CHAPTER III

EXPERIMENTS

3.1 Neutron Activation Analysis

3.1.1 Reagents and Chemicals

Uranium Standard Solution

A stock solution containing 100 μg U/cm^3 was prepared by dissolving 0.10549 g of the analar grade $UO_2(NO_3)_2 6H_2O$ in tri-distilled water or diluted solution of A.R. grade nitric acid and diluting to the mark of the 500.0 cm^3 volumetric flask.

A series of standard solutions with other concentrations are prepared by successive dilution of the 100 μg U/cm^3 stock solution with 1 % HNO_3.

Ethyl alcohol Absolute ethyl alcohol from Carlo Erba was used without further purification.

Mixed Solvent A Mixed solvent of 4 : 1 (V/V) solution of ethanol/HCl was prepared by mixing 4 volume of ethyl alcohol and 1 volume of A.R. grade concentrated hydrochloric acid from Mallinckrodt, Inc.

Anion exchange resin In order to exchange the uranium anions in the water samples, the strong basic anion exchange

resin, DOWEX 1-x8; 100-200 mesh, chloride form from J.T. BAKER CHEMICAL CO, was used. No pretreatment was commenced on the resin.

1 G of the anion exchange resin was packed into a thin-walled polyethylene column with 5 cm in length and 1 cm in diameter, The bottom of the column was closed with glass wool to support the resin. The whole column was soaked into a 250 cm^3 beaker containing 4 : 1 ethanol/HCl mixture for an hour. It is important that all resin in the column was soaked with the mixed solvent.

Stripped drill-hole water 500 cm^3 of the acidified drill-hole water sample was allowed to pass through a column of Dowex 1x8, 1 cm in diameter and 20 cm in height. The flow rate was set at 1-2.0 cm^3/min. After passing through the column, the effluent was considered to be uranium-free while other cationic matrix elements were retained.

Sample collection and Storage

The Office of Atomic Energy for Peace acts as a counterpart to the Department of Mineral Resources, Ministry of Industry in the Uranium Exploration Project. Geochemical samples and drilled hole samples are routinely analysed by the well-studied technique of neutron activation. Since in drilling, the diamond-drill must be flush-washed with water from time to time, it is felt that the uranium content in the washed water should also be an indication for the uranium

concentrate in that region. So, water sample at different depth from the earth surface were collected for investigation from the drill holes at Pratu Teuma region, Khonkhan province. The sampling operations were performed in May and June, 1978 by the Department of Mineral Resources. In addition to the drill-hole samples, fresh water from various rivers and canals was also collected and the uranium content investigated.

The samples were either stored in glass bottles (drill-hole water samples) or polyethylene container which were previously cleaned with concentrated nitric acid and distilled water. To avoid any loss of the trace uranium ion in solution by adsorption on the wall or an any particles in the water solution, 10 cm^3 of concentrated nitric acid per dm^3 was added into the water sample at the time of eollection.

3.1.2 Neutron Irradiation

All irradiations were performed in the Thai Research Reactor 1/Modification 1 (TRIGA MARK III) of the Office of Atomic Energy for Peace. The samples were either irradiated in the Rotary Specimen Rack or in the CA-2 position at power of 1 MW.

The Rotary Specimen Rack is in the reactor core. The approximate thermal neutron flux is about 2.9×10^{12} $n/cm^2.sec$. CA-2 is an irradiation facility which is shielded with cadmium to remove all the thermal neutrons so that the sample is subjected to irradiation with epithermal neutrons only.

3.1.3 Radiation Measurements

3.1.3.1 Gamma radiation measurements

Energies which are lower than 100 keV were detected by a cryogenically cooled HpGe detector with 25 mm^2 active area. The detector was connected to a charge sensitive preamplifier (CANBERRA MODEL 2000), a linear pulse amplifier (ORTEC MODEL 410), a 4096 multichannel analyzer (CANBERRA MODEL 8180) with associated power supply (CANBERRA MODEL 3005) and read out instruments (Teletype from Canberra Model ASR 33 or X-Y plotter from OMNIGRAPHIC, Houston Instrument). 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 3.1

Calibration curves for the detector were performed by using a variable x-ray energy source from the-Radiochemical Center, Amersham, England. The selected elements with their energies are listed in Table 3.1

A typical calibration curve at coarse gain 10, fine gain 10 and conversion gain 1024 is shown in Figure 3.3

Table 3.1 Standard x-rays for the calibration of the HpGe Detector

X-Rays	Energy (KeV)
Mo K_{α_1}	17.478
Ag K_{α_1}	22.162
Ba K_{α_1}	32.191
Tb K_{α_1}	44.47
Am-241 (γ-ray)	59.60

Energies which are higher than 100 keV were detected by a Ge (Li) detector with 22.5 cm^2 active area. The counting system was similar to the above described system. The full-width at half-maximum (FWHM) for the 1.332 MeV ^{60}Co-Gamma line is 1.73 keV.

3.1.3.2 Counting geometry

In order to obtain the maximum count rate, the sample and detector system were set up as shown in Figure 3.4[25]

The resin container was made up of a polyethylene cylinder which bottom was closed with a sheet of mylar film.

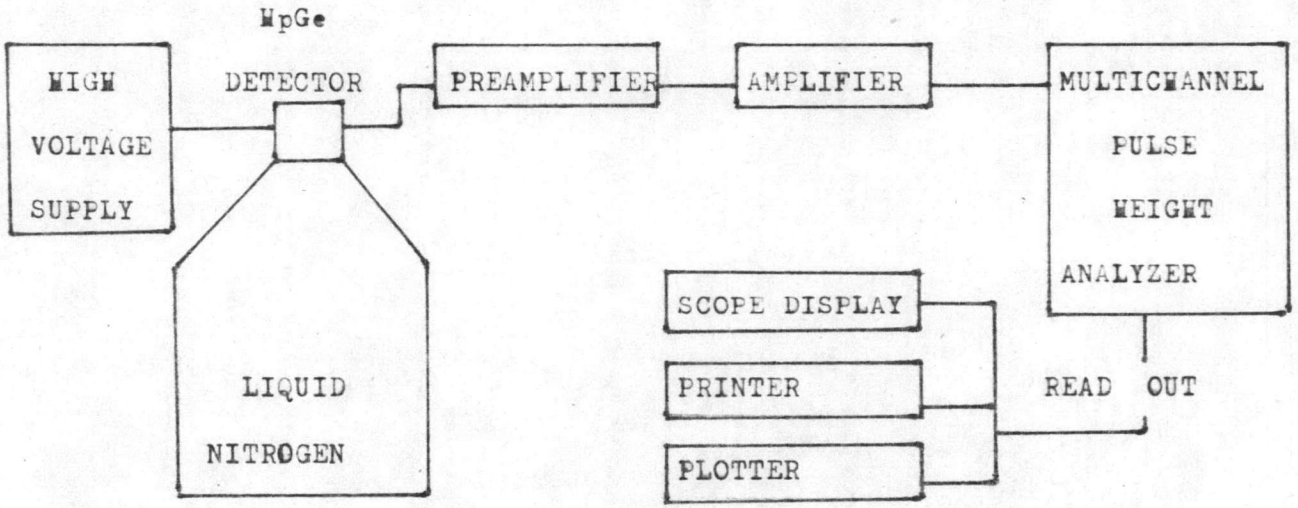
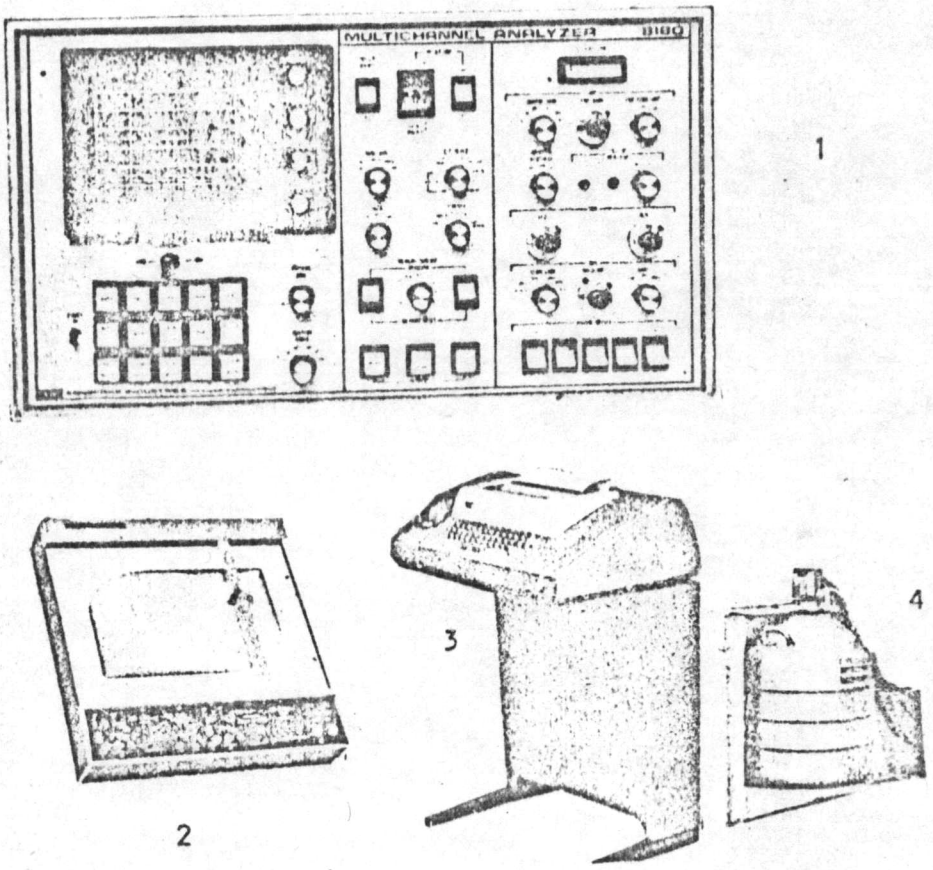


