) detector
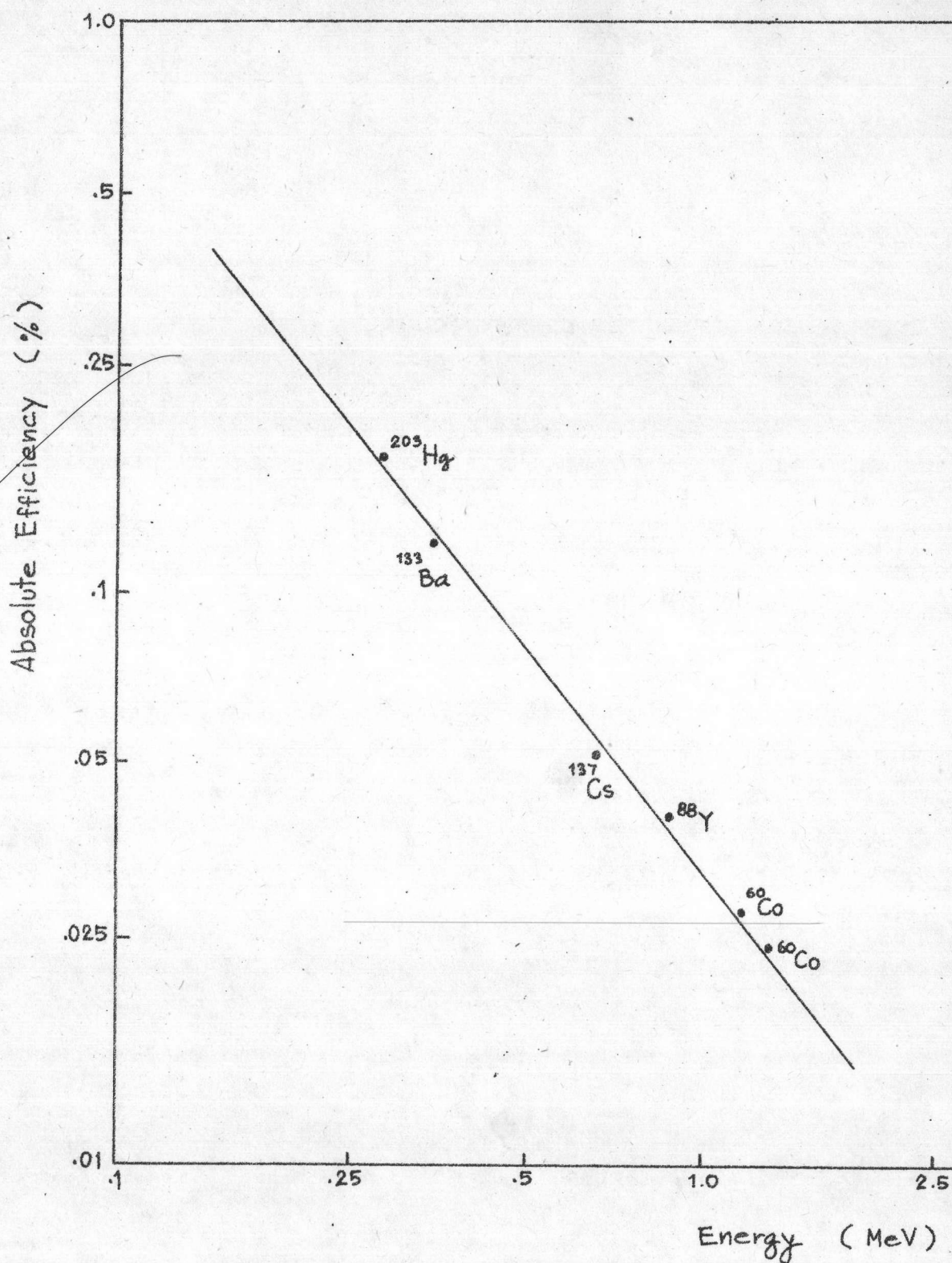with shielding and cooling
system.

Fig. 3-3   Photopeak efficiency of a Ge(Li) detector
as a function of gamma ray energy.

Table 3-1 Photopeak efficiency of the Ge (Li) detector

Standard nuclide	Energy (MeV)	Absolute activity (dps)	Measured activity (cps)	Absolute efficiency $= \dfrac{cps}{dps}$ X 100 %
^{203}Hg	0.279	14.80×10^{4}	280.32	0.190
^{133}Ba	0.356	38.21×10^{4}	406.08	0.110
^{137}Cs	0.661	36.88×10^{4}	183.47	0.050
^{88}Y	0.898	18.91×10^{4}	81.59	0.043
^{60}Co	1.173	40.61×10^{4}	119.66	0.030
^{60}Co	1.332	40.61×10^{4}	104.01	0.025

3.3 Identification of Nuclides

The identification of the nuclides in the observed spectra was based on the energies, half-lives and relative intensities of the peaks.

The spectrometer was first calibrated using the gamma energies from the standards which are listed in Table 3-2. Two calibration curves with different calibration coefficients which were used in this work are shown in Fig. 3-4 and Fig. 3-5

Table 3-2 Standard gamma energies

Nuclide	Energy of gamma ray (keV)
^{133}Ba	276.4, 302.8, 356.0, 383.8
^{137}Cs	661.6
^{60}Co	1173.1, 1332.4
^{88}Y	898.0
^{22}Na	511.0, 1274.5
^{54}Mn	834.8
^{203}Hg	279.1

The half-life of a gamma-peak was determined graphically by plotting the count rate or activity against time on a semilog paper. A straight line is obtained for a single radioactive species, from which the half-life can be found as the time taken for the activity to fall from any value to half that value. Fig. 3-6 shows a typical decay curve.

The relative intensities of the peaks of a radioactive nuclide were calculated and compared to the literature value[4].

