CHAPTER III

EXPERIMENTS

3.1 Sample Preparation

The ore was first crushed in a 6"x7" Jaw Crusher to 1/2 inch after which was fed into a 8" Pulverizer for grinding. By a vibrating screen the particle size was seperated into different fractions:+48, —48, —100, —150, and —200 mesh. The —200 mesh fraction, about 36 percent of the total weight, was chosen for use. The grinding and sieving processes were performed at the Department of Mining Engineering of the Chulalongkorn University.

3.2 Quantitative Analysis of Sandstone

3.2.1 Chemical and Spectrophotometric Analysis

The sample (—200 mesh) was fused, according to H.Bennett and R.A. Reed (15) , with sulphuric—nitric acid mixture to determine the following constituents: Al, Fe, Cu, Pb, Mn, K, Na, Mg and Ca. The content of Si was determined by decomposition with NaOH or fusion with a mixture of K_2CO_3 and Na_2CO_3. Conventional chemical and spectro — photometric methods were applied (15, 16, 17). Carbonate was analysed by back—tritration according to the method suggested by A.I. Vogel (18).

3.2.2 X-Ray Fluoresence Analysis [19, 20]

The X-ray analysis system is shown schematically in Figure 3.1. The main components used were an annular radioisotope source (8 mCi Cadmium 109), a cryogenically cooled Si(Li) detector (6.3 mm. active diameter), a spectroscopy amplifier (Ortec 472), a 4096 channel analyzer, together with associated power supply and readout instruments. The resolution of the system is 215 eV. (FWHM)* at 5.9 keV. Mn K_α line. The source sample set-up is shown in Figure 3.2.

Calibration curves for the detector were performed with a Variable Energy X-Ray Source from the Radiochemical Center, Amersham, England. The selected elements with their energies are in Table 3.1. A typical calibration curve of coarse gain 50, fine gain 1.0 and conversion gain 1024 is shown in Figure 3.3.

Table 3.1 The Variable Energy X-Ray Source for the
Calibration of Si(Li) Detector at gain 50 / 1.0

X-Rays	Energy (keV)	Peak Channel
Cu K_{α_1}	8.047	84
Cu K_{β_1}	8.904	102
Rb K_{α_1}	13.394	195
Rb K_{β_1}	14.960	240
Mo K_{α_1}	17.478	283

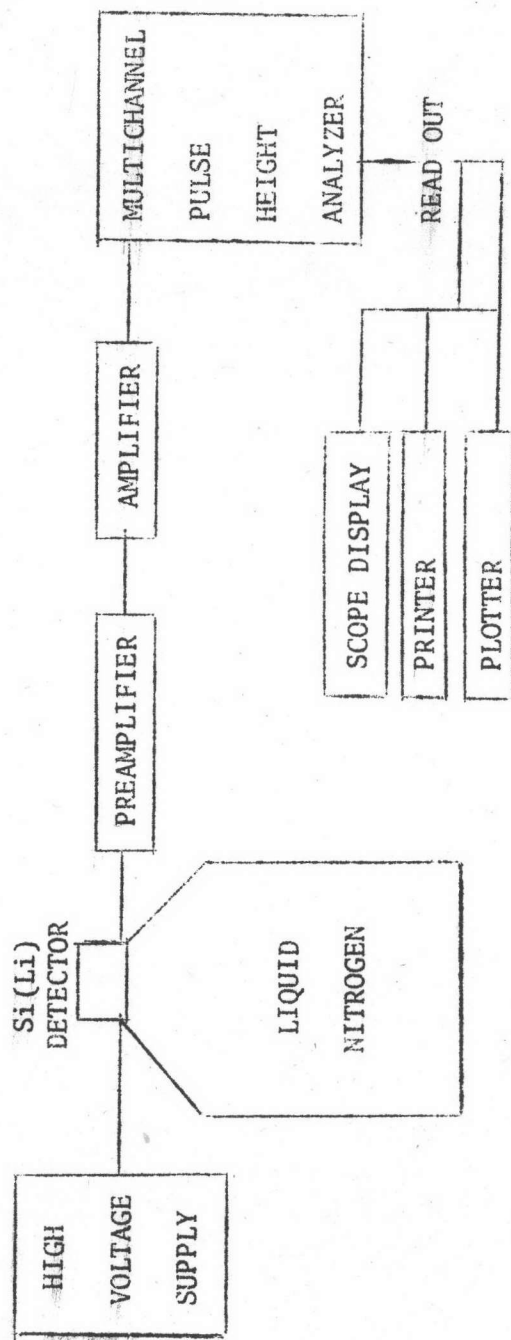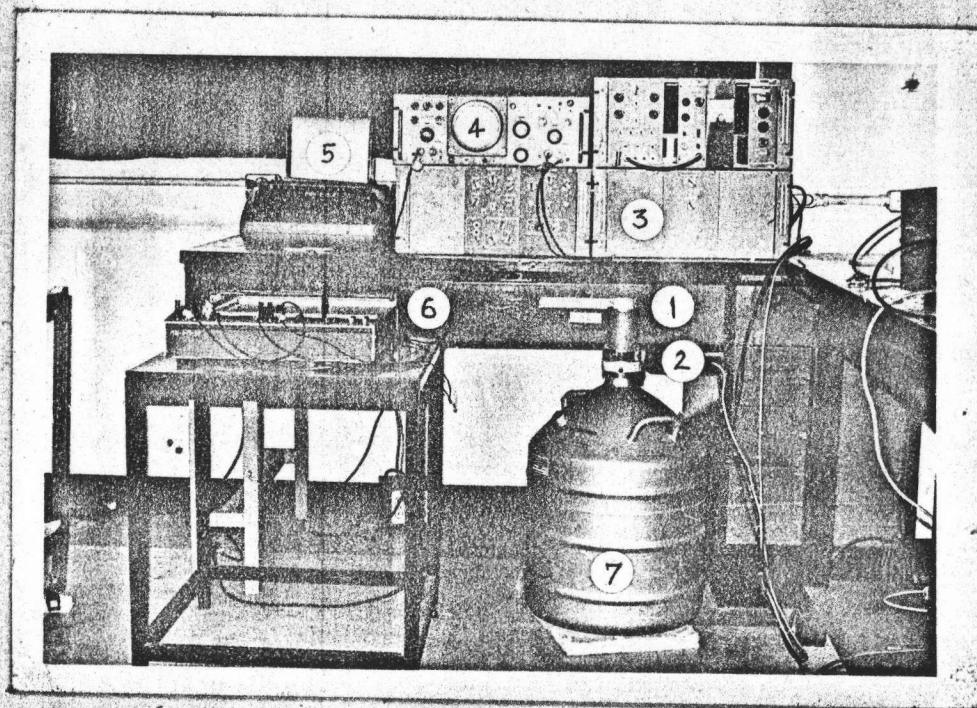* (FWHM   Full Width at Half Maximum)

