

CHAPTER III

EXPERIMENTS

3.1. Samples and their preparations

Two samples as received from the Department of Mineral Resources, whose composition as analysed by X-ray fluorescence are shown in Table 3 - 1, were used. The sample from Phuket was used in the small scale digestions whereas the sample from Ranong was used in the case of larger scale. In order to evaluate the chemical yield of each processing step, one standard monazite sample from the New Brunswick Laboratory (NBL 7A) which contains 9.7 per cent thorium oxide and 0.35 per cent uranium oxide was also processed in a small scale. All samples except the standard NBL 7A which particles are already very fine, were allowed to pass through a 200-mesh sieve after grinding by an automatic grinder for 2 hours. Minus 200-mesh monazite sand particles were used throughout this work.

Table 3 - 1 Compositions (%) of the samples of monazite used as analysed by X-ray fluorescence*

Element	Sample from	
	Phuket	Ranong
Ta	0.610	0.720
Th	6.600	8.350
Y	1.560	1.710
Zr	0.303	0.360
Sn	0.330	0.115
La	15.600	14.100
Ce	28.300	26.900
Gd	1.800	1.840
Dy	0.680	0.630

* The analyses were performed by the Physics Division, OAEP

3.2. Alkaline Treatment of Monazite

The flow diagram in Figure 2 - 1 was followed. In order to obtain the optimum conditions for the monazite opening process the effects of the reaction temperature, the concentration of caustic soda, the caustic soda to sand ratio and the time of reaction were studied using 0.5 g monazite per digestion. Having selected the optimum conditions for digestion a number of trials were made on a

larger scale, 50 g per batch. In the small scale digestion, the reaction was allowed to take place in a platinum crucible, and the mass was heated in an oven of which the temperature could be controlled exactly to $\pm 1^{\circ}\text{C}$. During the reaction the mass was occasionally agitated. For the larger scale digestion, a 500 ml stainless steel beaker with a stainless plate sealed on top as a cover was used. The diagram of the apparatus is shown in Figure 3-1. As is in the case of small scale digestions, the heater could be controlled exactly to $\pm 1^{\circ}\text{C}$.

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In the case of small scale investigations, the general method adopted in India (19) for the preparation of crude thorium hydroxide from the mixed metal hydroxide cake was followed. The mixed metal hydroxide cake (with undigested sand) was dried at 100°C and then dissolved in a small portion of 10 N hydrochloric acid. The pH of the slurry was adjusted to 3 to precipitate thorium as thorium hydroxide. After filtration to remove the large bulk of rare earths the precipitate was dissolved in a few drops of 10 N hydrochloric acid and the solution was diluted with water to make the pH value to 1.2. The undigested sand was removed by centrifugation and 15 ml 10 per cent oxalic acid was added to the solution. The precipitation of thorium oxalate was complete after the solution was heated at 70°C for about 2 hours. The oxalate obtained was converted to hydroxide by heating with 4 N sodium hydroxide solution at 90°C for about 1 hour. The resulted thorium hydroxide was dissolved in 4 N nitric acid, and the solution was ready for the subsequent step of purification of thorium by solvent extraction.