Figure 3.1 Block diagram of the gamma-counting system

Figure 3.2 The set-up of the gamma counting system



1. Multichannel Pulse Height Analyzer
2. X—Y Plotter
3. Teletype
4. Hyper Pure Germanium Detector

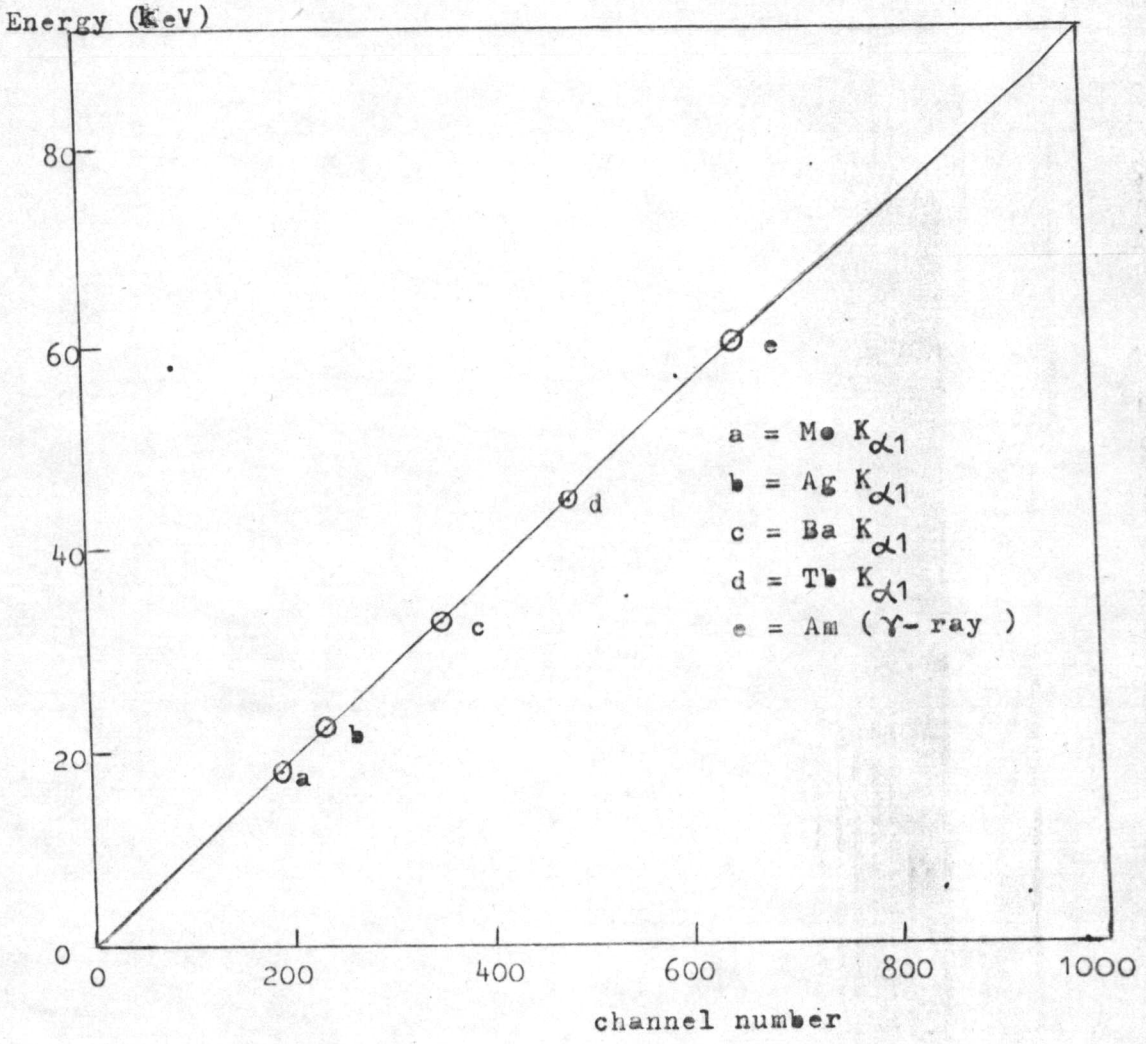


Figure 3.3 Calibration curve of the HpGe Detector at

gain 10 / 10

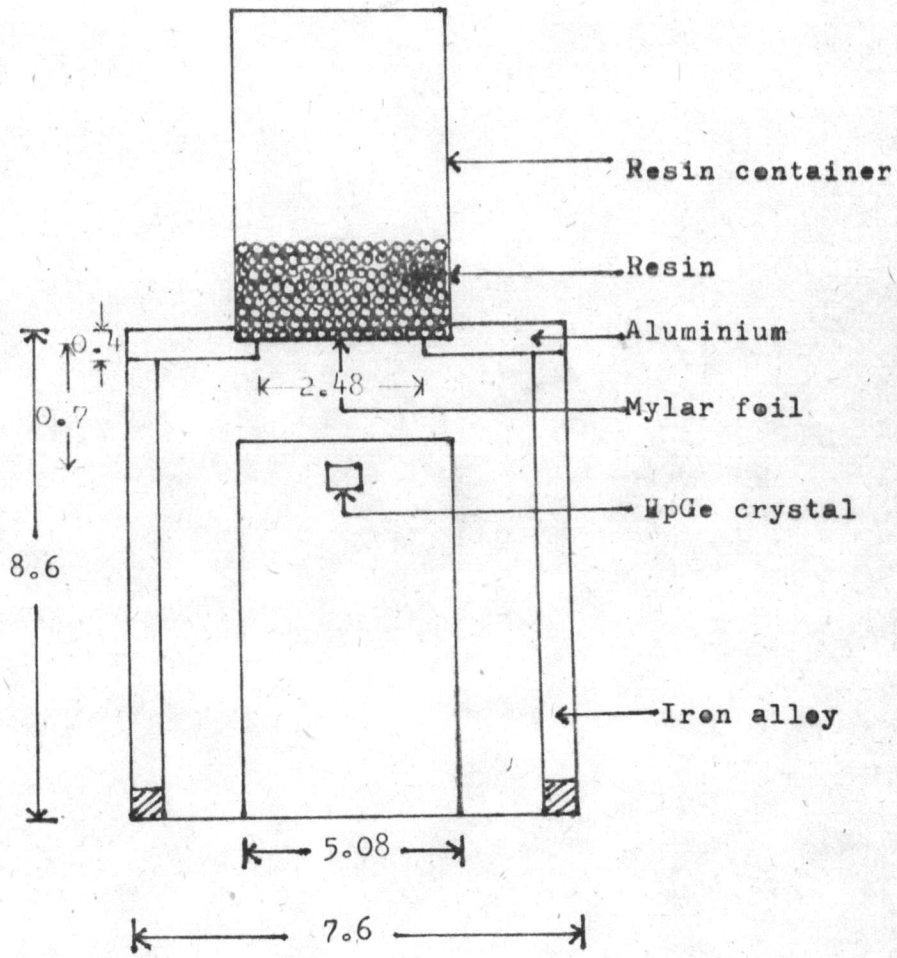


Figure 3.4 Counting geometry (in cm)

The cylinder was 2.5 cm in diameter and 5 cm in length. Mylar film was chosen to avoid adsorption of gamma-radiation. The container was mounted on a cylinder made of iron alloy with a thickness of 0.4 cm, a height of 8.6 cm and an outter diameter of 7.6 cm. The upper part on which the sample was mounted is made of aluminium. Different container sizes were tried. The above given dimension gave the maximum count rate.

3.1.4 Chemical Separation

4 cm^3 water was pipetted into a thin-walled polyethylene vial, 5 cm in length and 1 cm in diameter. The top side of the vial was heat-sealed.

Two samples and one uranium standard (50 $\mu g/dm^3$) were irradiated together in a polyethylene container for 10 minutes in the rotary specimen rack of the reactor. Immediately after irradiation, the vial were cut opened and the samples were separately added into 20 cm^3 4 : 1 ethanol/HCl solution. After mixing, the solution was allowed to flow through a column of resin. The required flow-rate was set by regulating the suction rate of a suction pump. The column was washed with 10 cm^3 portions of mixed solvent. Suction was continued until the resin was dried. The lower end of the column was cut off and the resin was punched into a polyethylene container by a glass rod. The sample was mounted on the detector and the radioactivity was counted for 200 seconds. The 74.5 keV r-ray from ^{239}U was utilized for the analysis. The total time

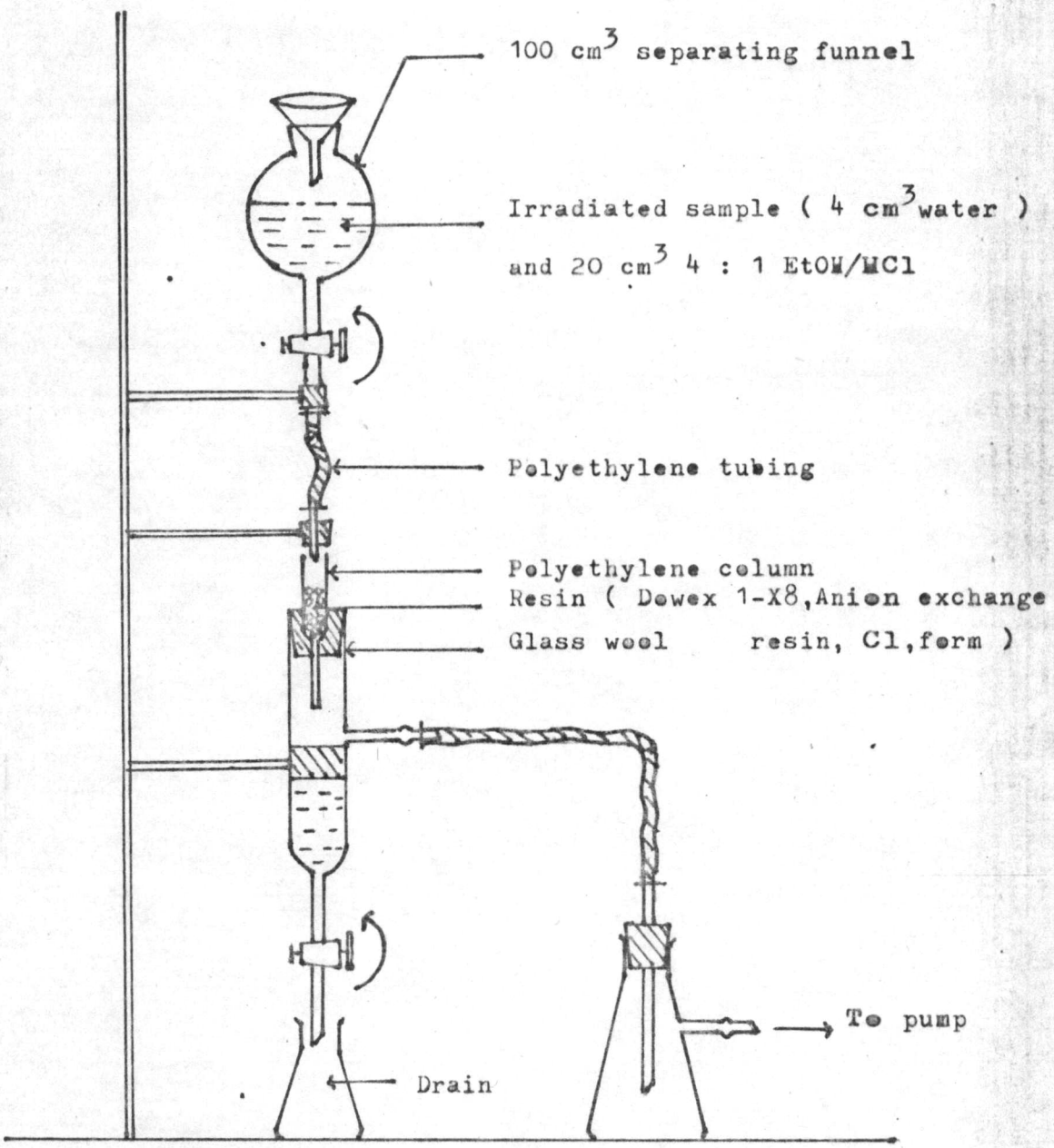


Figure 3.5 Schematic diagram of the experimental set-up

required for the chemical separation was less than 15 minutes for three samples.

The schematic diagram of the experimental set-up, and the flow diagram of the separation process are shown in Figure 3.5 and 3.6. In order to obtain the optimum conditions for the separation of uranium from water, the effects of amounts of resin and flow-rate were studied.