Figure 3.1   Block diagram of X – Ray fluorescence instruments.

Figure·3.2 The set-up of X—Ray Fluorescence Instruments.

1. Sample

2. Si(Li) Detector

3. Multichannel Analyzer

4. Scope Display

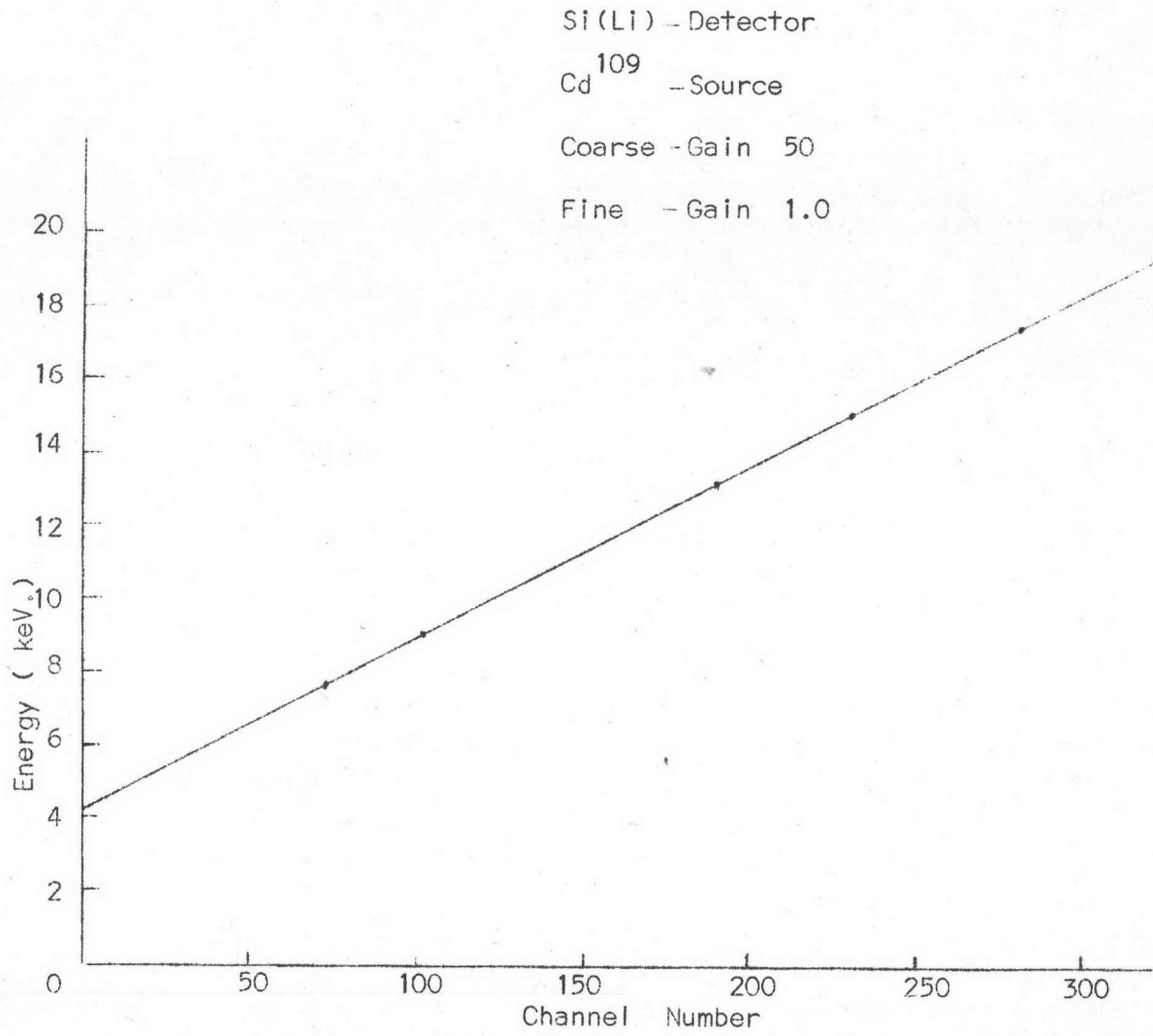5. Printer

6. .Plotter

7. Liquid Nitrogen Dewar

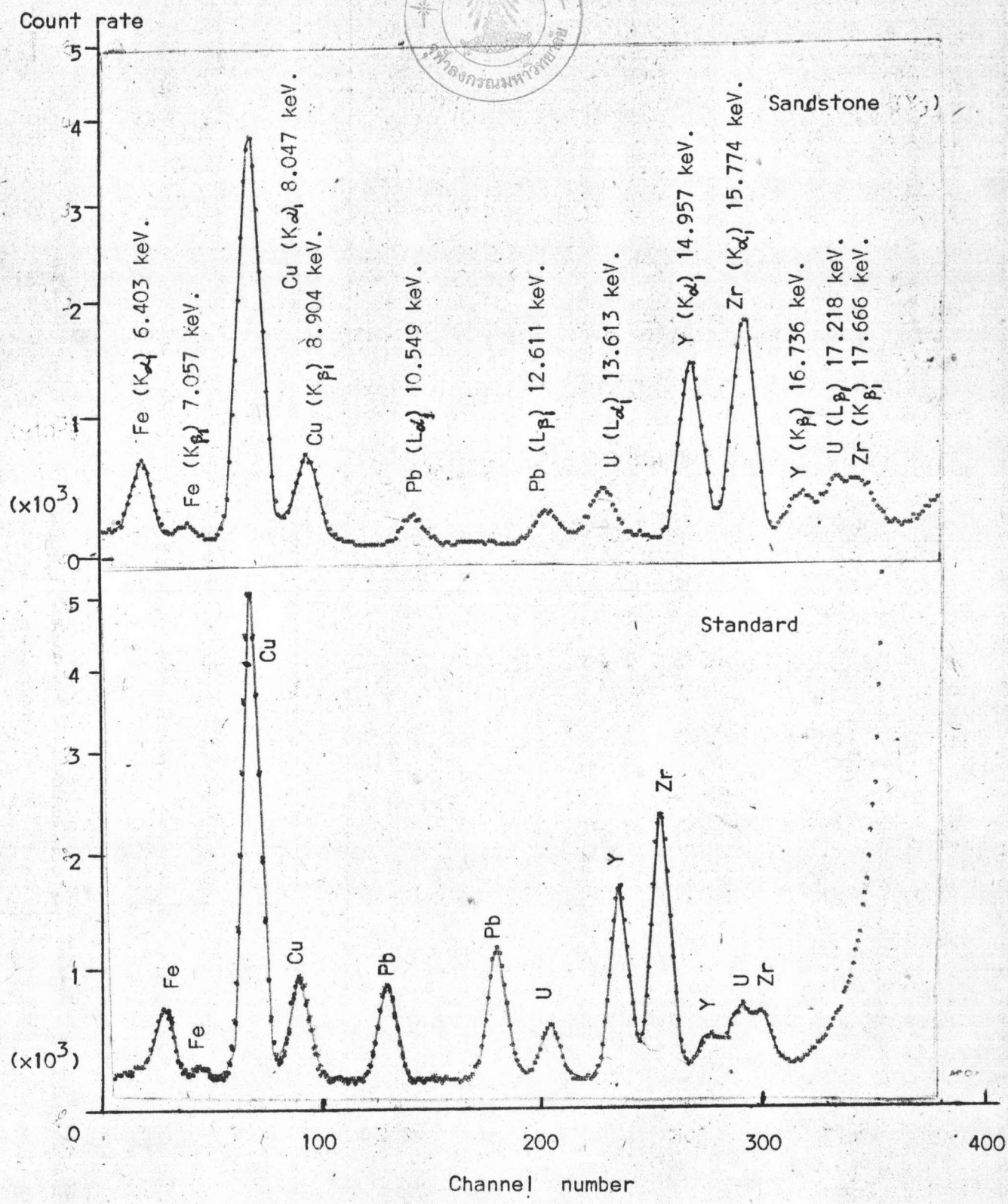Figure 3.3 Calibration Curve of X-Ray Fluorescence

Figure 3.4   X-Ray spectra of standard and sandstone.

In the X-Ray fluorescence analysis of sandstone, standard ore was prepared by mixing Specpure oxides of the elements which were made nearly similar to those of the ore compositions. The oxides were ground together for homogeneity. 15G of ground ore of 200 mesh was put in the polyethylene X-ray container after which was placed on the X-ray source. The ore components were analysed by comparing their peak intensity with the corresponding peak of the synthetic standard. Counting time was 800 seconds for all cases.

The X-ray spectra of the standard and sample are shown in Figure 3.4.