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4 Lederer, C.M., Hollander, J.M., and Perlman, I. Table of Isotopes. Sixth Edition, 1967. New York : John Wiley and Sons.
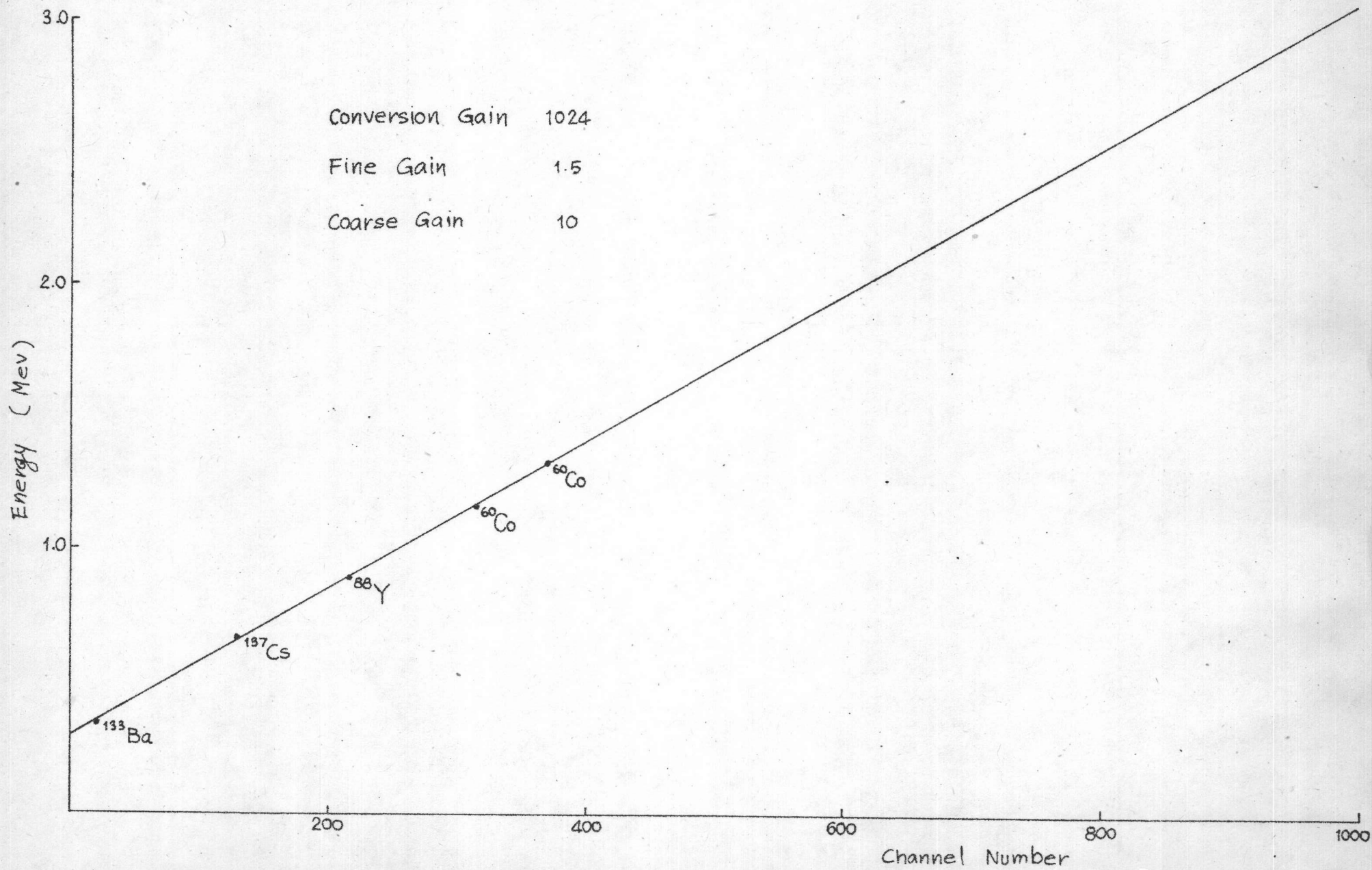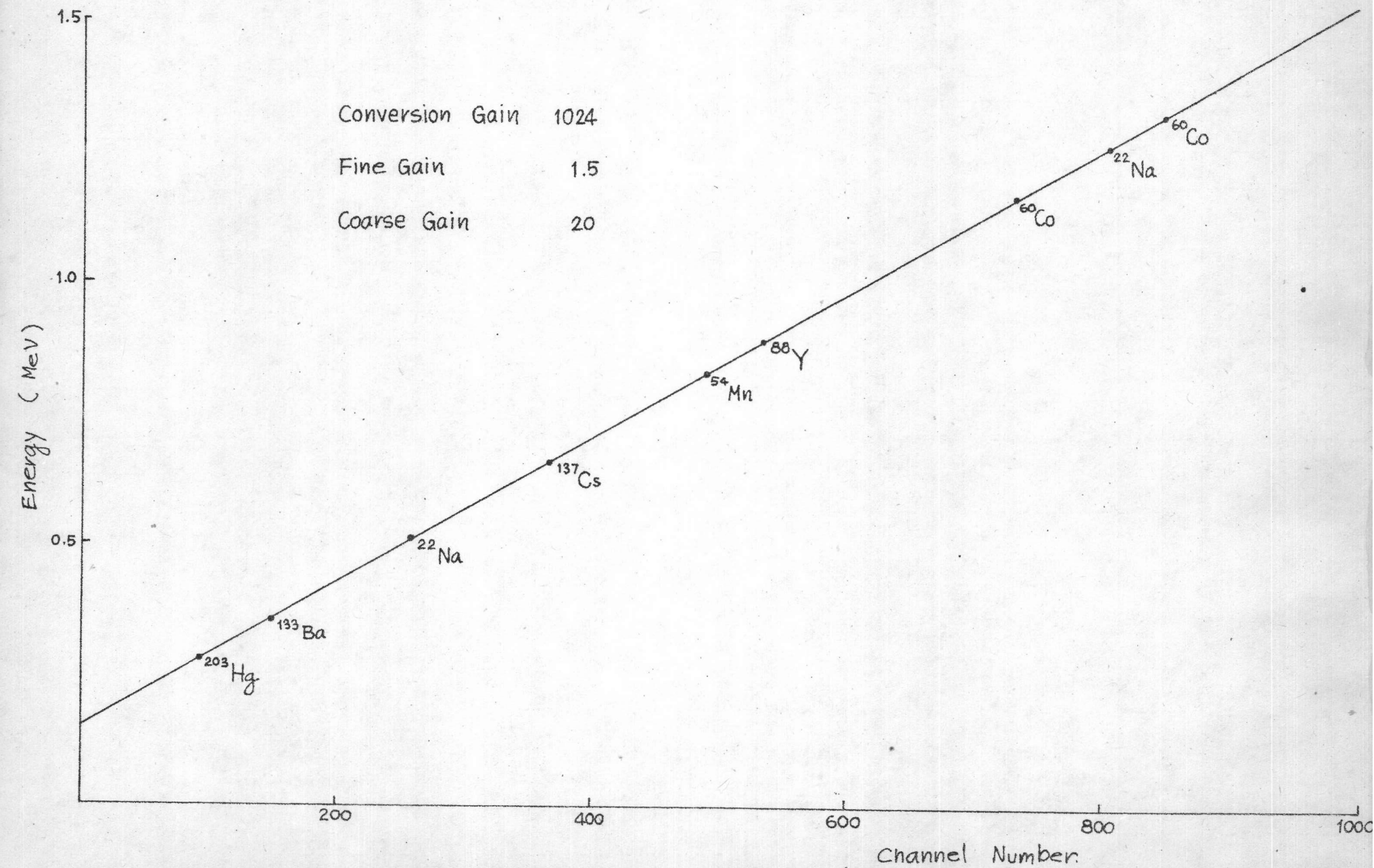
Fig. 3-4 CALIBRATION CURVE
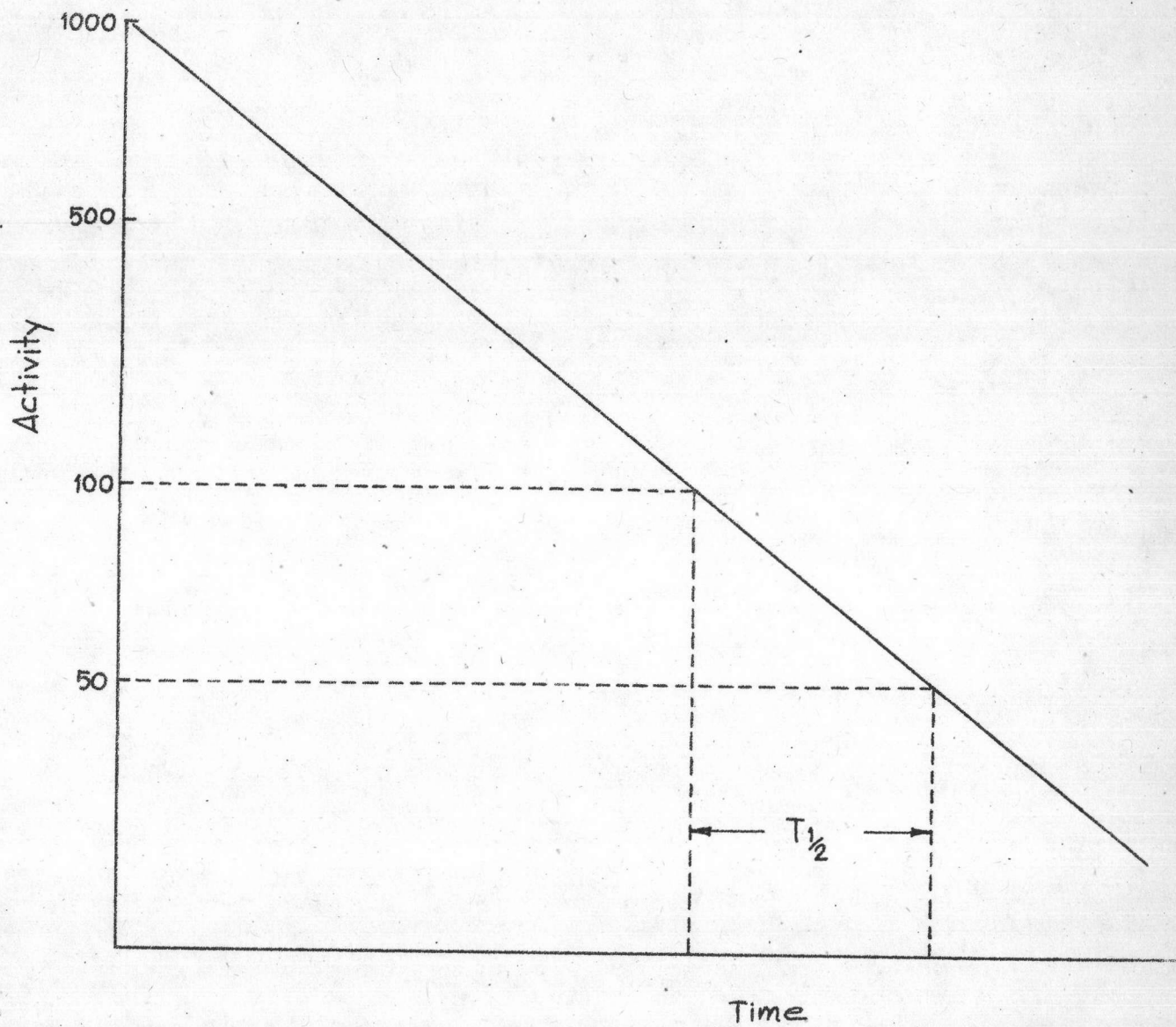
Fig. 3-5 CALIBRATION CURVE