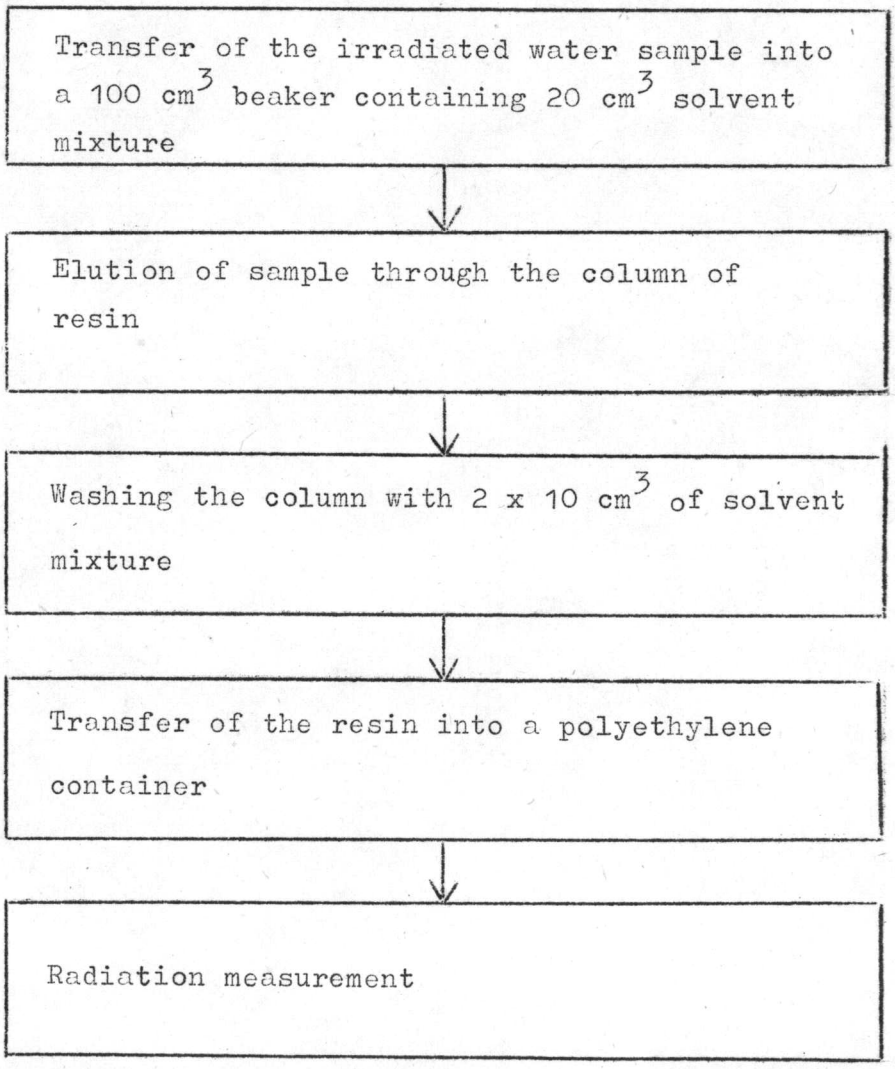


Figure 3.6 Simplified flow diagram of the uranium separation process.

3.1.5 Data Processing

The photopeak area was determined by the Covell's Method[21]. Figure 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 an either side of Co such that C_{+n} and C_{-n} contain counts above half-way between that in Co. The area above the line $C_{-n} - C_{+n}$ then can be expressed by the formula

$$\text{Area} = \sum_{m=-n}^{+n} A_m - (n + \tfrac{1}{2})(A_{-n} + A_{+n}) \qquad (3.1)$$

where

A_m = number of counts in the m^{th} channel

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

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

The content of uranium in a sample is calculated by the equation :

$$\frac{W_1}{W_2} = \frac{A_1 \pm \sigma_1}{A_2 \pm \sigma_2} \qquad (3.2)$$

where

W_1 = weight of uranium in sample

W_2 = weight of uranium in standard

A_1 = Photopeak area of uranium in sample

A_2 = Photopeak area of uranium in standard

σ_1 = Standard deviation of A_1

σ_2 = Standard deviation of A_2

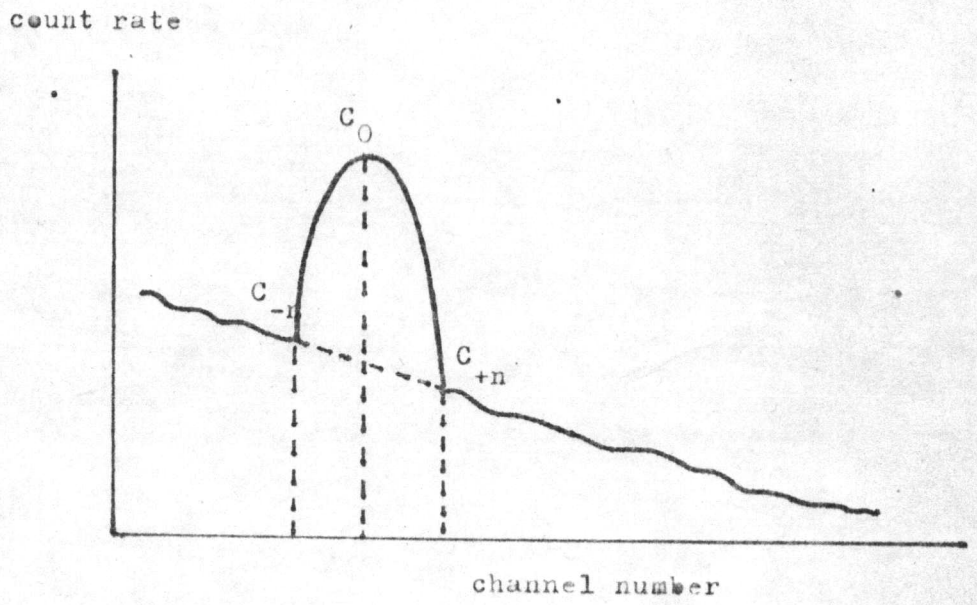


Figure 3.7 Gamma ray pulse height distribution curve

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

$$\frac{A_1 \pm \sigma_1}{A_2 \pm \sigma_2} = \frac{A_1}{A_2} \pm \frac{1}{A_2^2} (A_1^2 \sigma_2^2 + A_2^2 \sigma_1^2)^{1/2} \qquad (3.3)$$

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

$$W_1 = \left[\frac{A_1}{A_2} \pm \frac{1}{A_2^2} (A_1^2 \sigma_2^2 + A_2^2 \sigma_1^2)^{1/2} \right] W_2 \qquad (3.4)$$

3.1.6 Effect of Amounts of Resin on the Separation of Uranium

15 Cm^3 of a standard uranium solution containing 100 $\mu g/cm^3$ U was irradiated in the reactor for 10 minutes. 1 Cm^3 of the irradiated solution was pipetted into 20 cm^3 4 : 1 EtOH/HCl solvent mixture and mixed. The mixed solution was transfered to a 100 cm^3 separating funnel as shown in Figure 3.1 and the solution was allowed to pass through a column which resin weight was varied between 0.5-3.0 g. The flow rate was set at minimum at 2 cm^3/min. The column was washed with two portions, 10 cm^3 each, of mixed solvent. Suction was continued until the resin was dried. The effuent was transfered to a polyethylene container, 5 cm in diameter and 6 cm in height for radiation measurement. The percentage adsorption of uranium on resin was calculated by comparing the radioactivity of the effluent to that of a 50 cm^3 solution

containing 100 $\mu g/dm^3$ uranium which is obtained by diluting the same irradiated standard uranium solution with water.

The weight of resin versus the percentage adsorption of uranium on resin was plotted.

3.1.7 Effect of Flow-Rate

Experiments were performed in the same manner as described in section 3.1.6. The amount of resin was fixed at 1.0 g while the flow-rate of the mixed solvent was varied from 2 to 30 cm^3/min. The effuent was transfered to a polyethylene container for radiation measurement. The percentage adsorption of uranium on resin was calculated by comparing the activity of the effluent to that of standard uranium solution after dilution. The flow-rate versus the percentage adsorption of uranium on resin was plotted.

3.1.8 Limit of Detection

The detection limit of the technique for the determination of uranium in water was studied. A standard solution containing 100 $\mu g/dm^3$ uranium was irradiated in the Rotary Specimen Rack for 10 min. From the standard solution, solutions containing 10, 8, 5, 3, 1, 0.1 and 0.05 $\mu g/dm^3$ uranium were prepared. 4 cm^3 of each irradiated solution were taken and the separation diagram (Figure 3.6) was followed. The amount of resin was fixed at 1.0 g and the flow-rate at 2 cm^3/min. The relation between the uranium concentration and the activity

on the resin was plotted. The concentration which begins to deviate from the linear response is considered as the limit of detection.