3.2.3   Instrumental Neutron Activation Analysis (INAA) (21)

Methodology

The uranium content in samples and leach liquors were checked by instrumental neutron activation analysis (INAA) via the (n, γ) reaction of U^{238}. Standard uranyl sulphate solution containing 50, 100, and 200 $\mu g/cm^3$ were prepared by dissolving U_3O_8 (Specpure Grade) in diluted sulphuric acid. Standard uranium ores from NBL (NBL No.104 and No.105) which contains 0.01 and 0.001 % U respectively were used as solid standards. The amount of sample used for irradiation was normally 1 cm^3 for liquid and 5×10^{-3} g for solid. The samples were sealed in 1cm^3 polyethylene vials and subjected to irradiation. Two samples and one standard were irradiated per time. All irradiations

were performed at the TRIGA, Mark III (TRR 1/MT) reactor of the Office of Atomic Energy for Peace through the pneumatic system. Irradiation and decay time varied according to the operating power of the reactor (varied from 1 to 2 MW.) , position of the reactor core and the uranium concentration in the samples. Some typical conditions are given in Table 3.2.

Table 3.2 Conditions of sample irradiation for uranium
analysed by neutron activation analysis.

Type of sample	Neutron flux ($n.cm^{-1}.sec^{-1}$)	Optimum Range of Uranium Content ($\% U$)	Time of Irradiation (min)
Sandstone	10^{10}	0.01 − 0.03	15
Ore residues	10^{10}	0.001 − 0.01	30
Leach Liquors	10^{10}	0.001 − 0.03	4
Sandstones	10^{12}	0.01 − 0.03	5
Ore Residues	10^{12}	0.001 − 0.01	2.5
Leach Liquors	10^{12}	0.001 − 0.03	0.5

The samples and standards were counted for 200 seconds and the photopeak at 75 keV was used for the uranium content evaluation. The gamma spectrum of 0.01 % U standard uranium ore, sandstone sample, solid residue and leach liquor after irradiation at power 1MW, for the

time conditions described in Table 3.2 , and 5 min. decay time are shown in Figure 3.5, and 3.6 respectively. The decay curve of the 75 keV. peak as shown in Figure 3.7 gave a half-life of 24 min. which agrees well with the half-life of U^{239}.

As vanadium was also found present in the samples, its content was determined through the 1.43 MeV. gamma line of V^{52} proceed via the (n, γ) reaction of V^{51}.

Gamma Radiation Measurements

Energies which are lower than 100 keV. were detected by a cryogenically cooled HpGe detector with 25 mm.^{2} active area. Other components include a cooled input charge sensitive preamplifier, a linear pulse amplifier, a 4096 multichannel analyzer (Canberra 8180), together with associated power supply and readout instruments. The resolution of the system is 178 eV. (FWHM) for the 122 keV. Co—57 line. The block diagram of the set-up is shown in Figure 3.8.