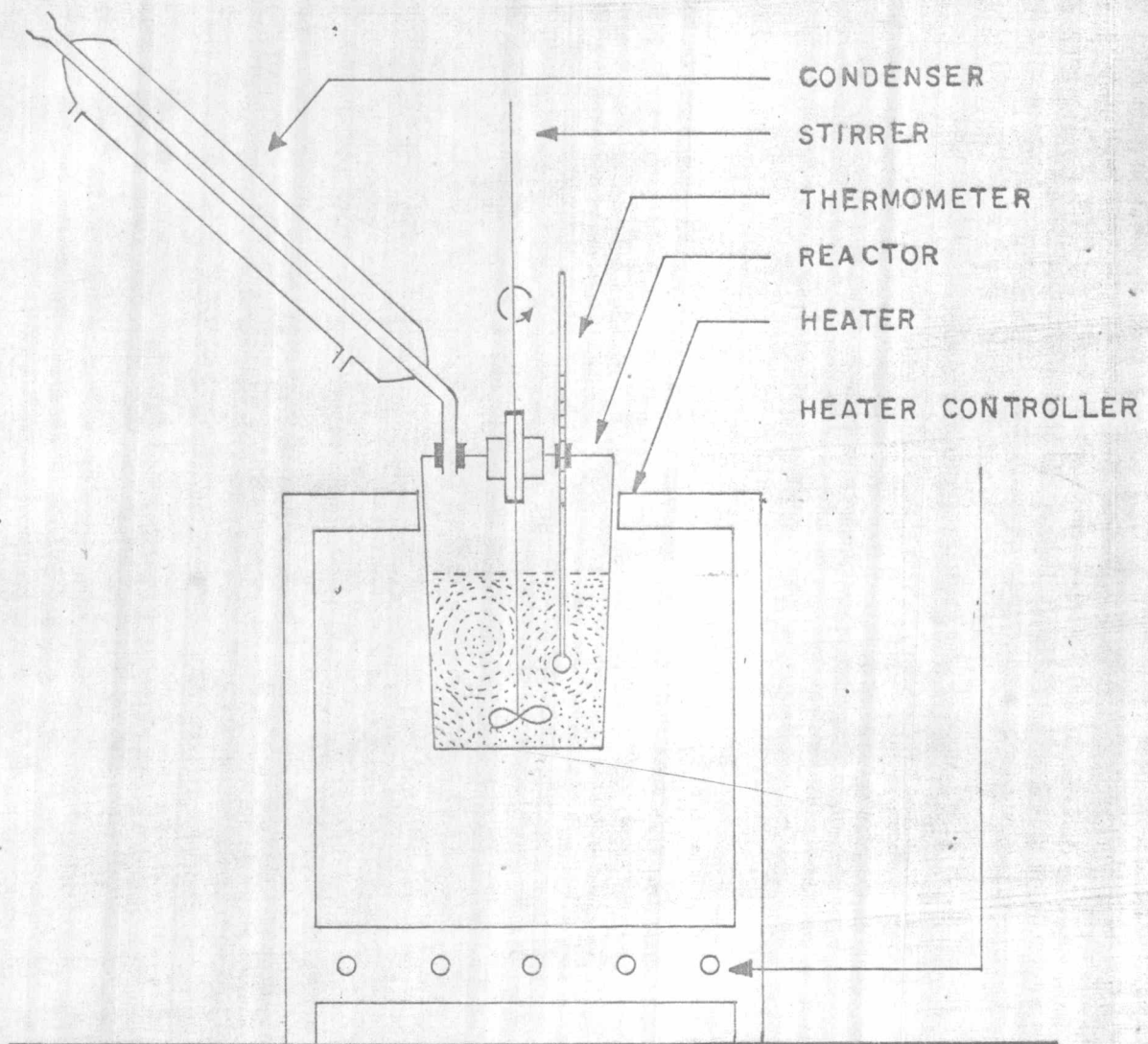


FIG. 3-1

SCHEMATICAL DIAGRAM OF THE APPARATUS

In the case of 50 g per batch digestion the step of oxalate formation was omitted. The mixed metal hydroxide cake was dissolved in 150 ml concentrated hydrochloric acid and the undigested sand was removed by filtration. Thorium hydroxide was precipitated when the pH of the solution was adjusted to 2 by adding 4N sodium hydroxide solution. The hydroxide was dissolved in 4N nitric acid for the subsequent step of purification.

3.3. Acid treatment of nonazite

The flow diagram in Figure 2-2 was followed. All parameters that were studied in the alkaline process were investigated. In the scale of 0.5 g per batch, the reaction took place in a 10 ml flask with a rubber stopper in which a glass-tube was provided and used as an air-condenser. The reaction mass was heated and stirred with a hot-stirred plate. In the larger scale case, a 250 ml flask was used and the set up of the whole apparatus was similar to the case of alkaline treatment. After digestion, water was added to the reaction mass in a ratio of 9 parts of water to 1 part of sand (weight by weight). The pH of the solution was adjusted to 2.0 by adding 4N sodium hydroxide. The resulting thorium hydroxide was dissolved in 4N nitric acid for further purification.

3.4. Solvent extraction of thorium nitrate solution

The effect of nitric acid concentration on the distribution coefficients of thorium in a 40 per cent TBP-xylene (volume/volume) solvent extraction system was checked. A 21 ml. portions of nitric acid solution concentration ranging from 0.07 N to 6.70 N containing 0.00256g thorium/ml were mixed with 14 ml. 40 per cent TBP-xylene which were previously saturated with nitric acid of the appropriate normality. The solutions were shaken with an automatic shaker for 1 hour. After the two phases were well separated, 1 ml. portion of the aqueous phase was pipetted and the amount of thorium content was analysed via activation analysis. The distribution coefficients were evaluated as the ratio of the thorium concentration ($\mu\text{g}/\text{ml}$) in the organic phase to the thorium concentration ($\mu\text{g}/\text{ml}$) in the aqueous phase. The results which are shown in Figure 3 - 2 agree well with those obtained by G.D. Calkins et al (8). Higher concentration of nitric acid results in a higher distribution coefficient but is not economically feasible. In the present work the aqueous feed solutions were prepared by dissolving the crude thorium concentrate obtained from the digestion of monazite in a solution of 4 N nitric acid.