Fig. 3-6   Half-life   determination   from
a   decay   curve.

3.4 Determination of Photopeak Areas

The areas of the photopeaks were determined by the Covell's Method[5]. Fig. 3 - 7 shows a typical gamma ray pulse height distribution curve. The channel which gives the highest count rate in the peak is termed Co, and n channels are counted off on either side of Co such that C_{+n} and C_{-n} contain counts about half-way between that in Co. The area above the line $C_{-n} - C_{+n}$ may then be expressed by the formula

$$\text{Area} = \sum_{m=-n}^{+n} A_m - (n + \tfrac{1}{2})(A_{-n} + A_{+n})$$

where :

A_m = number of counts in the mth channel

A_{-n} = number of counts in channel C_{-n}

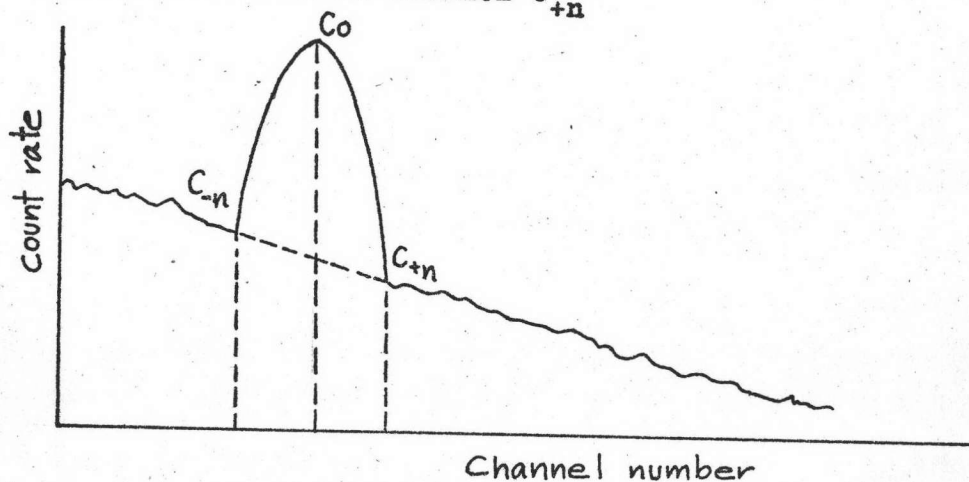A_{+n} = number of counts in channel C_{+n}

Fig. 3-7 Gamma ray pulse height
distribution curve.