Energies which are higher than 100 keV. were detected by a Ge(Li) detector with 18.1 cm^2. active area. The counting system was similar to the above described HpGe system. The resolution of 122 keV. Co^{57} is 1.08 keV.(FWHM).
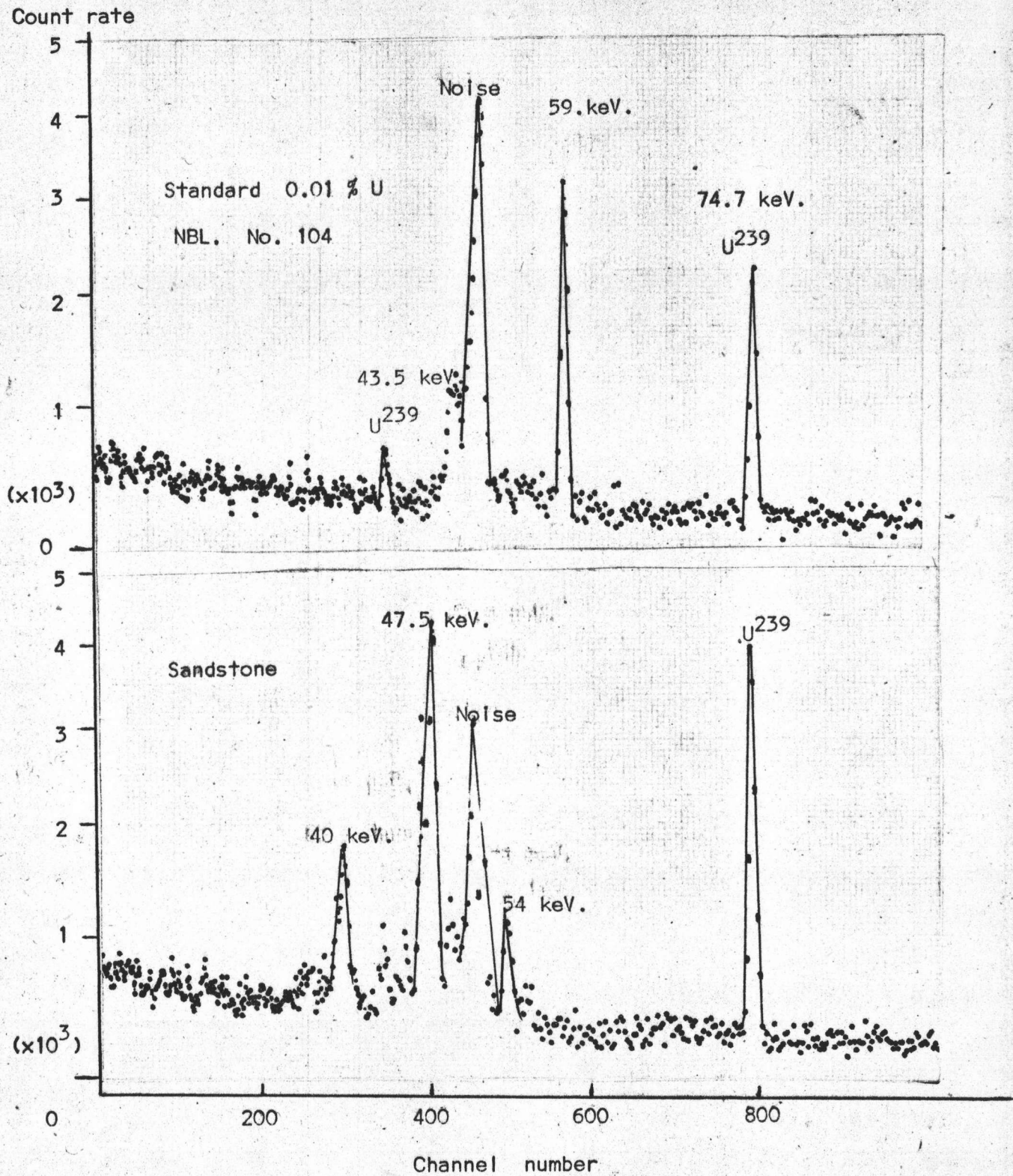
Figure 3.5 Gamma spectra of sandstone and standard NBL. No.104
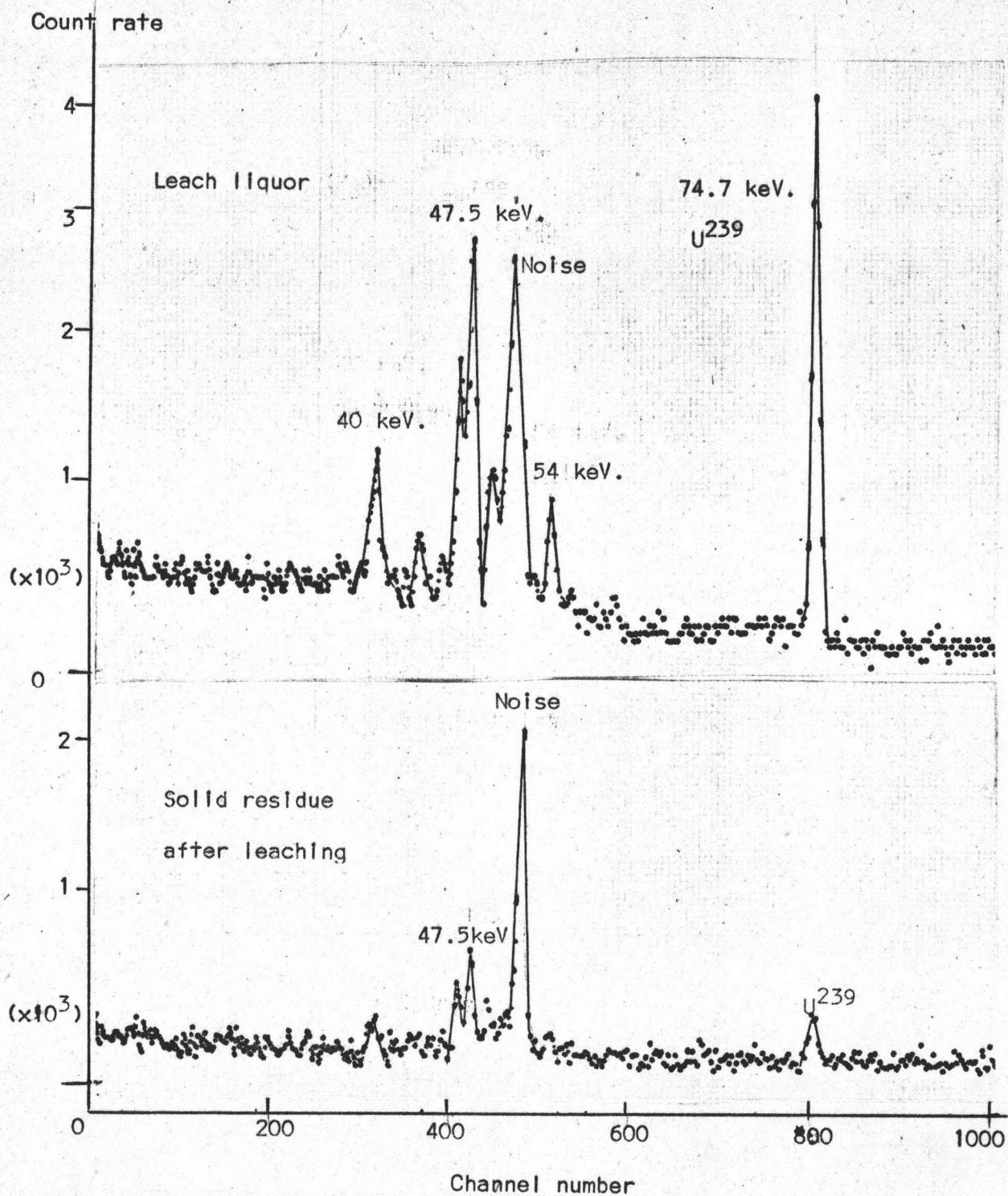
(0.01 % U)