The effect of shaking-time on the extraction of thorium with 40 per cent TBP-xylene as well as with 40 per cent TBP-kerosene was also studied. Solutions of thorium nitrate in 4 N nitric acid were shaken with the mentioned organic extractants for times varying from 5 to

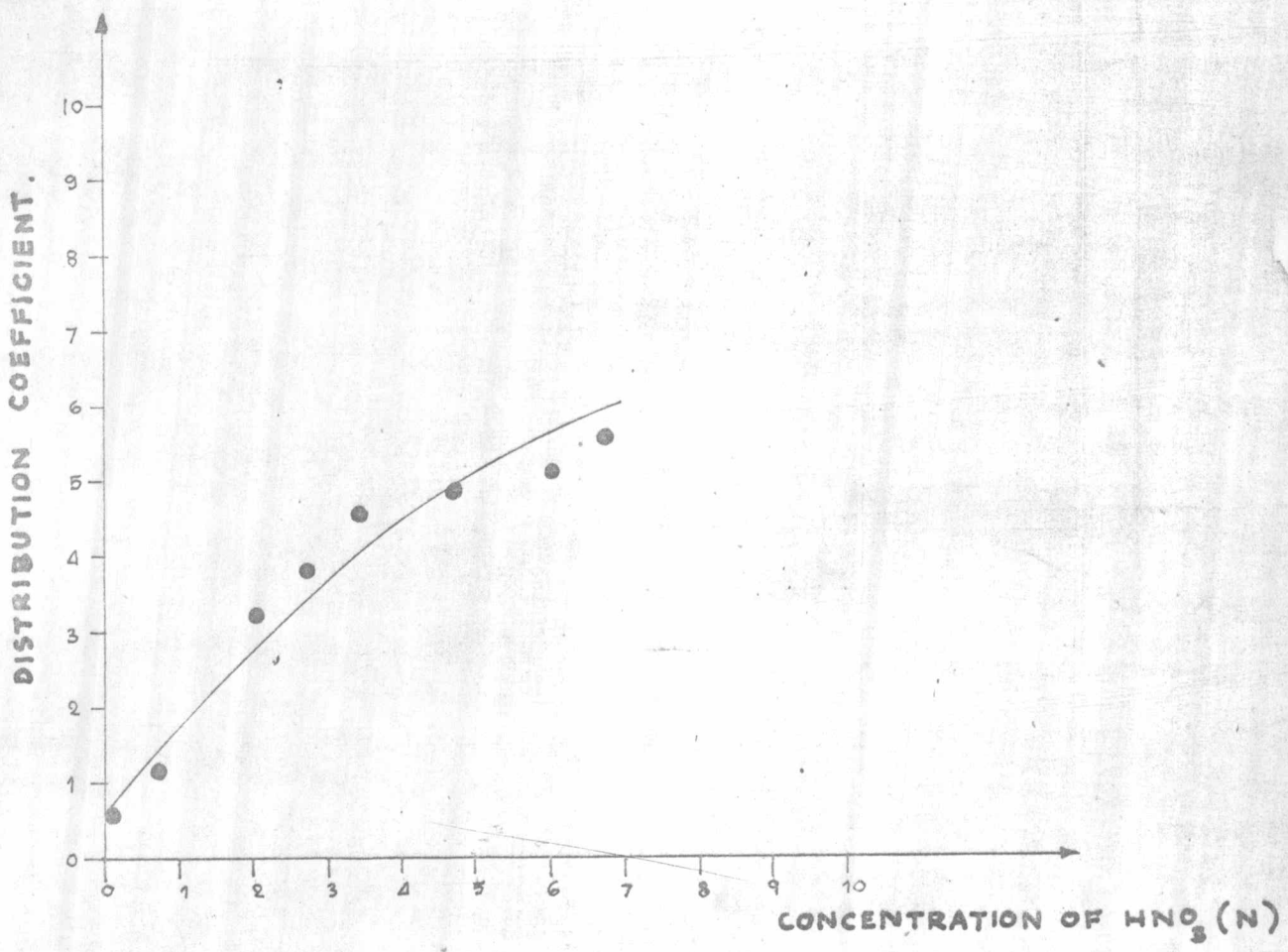


FIGURE 3-2 EFFECT OF ACID CONCENTRATION ON DISTRIBUTION COEFFICIENTS OF THORIUM IN A TBP-XYLENE-SOLVENT EXTRACTION SYSTEM.