5 Baedecker, Philip A. 1971. Digital Methods of Photopeak Integration in Activation Analysis. Analytical Chemistry, 43 : 405 - 410.

3.5 Sample Collection and Storage

Samples of surface water, at the depth of about 1 metre from the surface, were collected from the middle of the Chao Phya River at the following locations : Nonthaburi Bridge (Pathum Thani), Ban Sai Ma (Nonthaburi), Bangkok Bridge (Bangkok) and Samut Prakan (see Fig. 1-1). The sampling operations were performed on April 22, June 5, June 18, August 18, and August 24 of the year 1974. Two samples at one location were collected each time, one at the low-tide and one at the high-tide period. A total of 40 samples were obtained.

The samples, 4-5 litres each, were separately stored in polyethylene bottles which were previously cleaned with con-centrated nitric acid and distilled water. To avoid any loss of the trace elements by adsorption on wall or on any particles in the water solution, 10 ml of concentrated nitric acid per litre was added into the water samples[6]. A total content of 4-5 gm suspended materials was found in each sample (4-5 litres). These settled down after standing and the clear solution was pipetted and used for the analysis.

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6. Coyne, Robert V., and Collins, James A. 1972. Loss of Mercury from Water during Storage. Analytical Chemistry 44 : 1093 - 1096.

3.6 Removal of Sodium from the Sample

Many materials, including water, have high content of
sodium. After activation with thermal neutrons, a gamma
spectrum in which ^{24}Na is the prevailing radioisotope would
be obtained. The detection and measurement of other induced
radioactivities are often made difficult or impossible by the
presence of the radioactive sodium background. The elimina-
tion of sodium without affecting the concentration of other
elements would permit the simultaneous determination of many
trace elements by instrumental means.

The method developed by Girardi, F. and Sabbioni, E[7].
was used for the removal of sodium from water samples.

3.6.1 Preparation of Hydrated Antimony Pentoxide

Hydrated antimony pentoxide (HAP) was prepared by
adding $SbCl_5$ slowly into distilled water with vigorous stirring.
The white precipitate which resulted from hydrolysis of $SbCl_5$
was filtered by a water suction and washed 2-3 times with
distilled water. The precipitate was dried at 270°C for 5
hours in a muffle. It was then powdered and passed through
a sieve. The fraction between 100 and 300 micron was collec-
ted for use.

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7 Girardi, F., and Sabbioni, E. 1968. Selective Removal of
Radiosodium from Neutron-activated Materials by Retention
on Hydrated Antimony Pentoxide. Journal of Radioanalyti-
cal Chemistry, 1 : 169-178.

3.6.2 Removal of Sodium by HAP

The optimum conditions for the removal of sodium from water were first studied.

An activated stock solution of sodium was prepared by irradiating 10-15 ml of a sodium carbonate solution which contains 100 microgram sodium in one millilitre for 10 minutes. One millilitre of this solution was mixed with 10 ml 12M HCl and stirred with 200 mg HAP for 1 minute. The HAP was then filtered and washed with 5 ml. 8M HCl. The filtrate was collected and counted for sodium activity. Similar experiments were performed with agitation times of 2, 3, 4, 6, 8 and 10 minutes respectively. No sodium activity was found in any filtrate.

It is therefore obvious that 200 mg HAP could remove at least 100 microgram sodium from 8M HCl solution by simply agitating the mixture for 1 minute.

3.7 Sample Analysis

3.7.1 Qualitative Analysis of Water Samples

Since different nuclides have different half-lives, there exists an optimum condition for the detection of one nuclide. By varying the irradiation-and cooling- times as given in Fig. 3-8, 11 elements could be observed.

Group I. Nuclides obtained from short irradiation.
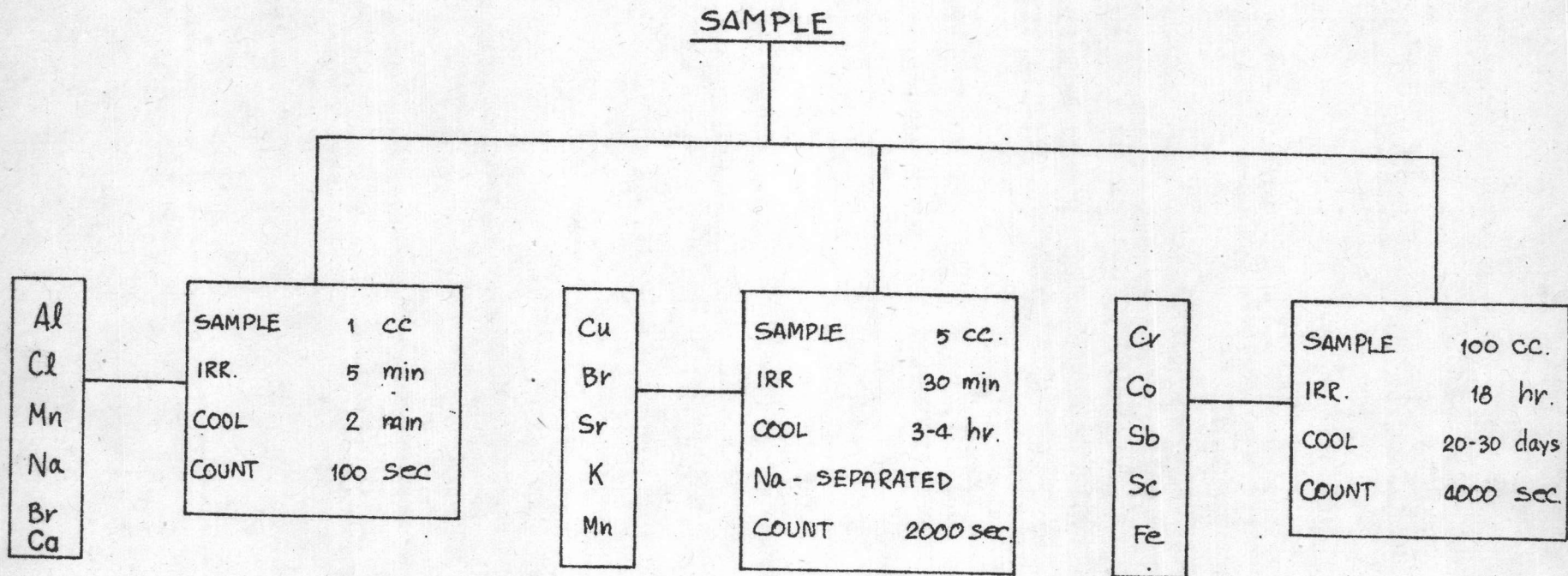
Fig. 3-8   IRRADIATION-COUNTING SCHEME

Water samples, 1 ml each, were pipetted into polyethylene vials and heat-sealed. These were subjected to irradiation in the pneumatic tube for 5 minutes. Two minutes after the end of irradiation, then samples were counted for 100 seconds. A typical spectrum of this group is shown in Fig. 3-9. The peaks were identified after their energies and half-lives. The half-life determination of the 0.846 MeV peak from ^{56}Mn is given in Fig. 3-10 as an example. The elements aluminum, bromine, calcium, chlorine, manganese and sodium were identified. The 1.293 MeV peak originated from Ar in the air inside the vial.