Figure 3.6 Gamma spectra of solid leached residue and leach liquor.
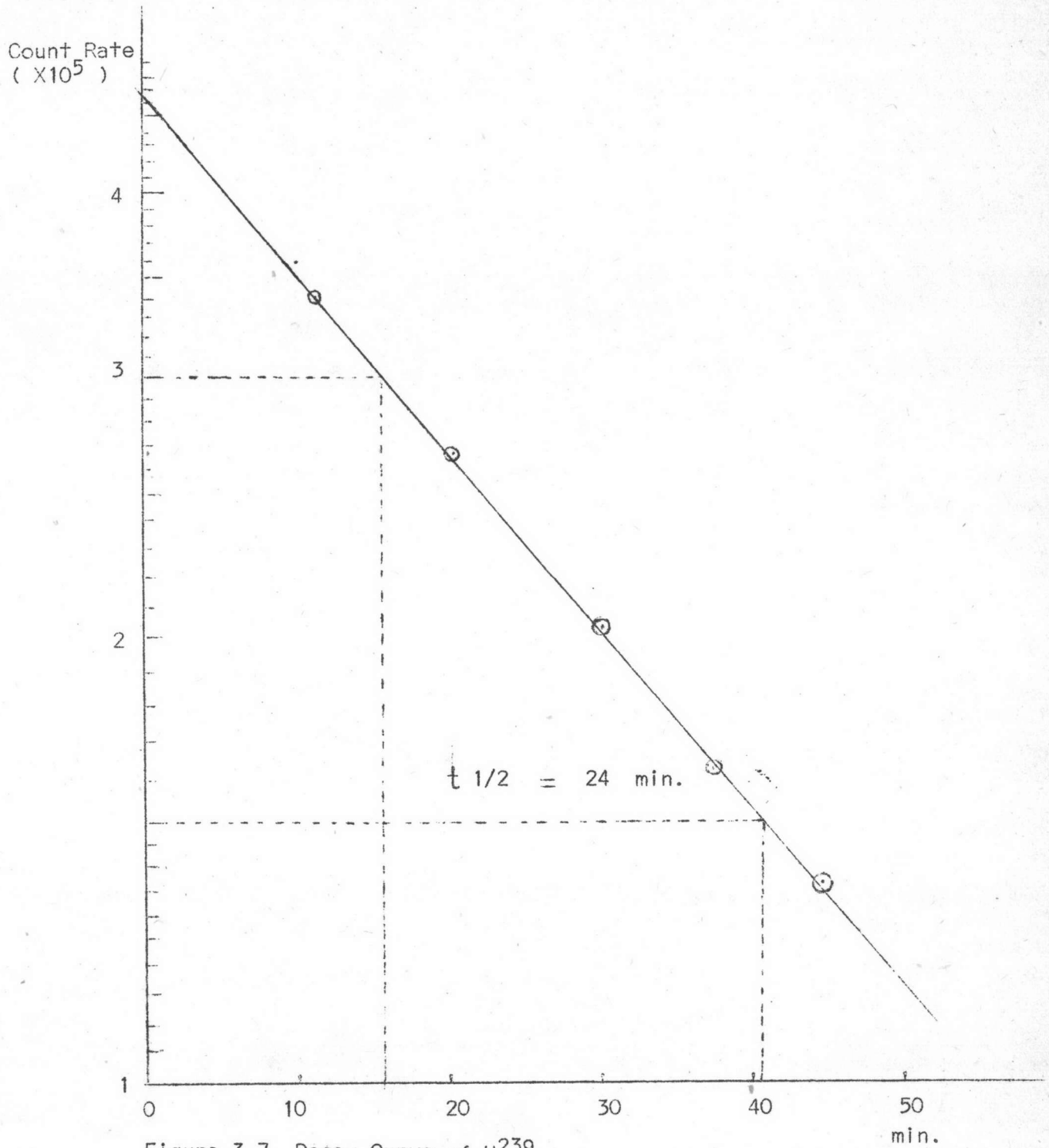