100 minutes. The amount of thorium remained in the aqueous phase was analysed and the per cent of extraction evaluated. From the results that are shown in Fig. 3-3, it would be seen that the equilibrium between the two phases can be reached even after shaking for only 5 minutes. Throughout the present study extractions were performed by shaking the aqueous and the organic phases for 1 hour.

The purification of thorium by solvent extraction was performed in three steps. Uranium was first removed from the feed solution by shaking with 5 per cent TBP (volume/volume). Thorium in the aqueous solution after removal of uranium was extracted with 40 per cent TBP. The impurities in the extract which composed mainly of rare earths were removed by scrubbing the extract with 1 N nitric acid. Finally, thorium was stripped into the aqueous phase with 0.02 N nitric acid. The operating conditions are shown in Table 3-2.

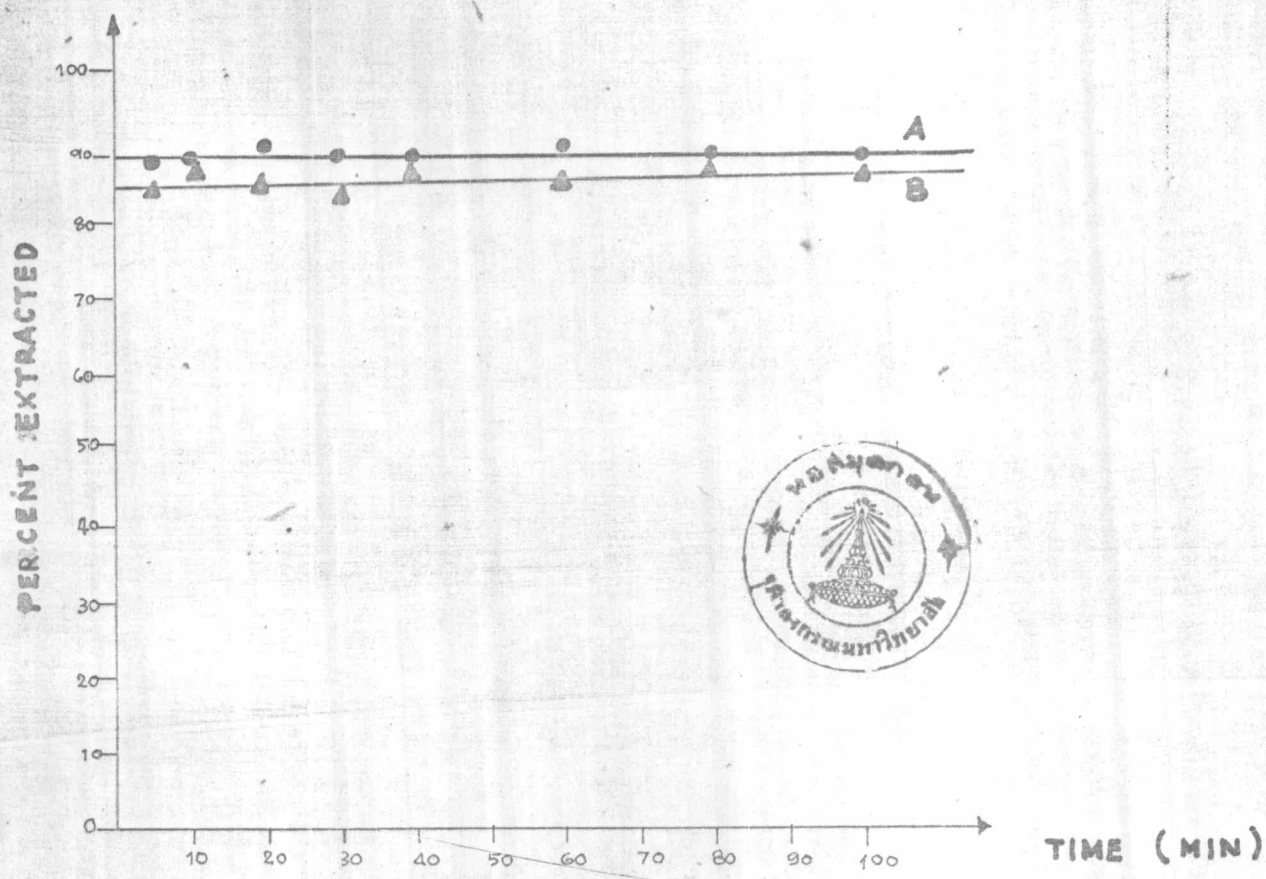


FIG. 3-3 EFFECT OF EQUILIBRIUM TIME ON PERCENT THORIUM EXTRACTED IN **2** TBP-XYLENE SYSTEM AND **3** TBP - KEROSENE SYSTEM.

