CHAPTER IV

RESULTS

4.1 Neutron Activation Analysis

4.1.1 Low-Energy Spectra of Uranium

The low-energy gamma spectra (0-100 keV) of a 10 $\mu g/dm^3$ standard uranium solution and a water sample after the separation process are shown in Figure 4.1 and 4.2 respectively in comparison with the spectrum of the same water sample before the separation process was commenced in Figure 4.3. It is obvious that if the separation process was omitted, the background of unwanted comtaminants would overwhelm the signal from uranium and it was impossible to analyse the uranium content accurately. The decay curve of the 74.5 keV peak from the separated sample is shown in Figure 4.4. The half-life from the decay curve was found to be 23.5 min which agrees well with the half-life of ^{239}U.

4.1.2 Effect of Amount of Resin on the Percentage Adsorption of Uranium

The results of this experiments are given in Table 4.1 and graphically shown in Figure 4.5

No significant difference in the adsorption yield was observed when the amount of resin is larger than 1.0 g.

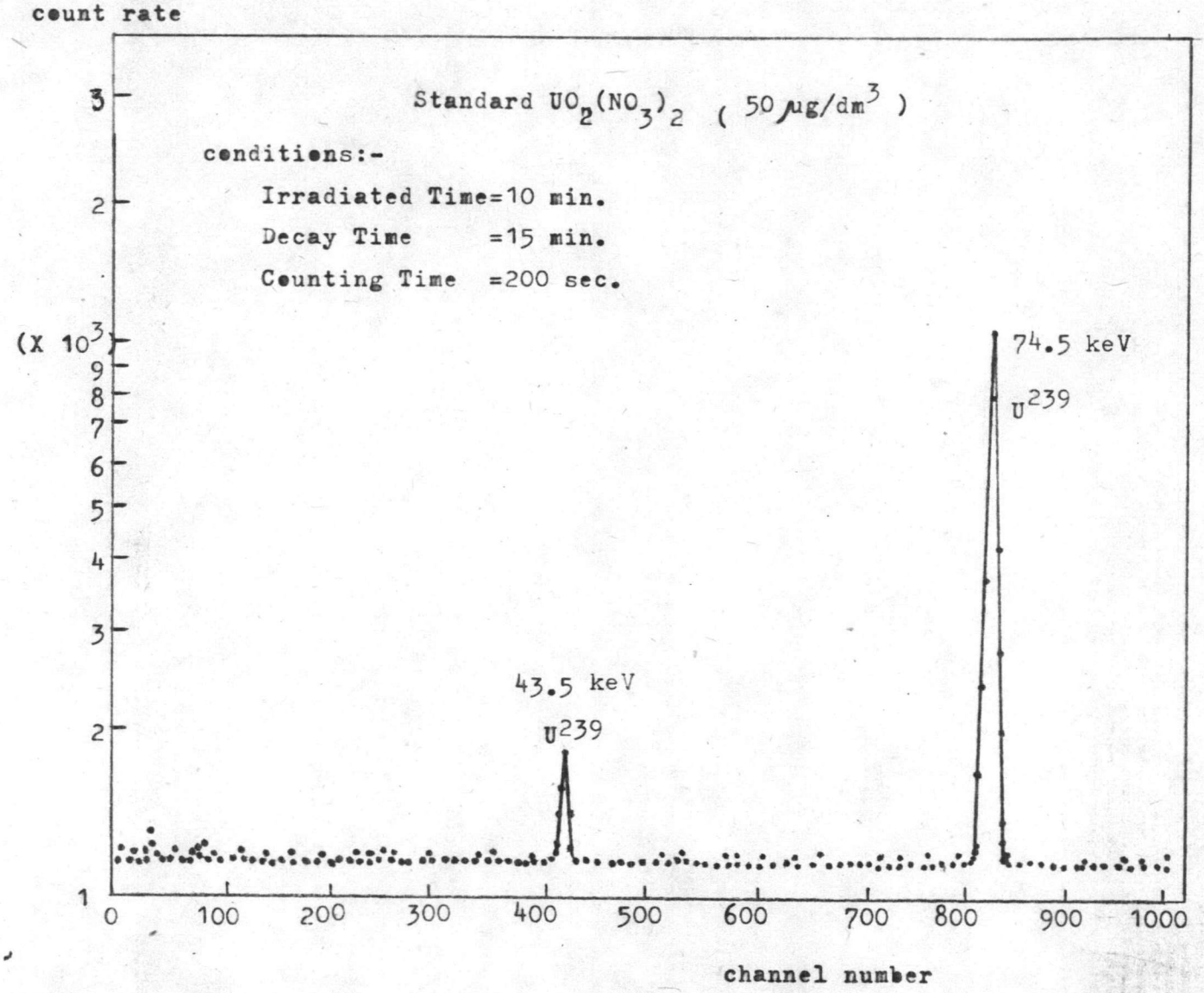


Figure 4.1 Gamma spectrum of the standard uranium solution after the separation process