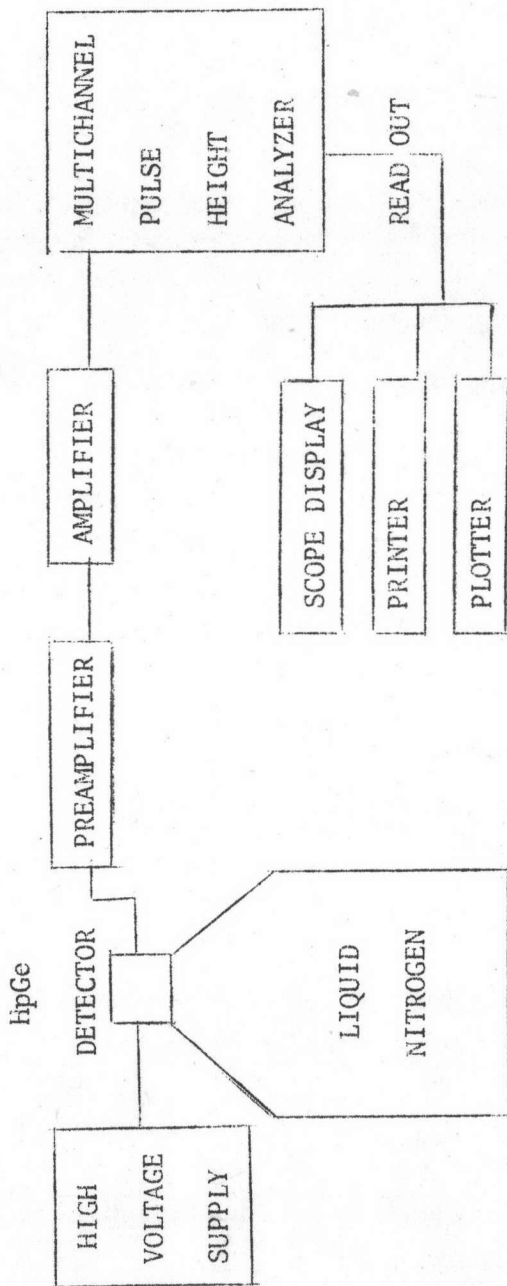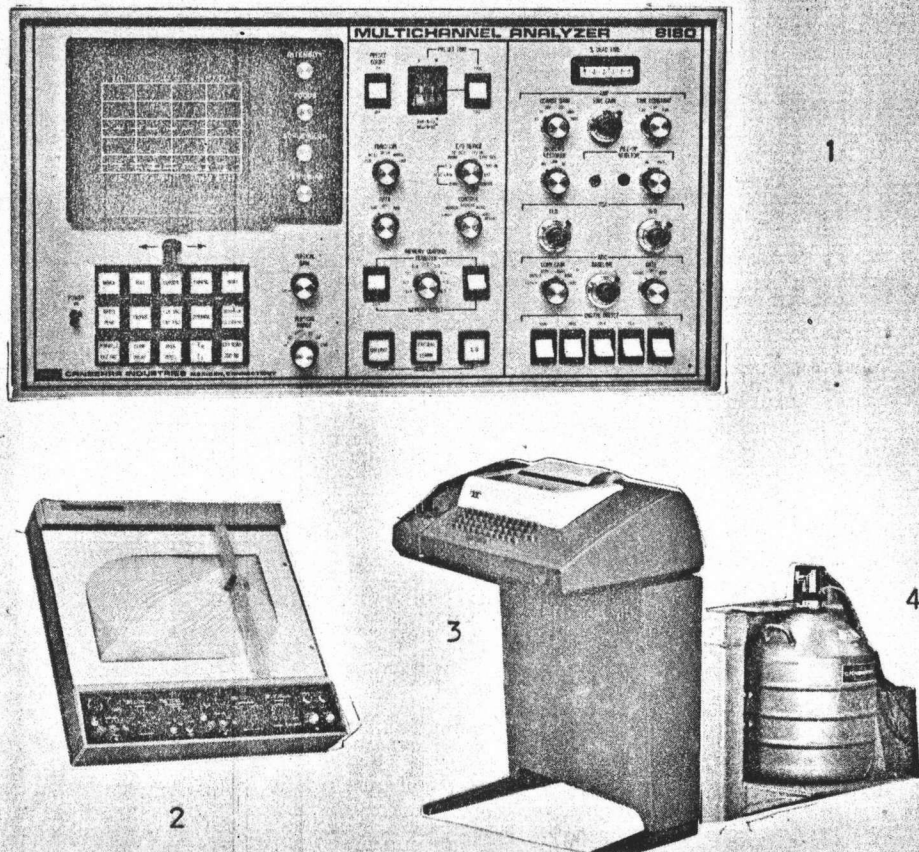Figure 3.7 Decay Curve of U^{239}