The limits of detection for the non-destructive determination of uranium through thermal-neutron and resonance-neutron-irradiations were also investigated. For thermal neutron irradiation, standard solution of uranium with concentrations ranging between 0.001-7.0 $\mu g/cm^3$ were prepared by diluting the standard stock solution with tri-distilled water. For resonance-neutron-irradiation, standards with concentrations ranging between 0.1-20.0 $\mu g/cm^3$ were prepared by diluting the same stock solution with stripped drill-hole water. 1 Cm^3 of each solution was pipetted into a 1 cm^3 polyethylene vial and heat sealed. The solutions were irradiated in the Rotary Specimen Rack (for thermal neutron-irradiation) and in the CA-2 position (for resonance neutron-irradiation) for 10-20 min. After irradiation the low-energy gamma spectra of the uranium were measured.

3.2 Fluorometry

3.2.1 Reagents and chemicals

All chemicals and reagents were of reagent grade, no further purification was attempted. Hygroscopic substances were kept in a desiccator containing anhydrous silica gel as a drying agent.

Flux mixture A mixture of 9 % sodium fluoride, 45.5 % sodium carbonate, and 45.5 % potassium carbonate was fused in a platinum dish, cooled, and ground to fine powder. It is essential to use a fused mixture, as mixtures prepared by ballmilling of the flux ingredients give poor reproducibility at low uranium concentration. The fused flux was then made to pellets for convenience of use. The required weight of the flux mixture was poured into the pellet puncher which was made of stainless steel. The schematic diagram of the puncher and its working mechanism are shown in Figure 3.8 and Figure 3.9 respectively.

Aluminium nitrate A saturated solution of aluminium nitrate was prepared by dissolving 500 g. of the salt in 250 cm^3 tridistilled water. The solution was heated until the salt was completely dissolved.

Preparation of Platinum dishes

The platinum dishes were fused with potassium pyrosulfate ($K_2S_2O_7$) at 700° C for 2-3 min, after which they were