Group II. Nuclides obtained from intermediate irradiation.

Water samples, 5 ml each, were pipetted into polyethylene vials and heat-sealed. These were subjected to irradiation in the core of the reactor for 30 minutes. After cooling for 3-4 hours, the samples were transferred into a 100-ml connical flask, 10 ml concentrated HCl was added and the solution was shaken with 200 mg HAP for 1 minute. The solution was filtered and the HAP was washed with small aliquots of concentrated HCl. The filtrate and washed solution were collected into a 20-ml polyethylene container and counted for 2000 seconds. A typical spectrum of this group before and after shaken with HAP are shown in Fig. 3-11 and Fig. 3-12 respectively. The elements bromine, copper, manganese, potassium and strontium were identified.

Fig. 3-9 SPECTRUM OF RIVER WATER (SHORT IRRADIATION)
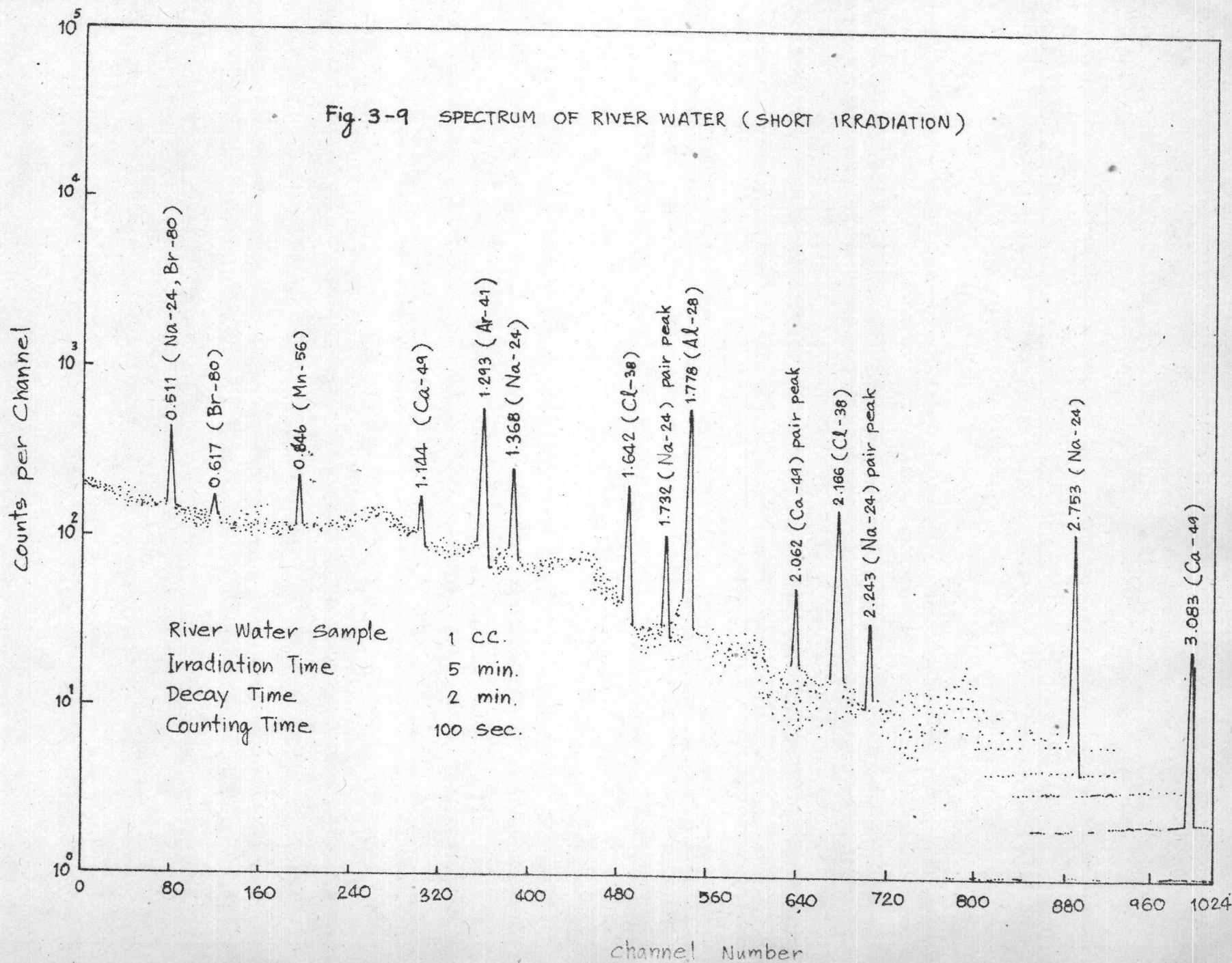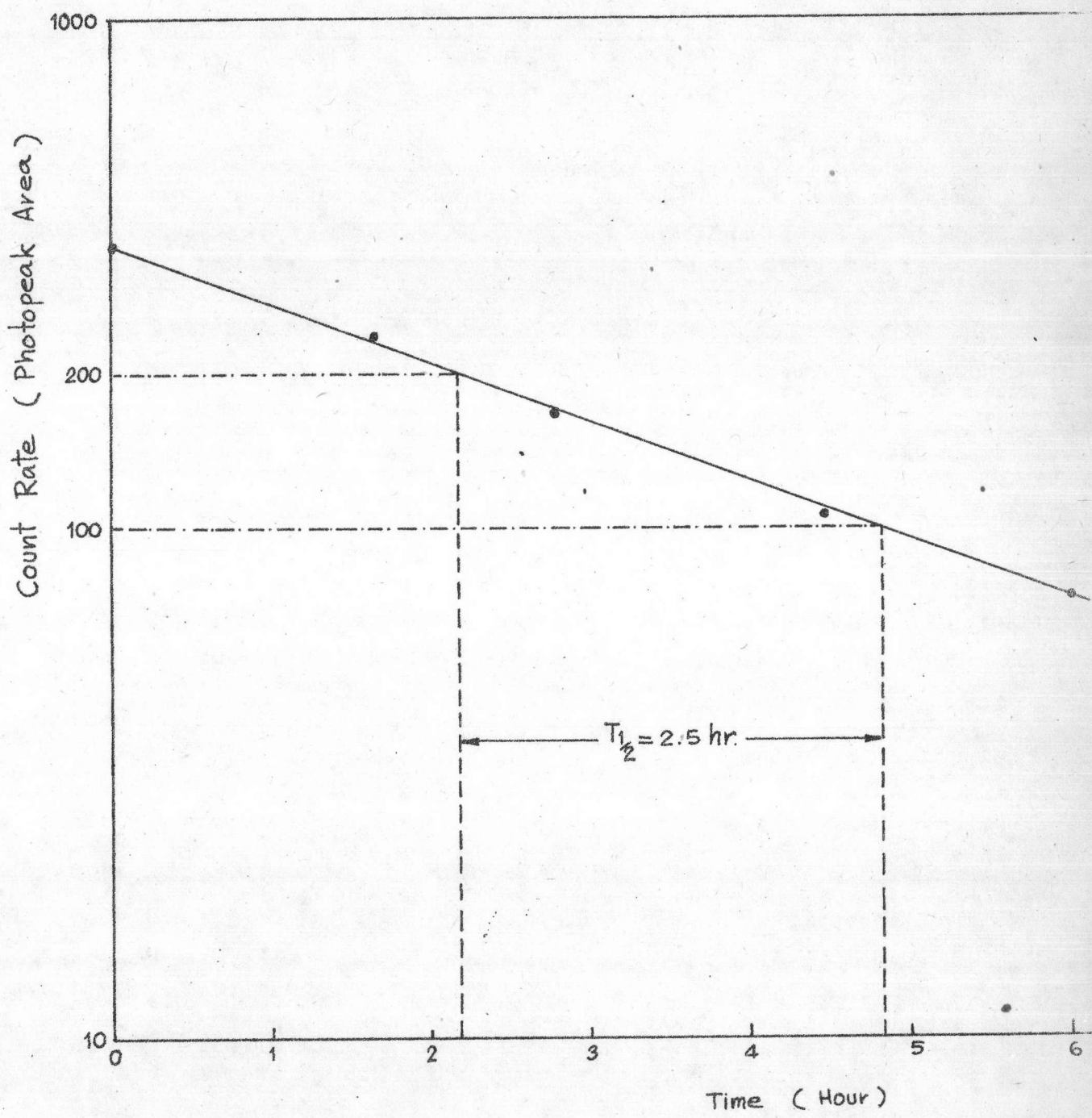
Fig. 3-10 Determination of the half-life of ^{56}Mn