Figure 3.8   Block diagram of gamma rays measurement instruments.

Figure 3.9 The set of gamma ray measurement instruments.

1. Multichannel Pulse Height Analyzer

2. X—Y Plotter

3. Teletype

4. Hyper Pure Germanium Detector

3.3 Ore Leaching

3.3.1 Procedure

The flow diagram in Figure 2.1 was followed. In order to obtain the optimum conditions for the uranium acid leaching the effects of the reaction temperature, the concentration of sulphuric acid, the amount of oxidant, particle size, and the time of reaction were studied using 100 g sand per leaching. Having selected the optimum conditions for leaching, a number of trial experiments were performed on larger scale, 1 kg per batch. A 2 liter conical flask and a mechanical stirrer were used in those cases.

After leaching, the solid—liquid was separated by vacuum filtration and the solid residue was washed with water. The leach liquor was gently evaporated to 100 ml. The concentration of uranium in the leach liquor was determined after which the solution was subjected to amine extraction.

3.3.2 Equipments for Batch Agitation :

1. 250 cm^3 conical flask with rubber stop—cork

2. 8 mm. diameter pyrex tube as air condenser

3. 100 $^{\circ}$C thermometer

4. heater with magnetic stirrer

The schematic diagram of the batch agitation apparatus is shown in Figure 3.10.