A : TBP - XYLENE SYSTEM.

B : TBP - KEROSENE. SYSTEM.

Table 3 - 2 Operating conditions for the purification of thorium by solvent extraction

	Diluent	Phase Ratio (Organic : Aqueous)	Number of Extractions	Remarks
<u>1. Step</u>				
<u>Removal of uranium</u>				
Small scale	Xylene	1 : 1 (19)	1	The extract after scrubbing with 1N HNO ₃ could be used for the recovery of uranium. The scrubbed solution was returned to the aqueous phase for the separation of thorium and rare earths.
Larger scale	Kerosene	1 : 1	2	
<u>2. Step</u>				
<u>Extraction of thorium</u>				
Small scale	Xylene	2.5 : 1(19)		The raffinate composed mainly of rare earths.
Larger scale	Kerosene	2.5 : 1		
<u>Scrubbing</u>				
Small scale	-	10 : 1 (19)	1	The scrubbed solution composed mainly of rare earths.
Larger scale	-	10 : 1	3 - 4	
<u>3. Step</u>				
<u>Stripping</u>				
Small scale	-	1 : 1 (20)	1	
Larger scale	-	1 : 1	4 - 5	

It should be mentioned that in the present investigations the crude thorium concentrate from the acid digestion was dissolved in 4 N nitric acid and used without prior treatment with hydroxide as feed solution.

3.5. Quantitative analysis of thorium

The thorium content in samples after each chemical processing step was checked via instrumental neutron activation analysis (INAA). Thorium nitrate solution (Spect Pure Grade) containing 1×10^{-3} g thorium/ml was prepared and used as standard for liquid samples, whereas standard monazite from NBL, which contains 9.7 per cent thorium oxide and 60 per cent rare earths, was used for solid ones. Since crude thorium concentrates contain as much as 50 per cent of rare earths, it is essential to use monazite whose thorium content was well analysed as a standard to prevent the difference in neutron flux in a standard and samples which may be caused by the high neutron absorption cross-section of some of the rare earths. In the case of the final thorium products which were obtained after purification through several extraction steps, such effect does not exist; spect pure thorium oxide powder was used as a standard. The amount of sample used for irradiation was normally 1 ml. for liquid and 5×10^{-3} g for solid. The samples were sealed in 1 ml. polyethylene vials and subjected to irradiations for 30 seconds, two samples and one standard in one irradiation, in the pneumatic tube of the Thai-Research Reactor 1 (TRR-1)

(1982 - 1) The neutron flux at the position of irradiation was about 5×10^{12} n/cm²-sec. The samples and standard were counted, for 2 minutes each, immediately after irradiation, and the photopeak at 29.2 KeV was used for evaluation of the thorium content. The gamma spectrum of the standard monazite from NBL after irradiation in the reactor for 30 seconds is shown in Figure 3 - 4. The decay curve of the 29.2 KeV peak as is shown in Figure 3 - 5. gave a half-life of 22 ± 1 min. which agrees well with the half-life of Th.²³³

It is therefore shown that the 29.2 KeV peak can be used selectively for the quantitative determination of thorium in monazite samples since no interferences from other nuclides were discovered.

The rare earth impurities in the final thorium oxide powders which were obtained from the monazite processing were also analysed. In this case, samples of 5×10^{-3} g each were weighed in polyethylene bags which were wrapped in aluminium foil to prevent deformations of the bags which may be caused by heating in the reactor core. The samples together with rare earth standards were submitted to irradiation in the reactor core for 20 minutes. The neutron flux of the core was about 1×10^{13} n/cm²-sec. The counting schedule for each element as well as the gamma photopeaks that were used for the evaluation are shown in Table 3 - 3.