Fig. 3-11 SPECTRUM OF RIVER WATER (INTERMEDIATE IRRADIATION)
Na- UNSEPARATED

River Water Sample   5 cc.
Irradiation Time   30 min.
Decay Time   2 hr.
Counting Time   200 sec.
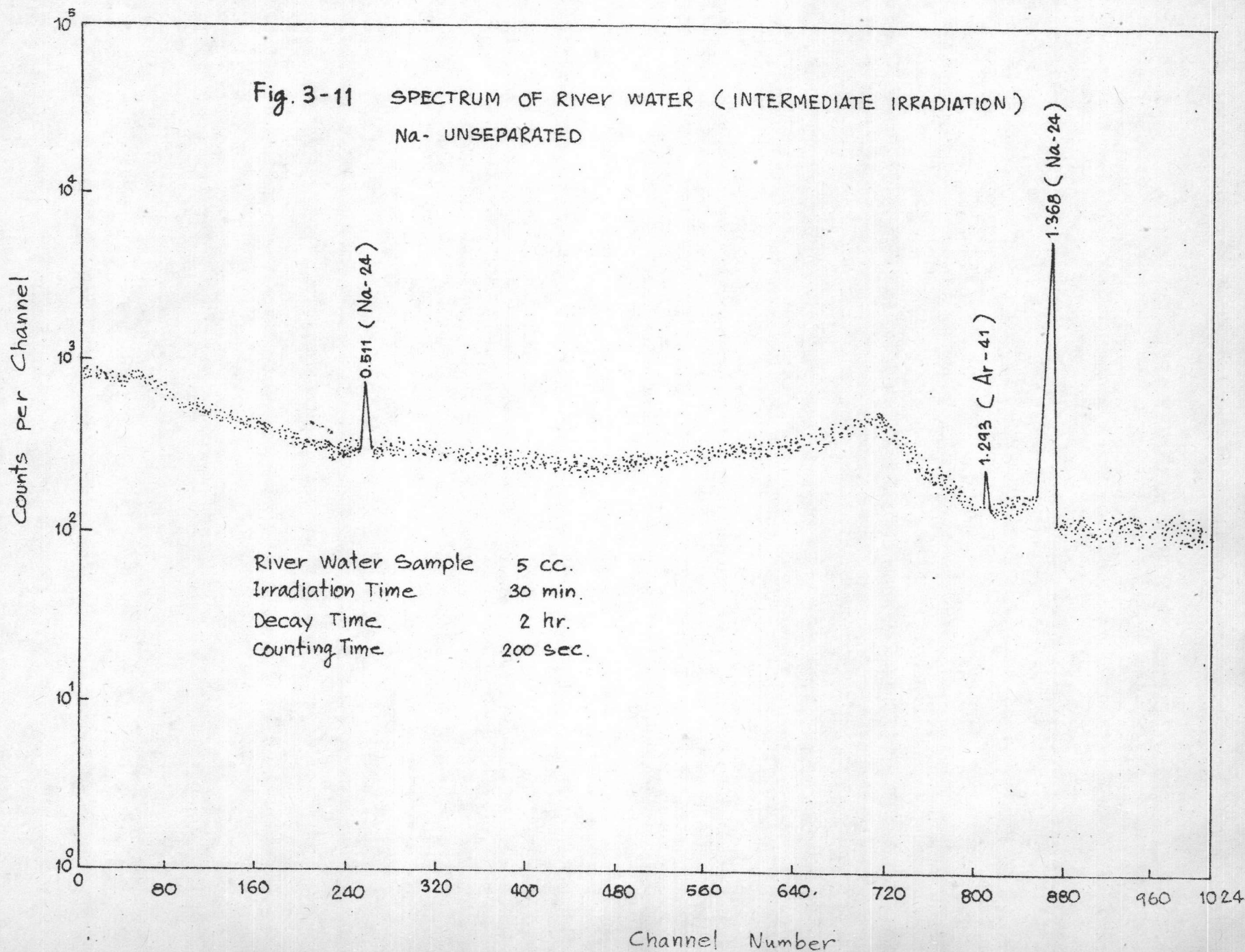
Fig. 3-12 SPECTRUM OF RIVER WATER (INTERMEDIATE IRRADIATION).
Na - SEPARATED

River Water Sample   5 cc.
Irradiation Time   30 min.
Decay Time   3-4 hr.
Counting Time   2000 sec.