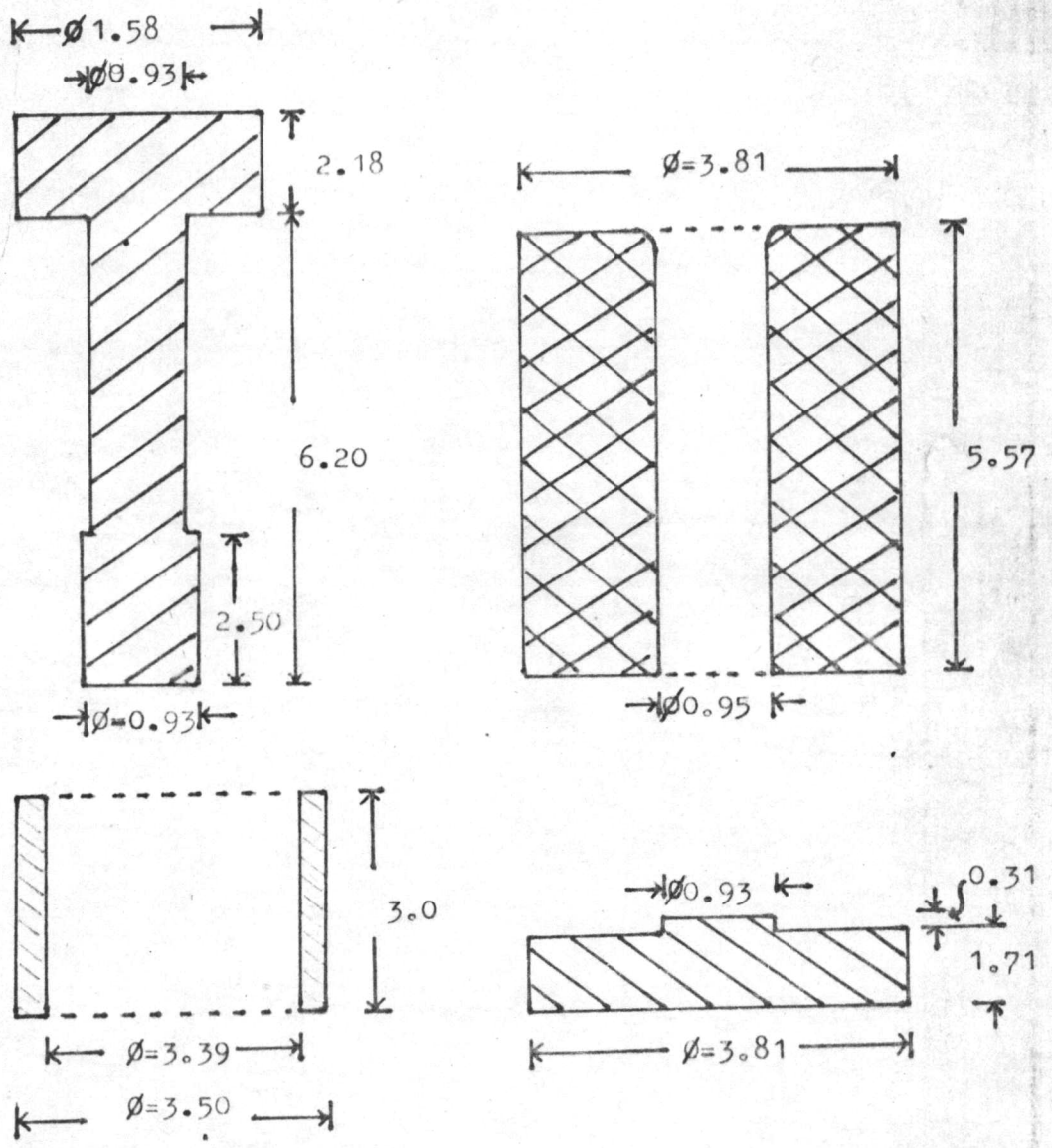


Figure 3.8 Schematic diagram of the pellet puncher

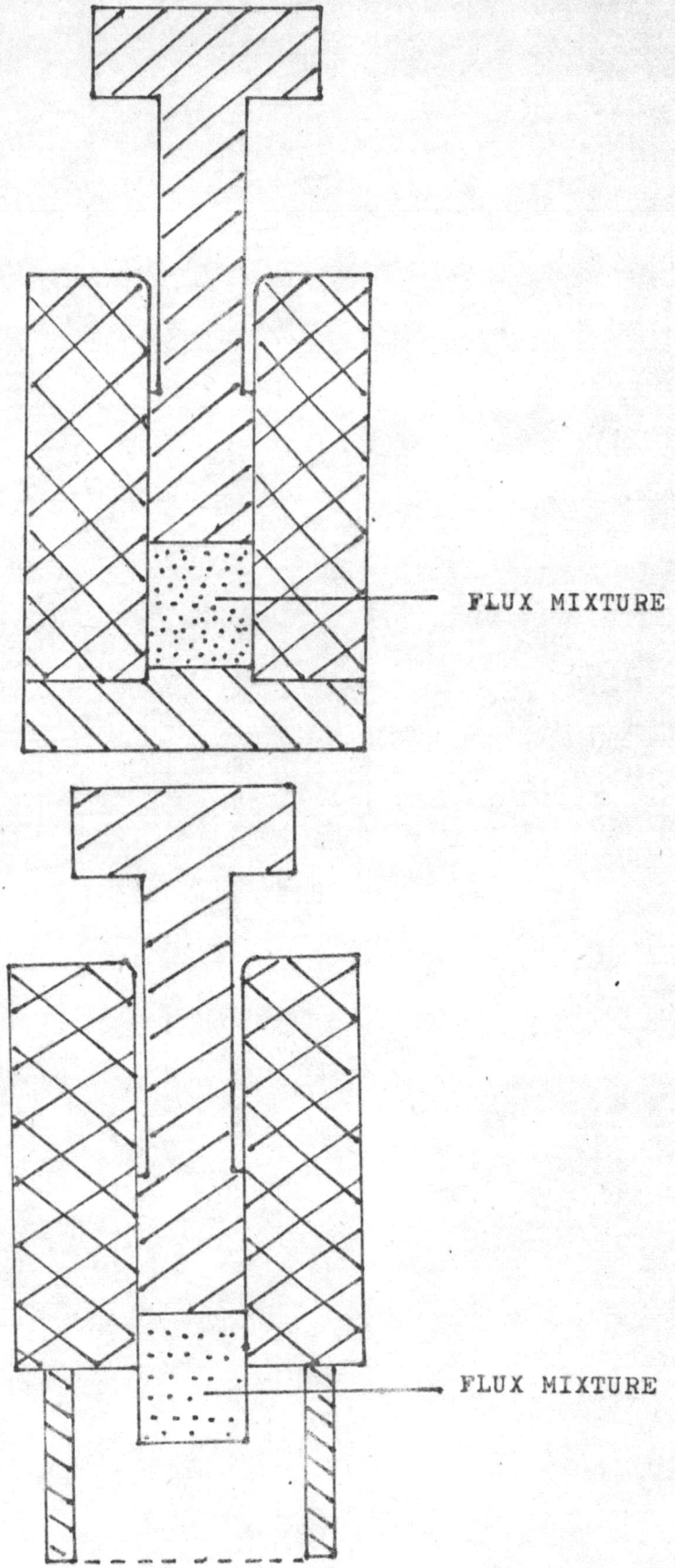


Figure 3.9 Working mechanism of the puncher

cooled and the residue was dissolved in hot water. The dishes were stored in 10 % HNO_3 and rinsed with water before use.

3.2.2 Apparatus

3.2.2.1 Platinum dishes : The dishes are 0.015 inch thick and 0.75 inch in diameter. All of them were provided by the Jarrell-Ash Co., Newtonville, Mass.

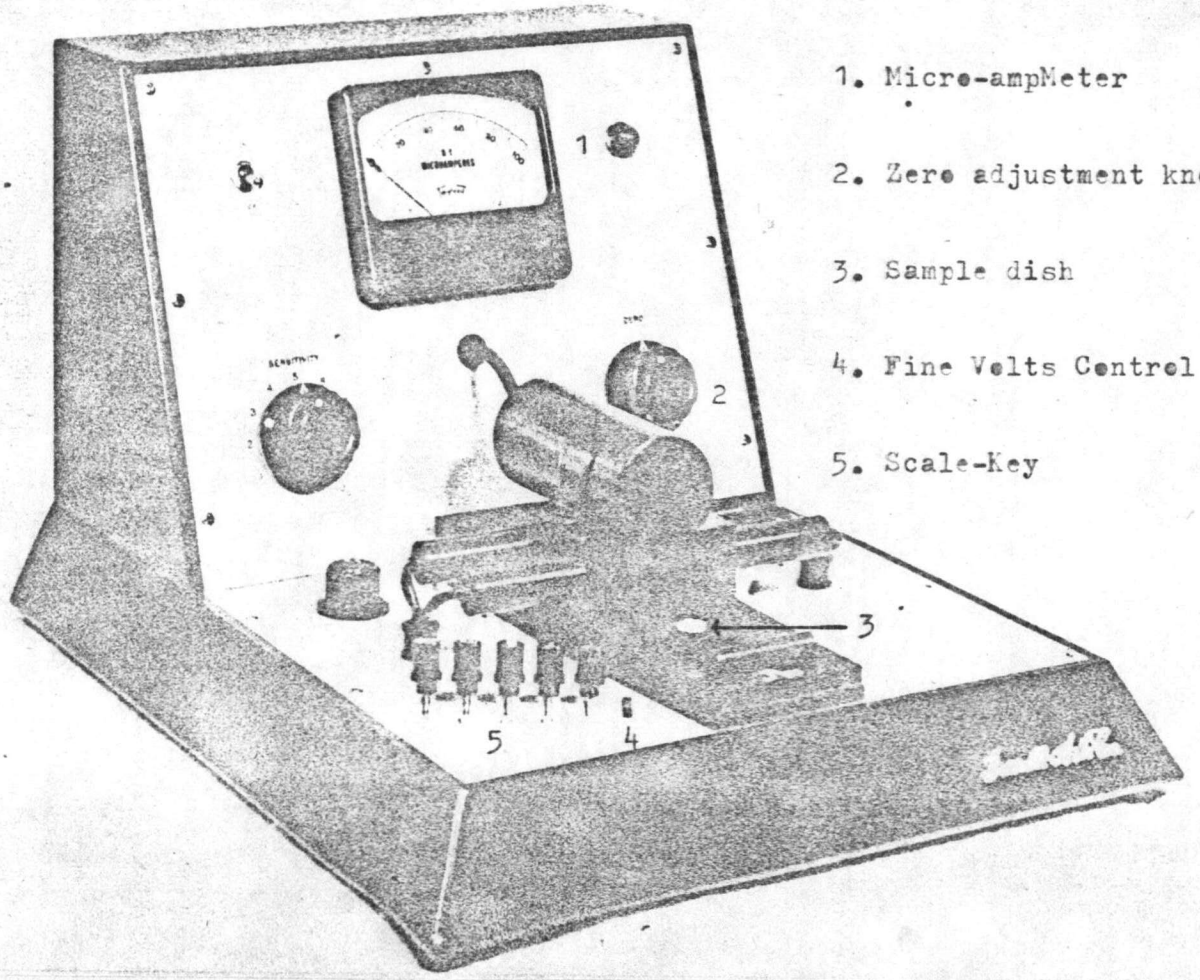
3.2.2.2 Fusion Burner : An electric muffle furnace with temperature control (from 0 to 1200°C) was used.

3.2.2.3 Fluorometer : A Galvanek-Morrison Fluorometer, Mark V (see Figure 3.15), from Jarrel Ash Co., Newtonville, Mass. was used. The G-M Fluorometer is a fluorometer for solids or liquids of varying depths. The fluorescent lamps are mounted within a half inch of the sample wheras the secondary filter and detector are above it.

Two 4 watt, FT5, Sylvania black light, type 360, fluorescent lamps are used to provide ultraviolet light as light source. The schematic diagram of the set up of the fluorometer and the spectral energy distribution of the lamps are shown in Figure 3.10 and Figure 3.12

3.2.3 Fluorometric Determination of Uranium

3.2.3.1 Extraction 2 cm^3 of the sample (or standard) solution was pipetted into a 50 cm^3 extraction glass bottle which contained 15 cm^3 saturated aluminium nitrate



1. Micro-ampMeter
2. Zero adjustment knob
3. Sample dish
4. Fine Volts Control
5. Scale-Key

Figure 3.10 Galvanek-Morrison Fluorometer, MARK V, Jarrell-Ash Company.