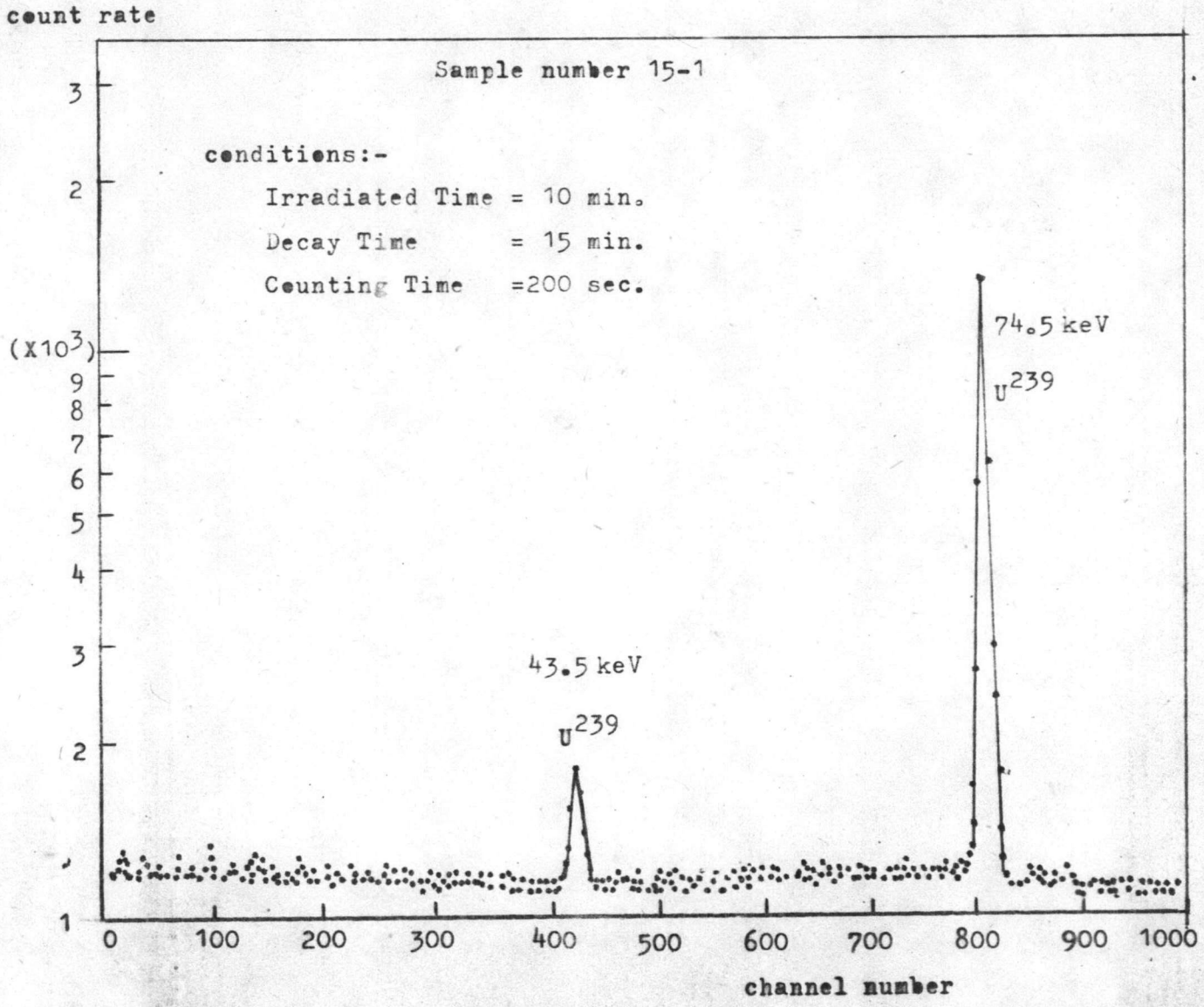


Figure 4.2 Gamma spectrum of the sample after the separation process