Counts per Channel

Channel Number.

33
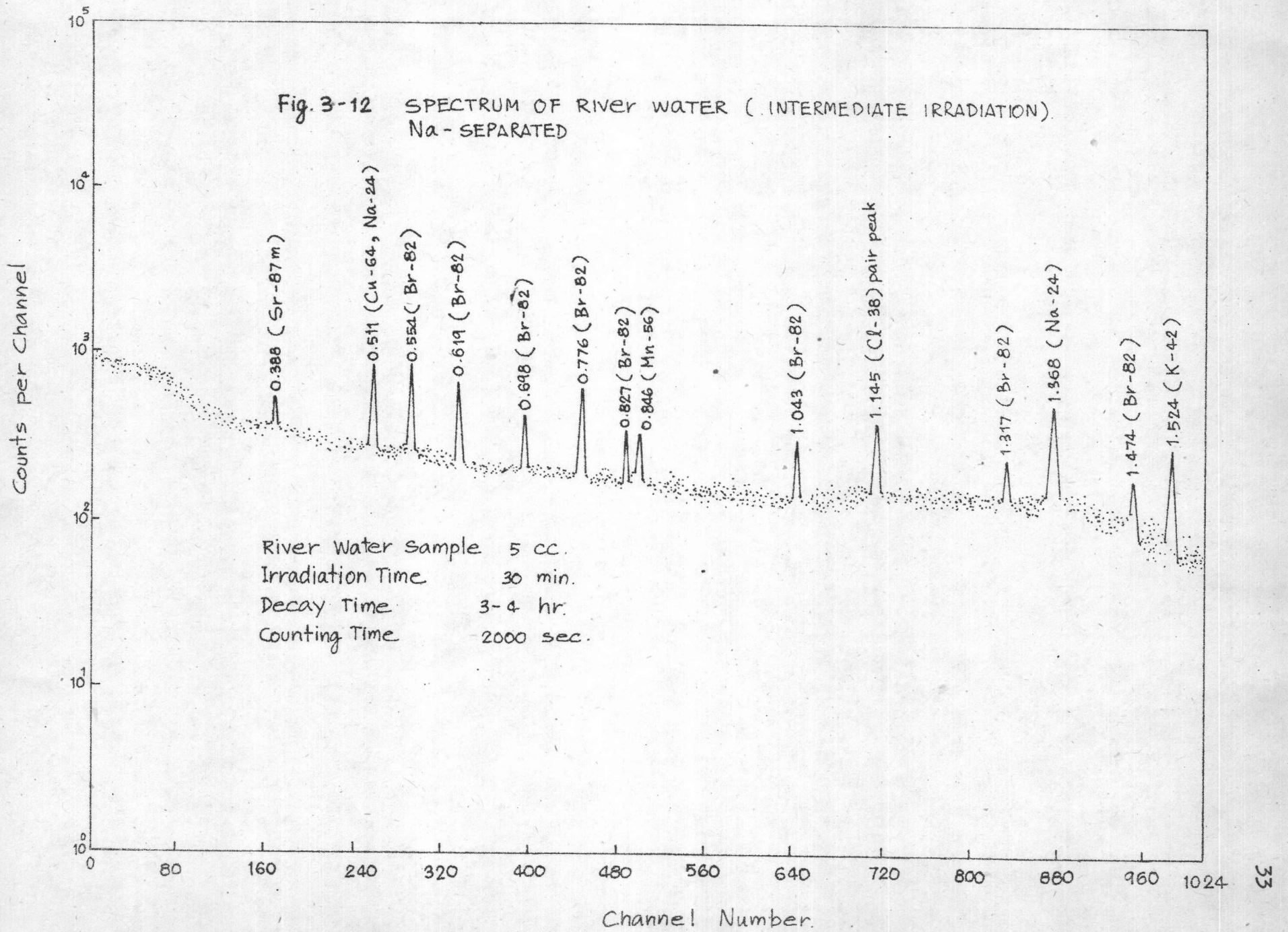
Group III. Nuclides obtained from long irradiation.

The higher the concentration levels of the trace elements to be determined, the more reliable the results would be. To achieve this, 100 ml of each sample were evaporated to dryness under an infrared lamp. The residue was dissolved in 1-2 ml concentrated nitric acid and transferred into a polyethylene vial. The evaporating dish was rinsed with small aliquots of water. A total volume of 5 ml was obtained. From extraperformed experiments, it was assured that no elements would volatile under this evaporating coundition. The samples were heat-sealed and put into an aluminium can. They were subjected to irradiation in the reactor core for 18 hours. After a cooling time of 7 days, the samples were taken from the aluminium can and any outer contamination was removed by washing the vials with dilute nitric acid and water. The samples were cooled further for 20 days and counted for 4000 seconds each. No extra processing prior to measurement was performed. A typical spectrum of this group is shown in Fig. 3-13. The half-life determination was omitted for very long half-lived nuclides, such as ^{60}Co. The intensity-ratio of their energies was determined instead. The elements antimony, chromium cobalt, iron and scandium were identified.

Fig. 3-13 SPECTRUM OF RIVER WATER (LONG IRRADIATION)