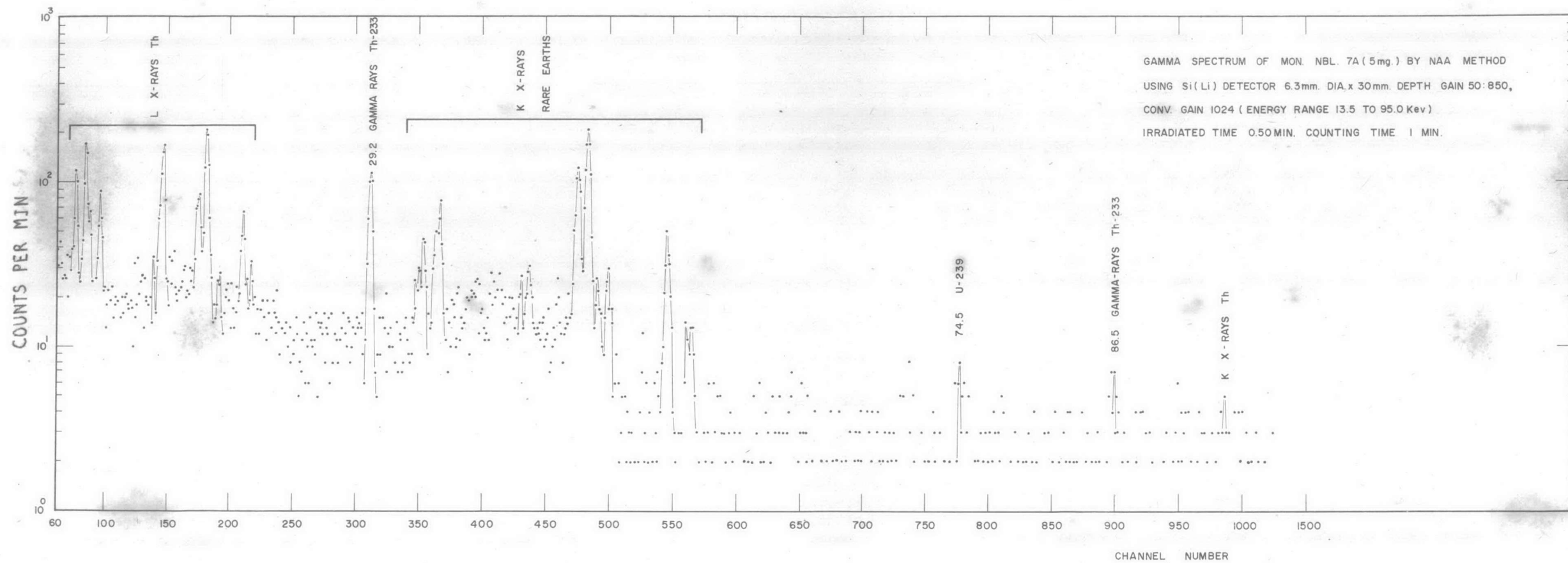


Fig. 3-4 Gamma spectrum of monazite NBL 7A by neutron activation analysis

FIGURE 3-5 HALF-LIFE OF THORIUM-233

SI(LI) DETECTOR

COARSE GAIN 50

FINE GAIN 0.85

CONVERSION GAIN 1024

IRRADIATED TIME 1.0 MIN

COUNTING TIME 1.0 MIN

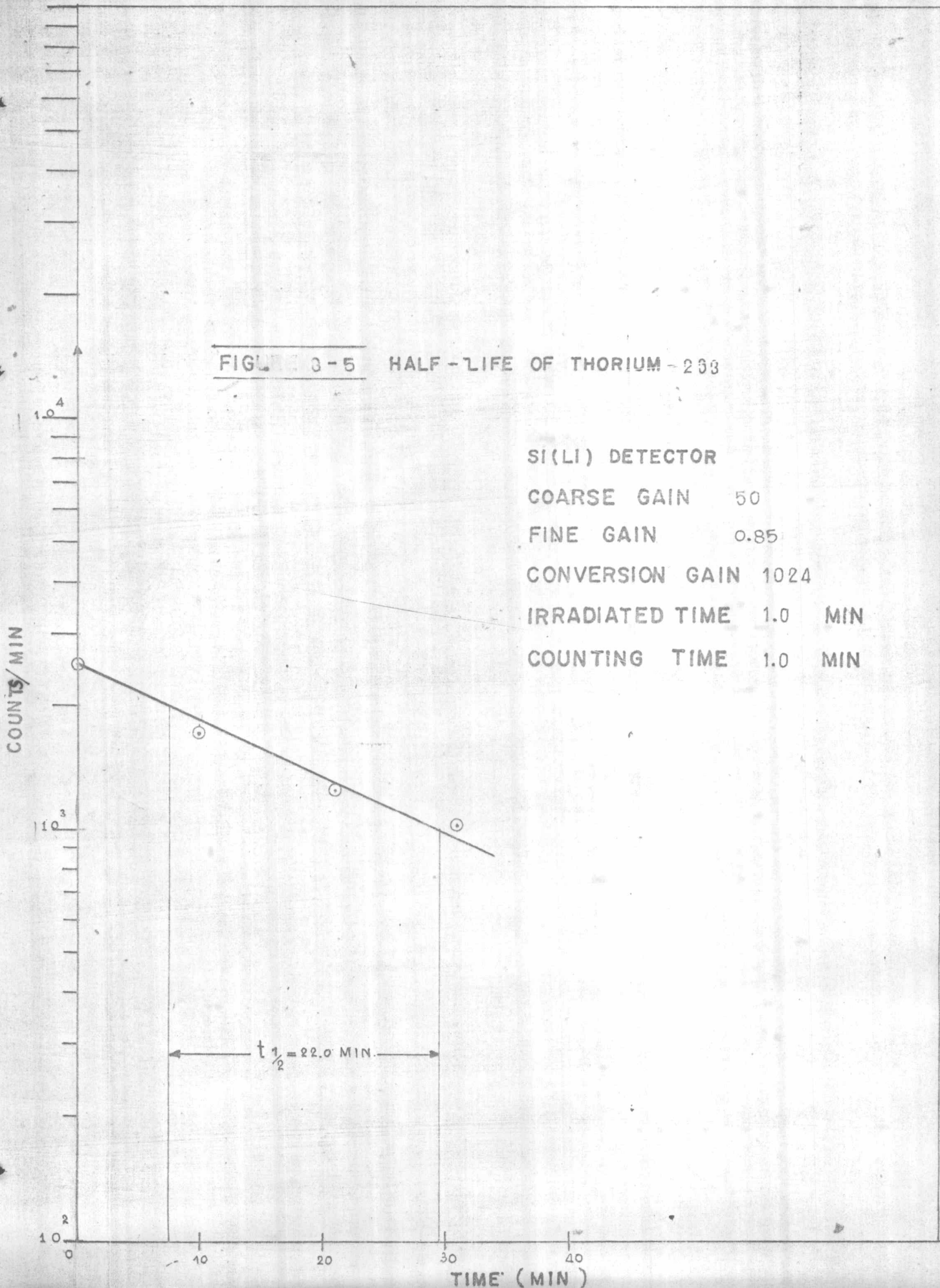


Table 3 - 3 Half-life, photopeaks and counting schedule of
nuclides of rare earth elements used in NAA
determination
(NAA = Neutron Activation Analysis.)

Element	Radio-nuclide	Half-life	Decay-times days	Principal gamma-ray peaks KeV
La	La-140	40.22 h	1 3	1595.4 486.8, 815.5, 328.6
Ce	Ce-141 Ce-143	32.50 d 33.00 h	8 3	145.4 293.1
Pr	Pr-142	19.20 h	0 1	1575.5 1575.5
Nd	Nd-147	11.01 d	8 26	91.4, 531.0 91.4, 531.0
Sm	Sm-153	46.80 h	0, 1, 3, 8*	103.2
Eu	Eu-152 m Eu-152	9.30 h 12.70 y	0, 1* 26	121.8, 841.6 121.8
Gd	Gd-159	18.00 h	1	363.5
Tb	Tb-160	72.10 d	8 26	879.4, 298.6 298.6, 879.4
Dy	Dy-165	2.32 h	0	94.6, 279.5
Ho	Ho-166	26.9 h	1, 3*	80.6
Er	Er-171	7.52 h	0, 1	308.1
Tm	Tm-170	134.00 d	26	84.4
Yb	Yb-169 Yb-175	31.80 d 101.00 h	26* 3, 8*	177*, 97.8, 307.5 282.9, 396.1
Lu	Lu-177	6.74 d	3, 8	208.4