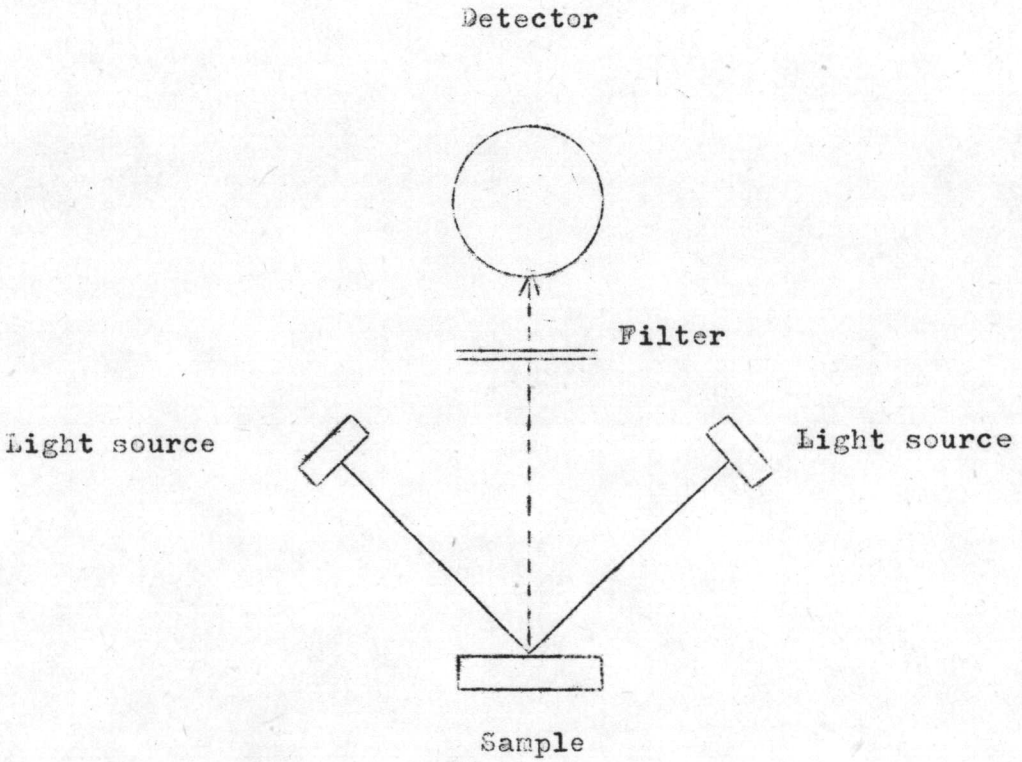
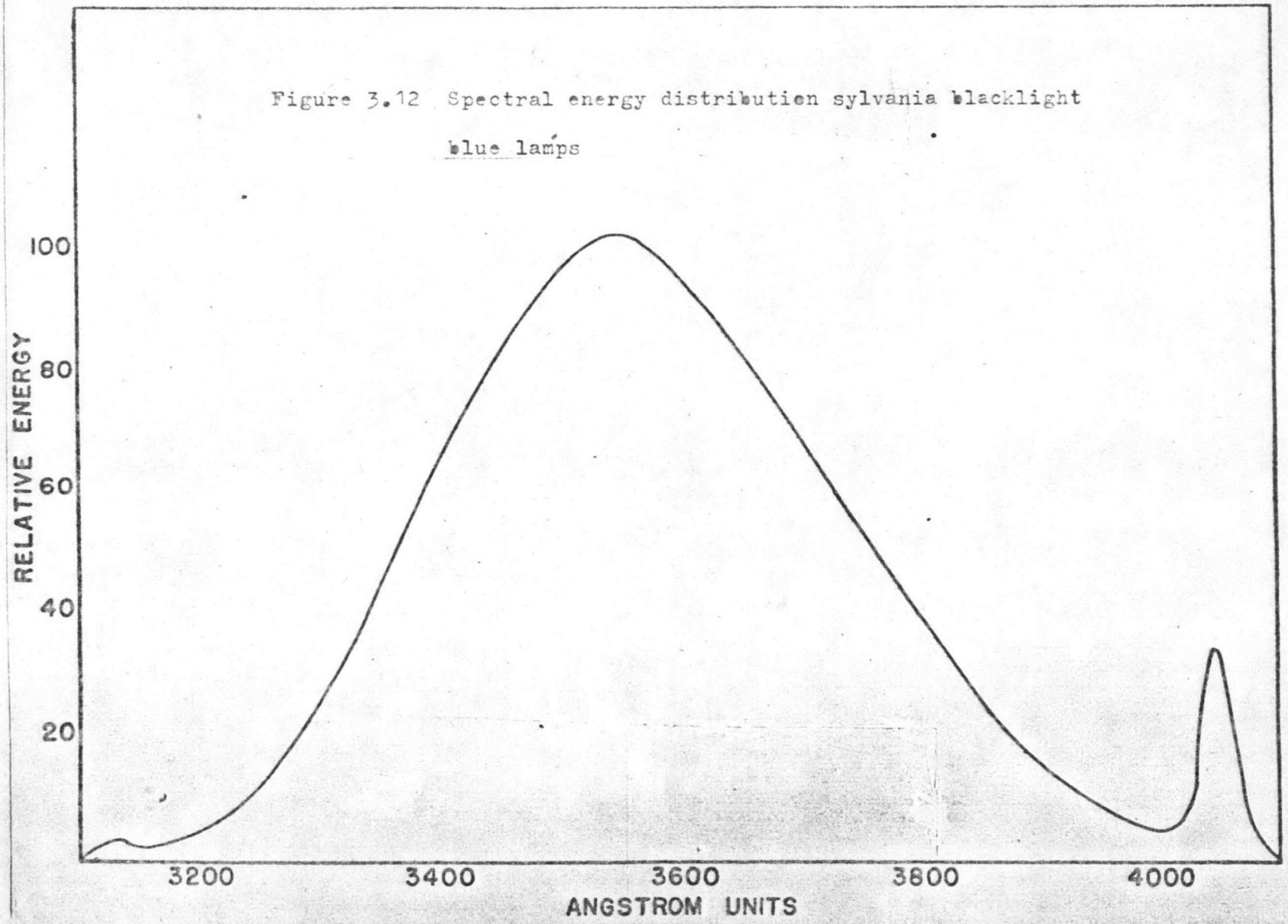


Figure 3.11 Schematic diagram of a fluorometric measurement for solids sample

Figure 3.12 Spectral energy distribution sylvania blacklight blue lamps



solution and the mixture was mixed thoroughly. Exactly 10 cm^3 ethyl acetate was added as extraction solvent. The bottle was closed and shaken on an automatic shaker for 10 minutes. After phase-separation, 0.2 cm^3 of the ethyl acetate layer was pipetted into a platinum dish and the solvent was allowed to dry under an Infrared lamp.

At the time of experiment, only 12 platinum dishes were available. Among these, 4 had to be reserved for a standard solution, 2 for blanks, 1 for instrument-adjustment, so that only 5 samples could be analysed per batch.

A pellet of the flux mixture was placed on each dish which contained the organic extract residue and the dishes were allowed to fuse in an electrical muffle furnace for 10 min. The dishes were placed on an iron tray. The temperature of the muffle was preheated to 700°C. The tray was shaken from time to time to dissolve and uniformly distribute the solid residue in the fusion dishes. The dishes were allowed to cool in a desiccator for at least 15 min. before subjected to fluorometric reading. The simplified flow diagram is shown in Figure 3.13

From trial experiments it was observed that the fluorescence intensity of the button (fused flux pellet) increases with the delay time at the first 15 min. and remains constant afterwards for about an hour.

3.2.3.2 Preconcentration technique

For the analysis of very low uranium concentration, preconcentration was performed prior to solvent extraction.

250 Cm^3 water was transfered into a 600 cm^3 beaker and 2 cm^3 15 M HNO_3 and 2 cm^3 72 % $HClO_4$ were added. The beaker was placed on a hot plate and the solution was evaporated almost to dryness. 25 Cm^3 of the salting solution was added and the solution was transfered to a 50 cm^3 separating funnel after which 5 cm^3 ethyl acetate was added. The mixture was shaken for 10 minutes, and the phases were allowed to separate. The aqueous phase was discarded. An aliquot of 0.2 cm^3 of the organic phase was pipetted into a platinum dish and the solvent was allowed to dry under an Infrared lamp.