River Water Sample   100 cc.
Irradiation Time   15 - 18 hr.
Decay Time   20 - 30 Days
Counting Time   4000 sec.
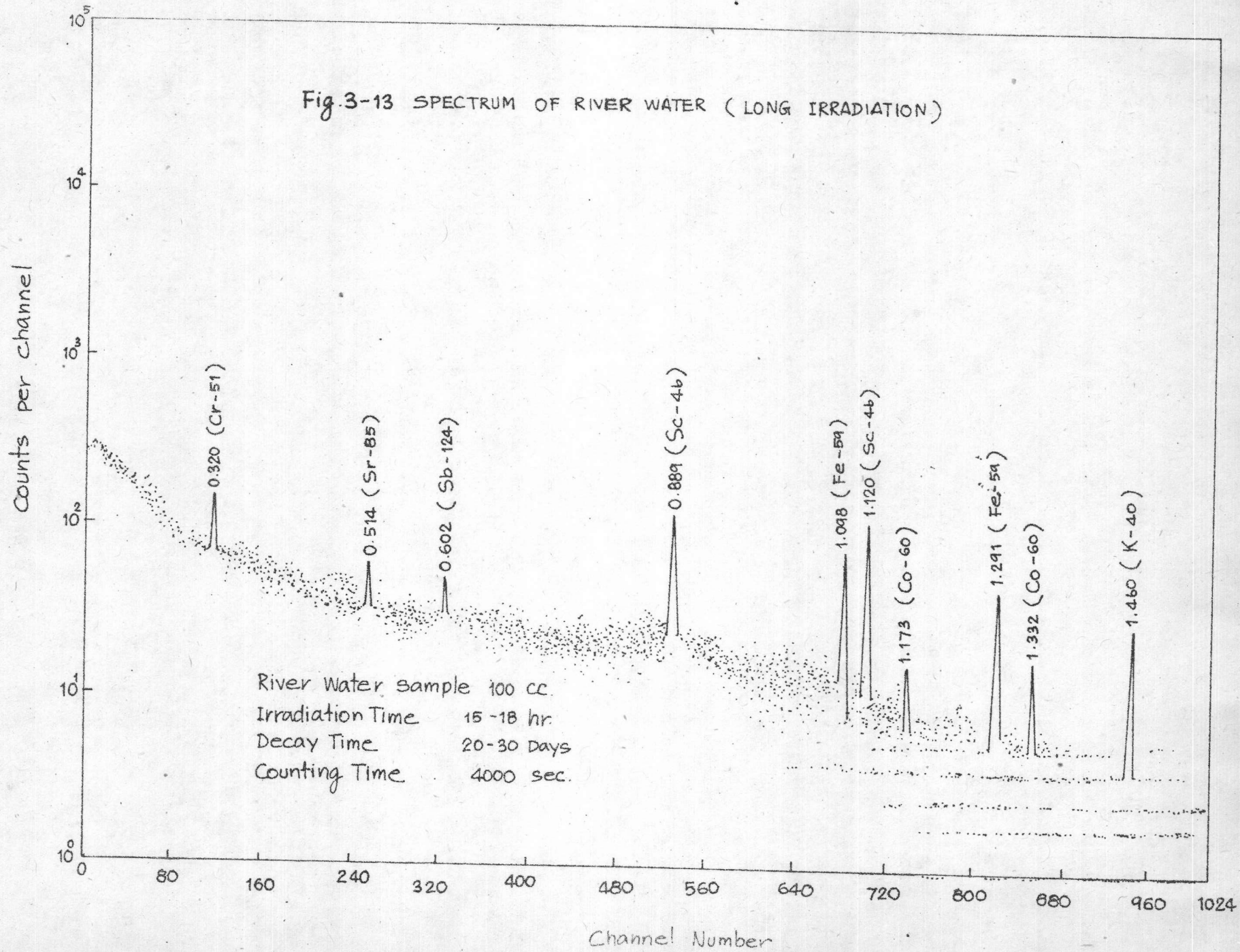
3.7.2 Quantitative Analysis of Water Samples

Three mixed standard solutions were prepared by dissolving specpure grade powders in water or A.R. grade nitric acid. Their compositions are tabulated in Table 3-3

Table 3-3   Composition of the mixed standard solutions

Solution I (short-lived)		Solution II (intermediate)		Solution III (long-lived)	
Element	Concentration (ppm)	Element	Concentration (ppm)	Element	Concentration (ppm)
Al	0.169	Br	0.750	Co	0.80
Cl	0.249	Cu	0.390	Cr	2.00
Mn	0.193	Mn	0.193	Fe	5.00
Na	0.420	Sr	0.210	Sb	0.80
				Sc	0.04

The elements Al (short-lived group), Sr, Br, Cu, Mn (intermediate-lived group), Co, Cr, Fe, Sb, Sc (long-lived group) were quantitatively determined. The nuclides and the gamma rays used in the analysis are tabulated in Table 3-4 together with their half-lives and reaction cross-sections.

Table 3-4 Radioisotopes used in the analysis

Element	Isotope	Cross-section (barn)	Half-life	Gamma rays used (keV)
Al	^{28}Al	0.21	2.31 min.	1778.9
Sr	^{87m}Sr	1.30	2.84 hr.	388.5
Cu	^{64}Cu	4.51	12.80 hr.	511.0
Br	^{82}Br	3.30	35.87 hr.	776.6
Mn	^{56}Mn	13.30	2.58 hr.	846.9
Cr	^{51}Cr	15.90	27.8 day	320.0
Sb	^{124}Sb	3.30	60.9 day	602.6
Sc	^{46}Sc	23.00	83.9 day	889.4
Fe	^{59}Fe	1.10	45.1 day	1098.6
Co	^{60}Co	37.00	5.2 yr	1173.1

The conditions of irradiation, cooling and counting followed the scheme presented in Fig. 3-8. The samples were prepared and processed in the same manner as described in section 3.7.1. For the quantitative determination of the short-lived and the intermediate groups, one sample and one mixed standard were subjected to irradiation together, whereas in the case of the long-lived group four samples and two mixed standards (two samples and one standard in one vertical position) were irradiated at the same time. The volume of the mixed standard solutions for irradiation was always 1 ml. To

avoid counting error which may occur if the volumes of the standard and the sample are different, 4 ml distilled water were added into the vial of the mixed standard III befor irradiation. A total volume of 5 ml was obtained. After irradiation, the mixed standard solution II was processed in the same manner as the samples. Except for the long-lived group, the photopeak areas of the samples and standards were always corrected to the same measuring time.

The content of an element in a sample is simply calculated by the equation :

$$\frac{W_1}{W_2} = \frac{A_1 \pm \zeta_1}{A_2 \pm \zeta_2}$$

where :

W_1 = weight of the element in the sample

W_2 = weight of the same element in the mixed standard

A_1 = area of the photopeak of the element to be determined in the sample

A_2 = area of the photopeak of the same element in the mixed standard

ζ_1 = standard deviation of A_1

ζ_2 = standard deviation of A_2

The net standard deviation which results from the division of A_1 by A_2 can be calculated from the equation;

$$\frac{A_1 \pm \zeta_1}{A_2 \pm \zeta_2} = \frac{A_1}{A_2} \pm \frac{1}{A_2^2}(A_1^2 \zeta_2^2 + A_2^2 \zeta_1^2)^{\frac{1}{2}}$$

Therefore the weight of an element in a sample can be
determined by the equation;

$$W_1 = \left[\frac{A_1}{A_2} \pm \frac{1}{A_2{}^2} \left(A_1{}^2 \, \zeta_2{}^2 + A_2{}^2 \, \zeta_1{}^2 \right)^{1/2} \right] \cdot W_2$$

Photopeak areas were calculated manually with an elec-
tronic calculator. A simple mathermatical program was
written for the calculation of the concentrations (W_1). A
small computer, PDP 8/e, was available for this purpose.