* Decay times used in calculating element concentration

3.6. Radiation measurements

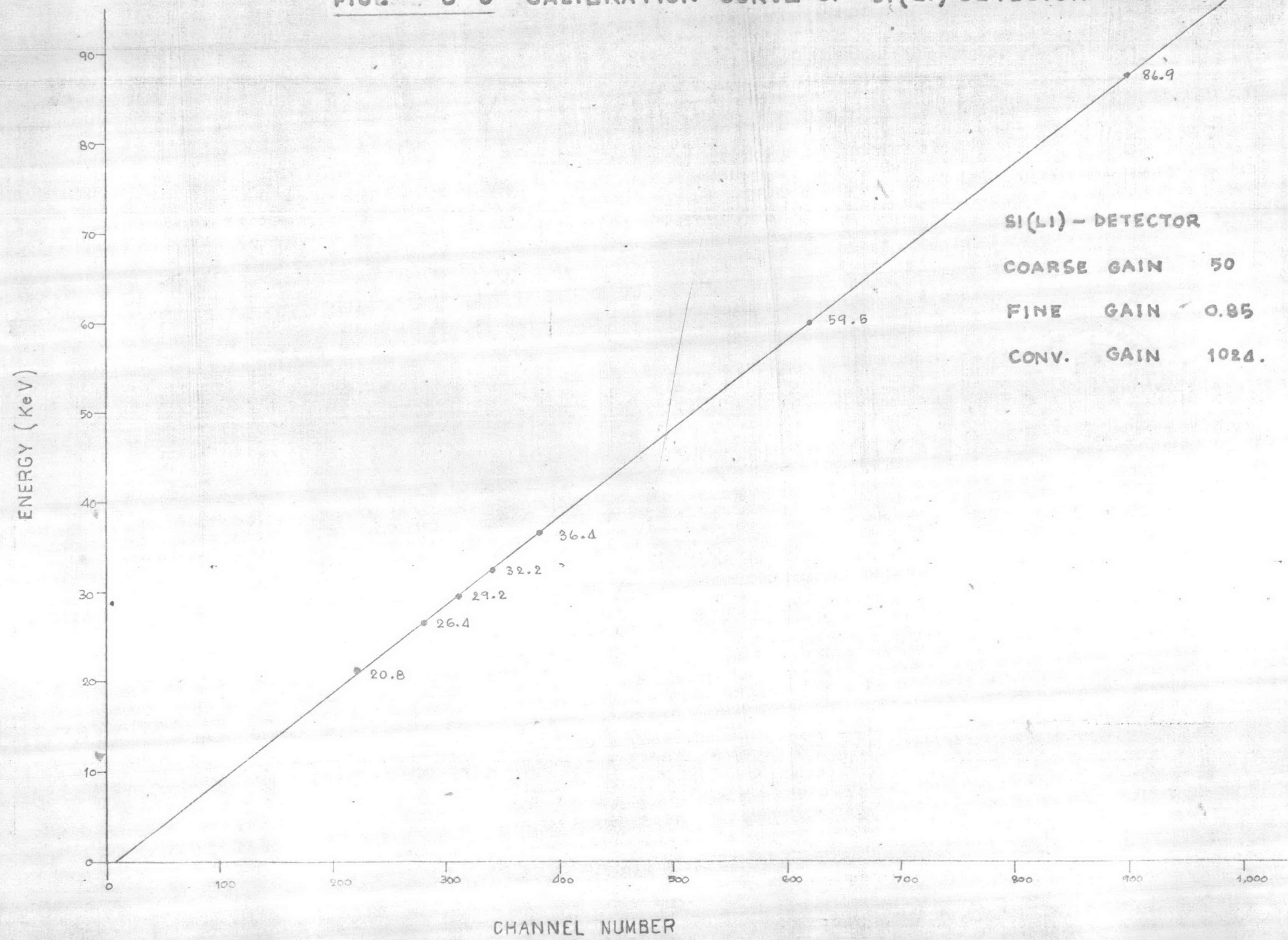
All energies which are lower than 100 KeV were detected with a Si (Li) detector with 6.3 mm active diameter and a resolution of < 215 eV FWHM at 5.9 KeV Mn K_{α} - line. The detector was connected to an amplifier from Ortec (Model 761 A) and a pulser from the same producer (Ortec 419) High-Voltage was supplied to the system via a bias supply from Ortec (Model 446) which voltage was set at 1500 volt. The pulses after passing through the amplifier were analysed by a computer based pulse-height analyser from PDP (Model 8E). The calibration curve of the detector as calibrated with Am²⁴¹ (20.8 KeV, 26.4 KeV and 59.5 KeV), Th²³³ (29.2 KeV and 86.9 KeV) and Cs¹³⁷ (32.2 KeV and 36.4 KeV) is shown in Figure 3 - 6.

For higher energies a 26.2 cc Ge (Li) with a resolution of 2.2 KeV FWHM at 1.33 MeV photopeak of Co⁶⁰ was used. The detector was connected with a preamplifier (Nuclear Data Model 120), a linear amplifier (Nuclear Data Model 451) and a biased amplifier (Nuclear Data Model No. 8001 - 0822). The pulses were analysed by a multi-channel analyser from Nuclear Data (Model 2002)
(FWHM = FULL WIDTH at HALF MAXIMUM)

3.7. Chemical reagents

In the case of small scale investigations, analar grade reagents were used, whereas in the case of a larger scale all reagents

FIG. 3-6 CALIBRATION CURVE OF SI(LI) DETECTOR.



were commercial grade, with the exception of TBP and nitric acid which were of analar grade.