3.2.3.3 Measurement of Fluorescence

Instrument Adjustment The instrument is turned on to warm for one hour before use. When the instrument is on but not in actual use, it is advisable to have the sample slide pushed to the rear stop so that no fluorescence is produced from the empty aluminium holder. This avoids a fatigue effect in the phototube.

A suitable standard (usually 1.0 $\mu g/cm^3$ uranium on a 0.3 gram flux mixture) is inserted into the dual-flux sample dish and the slide is pushed into the reading position. Now the standard is under the Ultraviolet light. The "Sensitivity"

control is increased while depressing the 0.1 scale key until the meter reads at mid-scale. The meter is set to read full-scale or 100 by adjusting the "Fine Volts" control. The sample slide is pulled out to the loading position and the "Zero" adjusting knob is rotated until the meter reads zero. The voltage and zero adjustments are repeated alternatively until the readings are constant this should be done at least three times. The instrument is now ready for unknown samples. When the sample slide is pushed in, the lowest sensitivity scale is automatically switched in. It is advisable to start the scale keys from the highest value by going from right to left. This is to prevent the meter from being damaged by a high concentration sample.

Calculations For each set of 12 buttons, the uranium content in the samples can be calculated by comparing their fluorometric reading with that of the known standard uranium solution. In order to obtain accurate results, four buttons were prepared from the standard solution and the readings were averaged. The uranium content of the samples was calculated according to the following relation :

$$\mu g/dm^3 \text{ of U in sample} = \mu g/dm^3 \text{ of U in standard} \times \frac{\text{sample reading - blank reading}}{\text{standard reading - blank reading}}$$

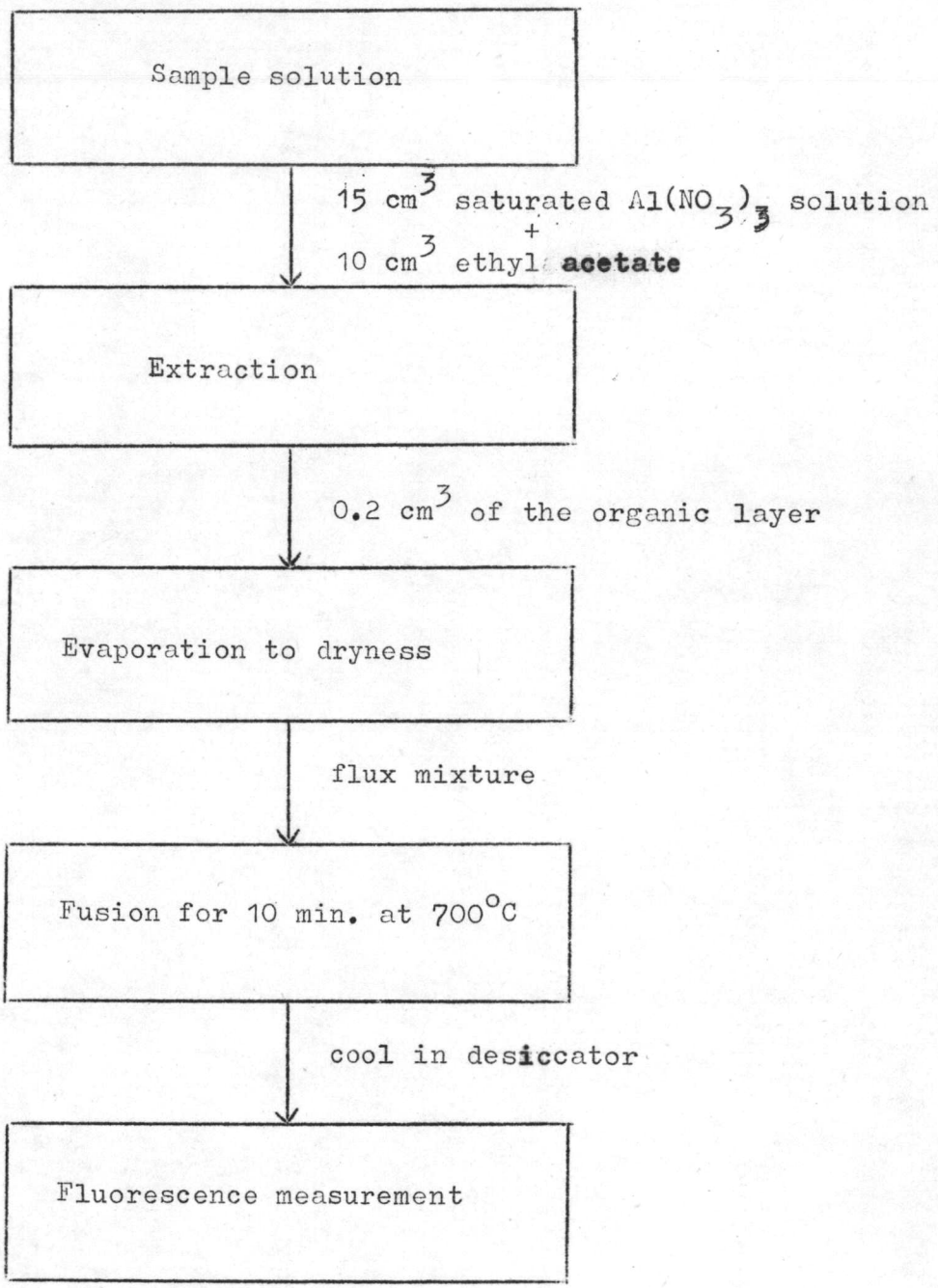


Figure 3.13 Simplified flow diagram for the determination of uranium by Fluorometry.

3.2.4 Effect of amounts of Flux Mixture

The effect of amount of flux mixture was studied on two different uranium concentrations, i.e. 50 $\mu g/dm^3$ and 10 $\mu g/cm^3$. Experiments were performed in the same manner as described under section 3.2.3.1. The amount of the flux mixture was varied between 0.02 and 0.40 g. The amount of the flux mixture versus the value of fluorometric reading in microamp (μA) was plotted.

3.2.5 Relation between fluorometric reading and uranium concentration

The linearity of the function between the fluorometric reading and the uranium concentration was tested. Uranium was extracted from standard solutions as described in section 3.2.3.1. The amount of the flux mixture was fixed at 0.3 g while the concentration of the uranium solution was varied between 10 $\mu g/dm^3$ to 1 $\mu g/cm^3$.

3.2.6 Extraction Yield of Uranium by Ethyl acetate

The extraction yield of uranium by ethyl acetate was investigated. The extraction procedure described in section 3.2.3.1 was applied. The amount of the flux mixture was fixed at 0.3 g and the uranium concentration was 1000 $\mu g/dm^3$. The extraction yield was calculated by comparing the fluorometric reading of 0.2 cm^3 of the extracted organic solution and that of a 0.2 cm^3 1000 $\mu g/dm^3$ standard uranium solution.

The recovery yield (%) of a single stage extraction by ethyl acetate can be calculated by the following equation :

$$\mu g/dm^3 \text{ of U in unknown} = \mu g/dm^3 \text{ of U in standard} \times \frac{\text{av. unknown reading - blank}}{\text{av. standard reading - blank}},$$

$$\text{or yield (\%)} = \frac{1000}{2} \frac{(FR-B)_1}{(FR-B)_2}$$

where

$(FR-B)_1$ = average fluorometric reading of unknown

$(FR-B)_2$ = average fluorometric reading of standard

3.2.7 Limit of Detection

The detection limit for the determination of uranium in water under the present working conditions of uranium was studied. Standard uranium solutions of various concent - rations were subjected to extraction in the same manner as described in section 3.2.3.1. The amount of the flux mixture was fixed at 0.3 g. while the concentration of the standard uranium solutions was varied from 0.05 to 20 $\mu gU/dm^3$. The concentration of uranium versus the value of fluorometric reading was plotted. The concentration at which the line begins to deviate from linearity was considered as the minimum detectable concentration.