Figure 3.10 Schematic diagram of the batch agitation apparatus

— Air Condenser

— Thermometer

— Conical Flask

— Magnetic Bar

— Heater with Magnetic stirrer
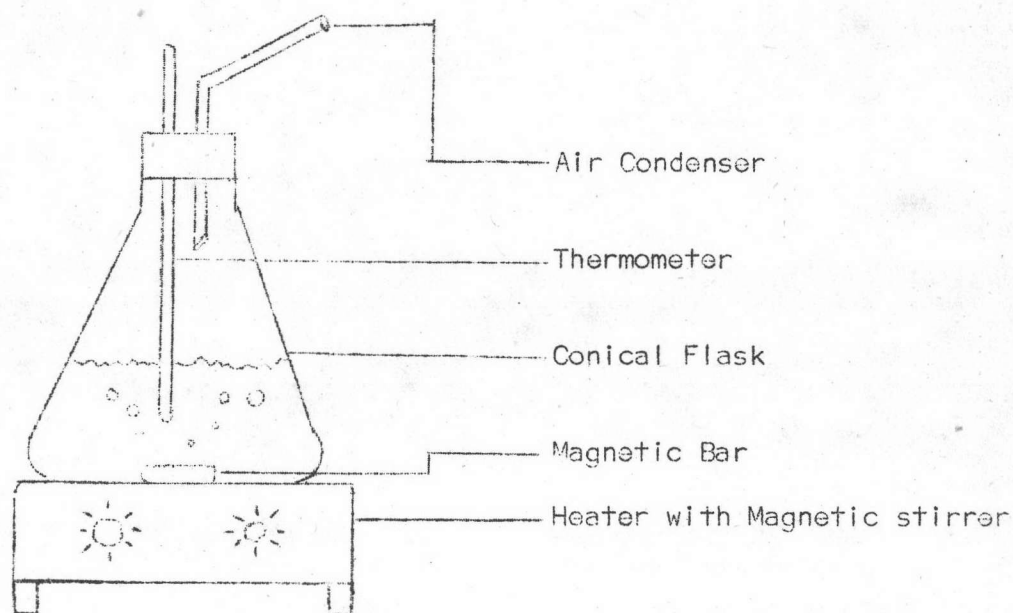
3.4   Amine Extraction of Sulphuric Leach Liquor

Uranium in the sulphuric acid leach liquor was recovered by extracting with tertiary amine, Alamine 336. The extraction conditions applied in the present study were based on the investigation of the Instituto de Energea Atomica of Brazil (12).

The organic phase was prepared by mixing 7.5 % (v/v) Alamine 336 in Solvent 3040. The organic to aqueous volume ratio was 0.3 . The pH of the leach liquor was found to be the optimum pH for extraction, as shown in Figure 3.11. Under such conditions D.R. George and J.R. Ross (22) found that up to 95 % uranium could be extracted in three stages. The load in organic phase was found to be 0.5 g U_3O_8/l.

Leach liquor, 100 cm^3 each, containing 0.222 g U/l was subjected to solvent extraction.   The extraction was carried out at room temoerature, 30° C with 30 cm^3 of 7.5 % (v/v) Alamine 336 in Solvent 3040 which was previously saturated with diluted sulphuric acid at pH 1 .   The extractions were performed by shaking the aqueous and organic phases for 15 min.   The organic phase was then subjected to one_stage scrubbing with tri_distilled water to remove impurities such as iron and small amount of extracted sulphuric acid (13,23). Uranium was then stripped twice by 0.1 mol/l (NH$_4$)$_2$CO$_3$ according to F.J. Hurst and D.J. Crouse (14).   The pH of the stripped liquor was adjusted to 7.5 by merely evaporation.   Uranium was finally precipitated as ammonium uranyl tricarbonate.
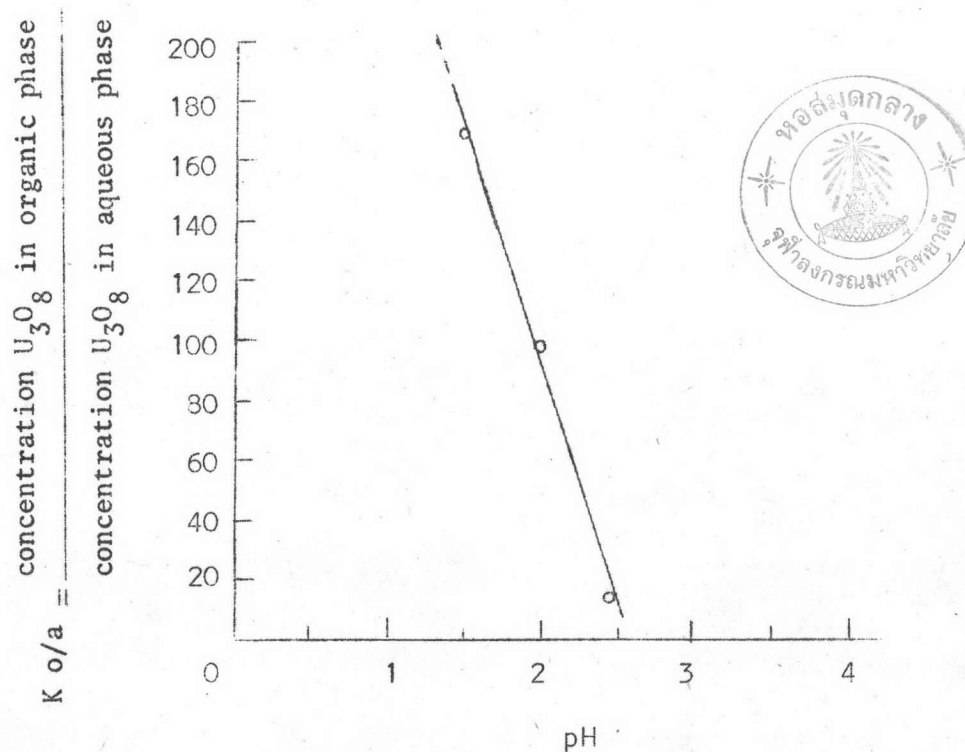

Figure 3.11   Effect of pH on the extraction of uranium with

tertiary amine (22)