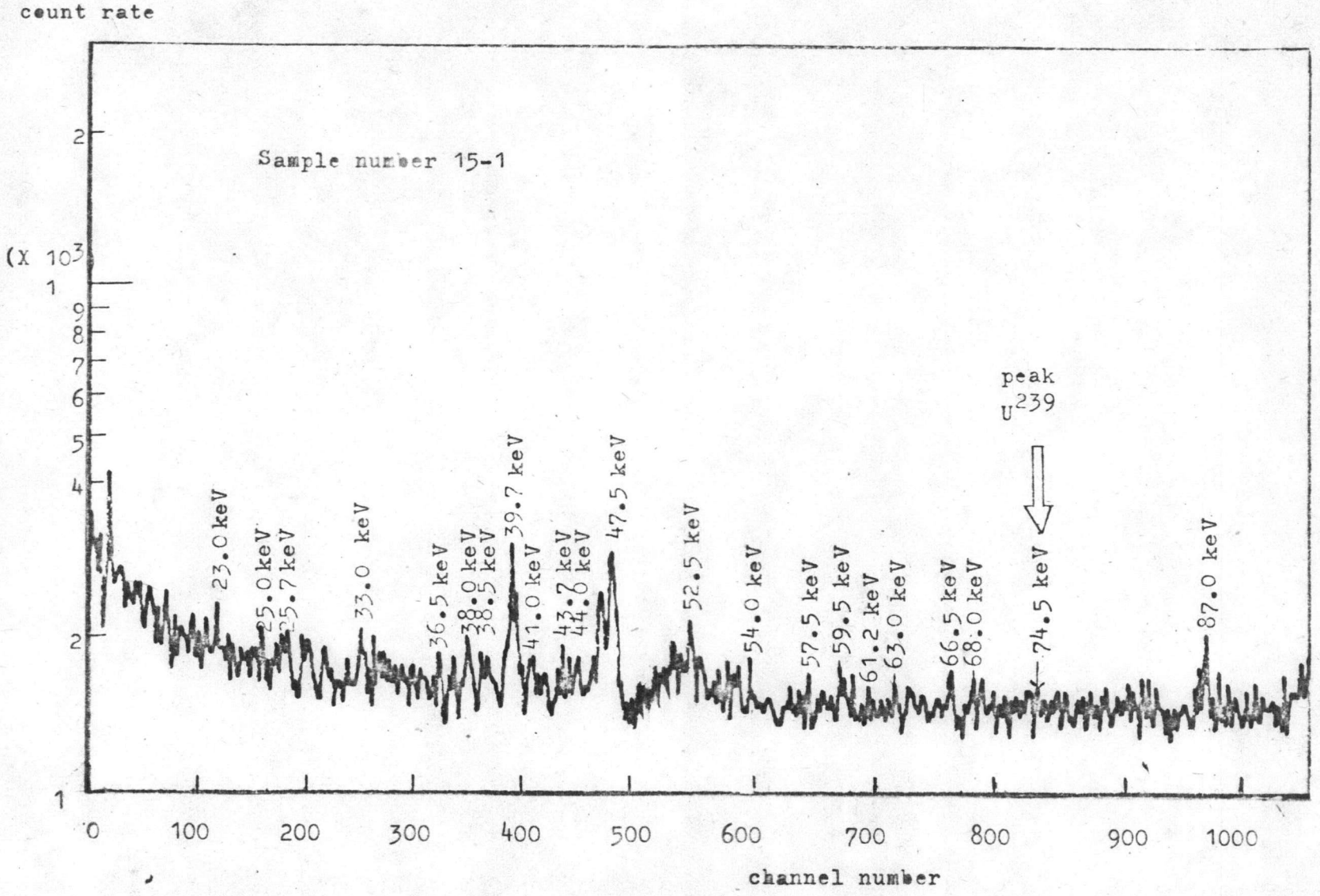


Figure 4.3 Gamma spectrum of the sample before the separation process

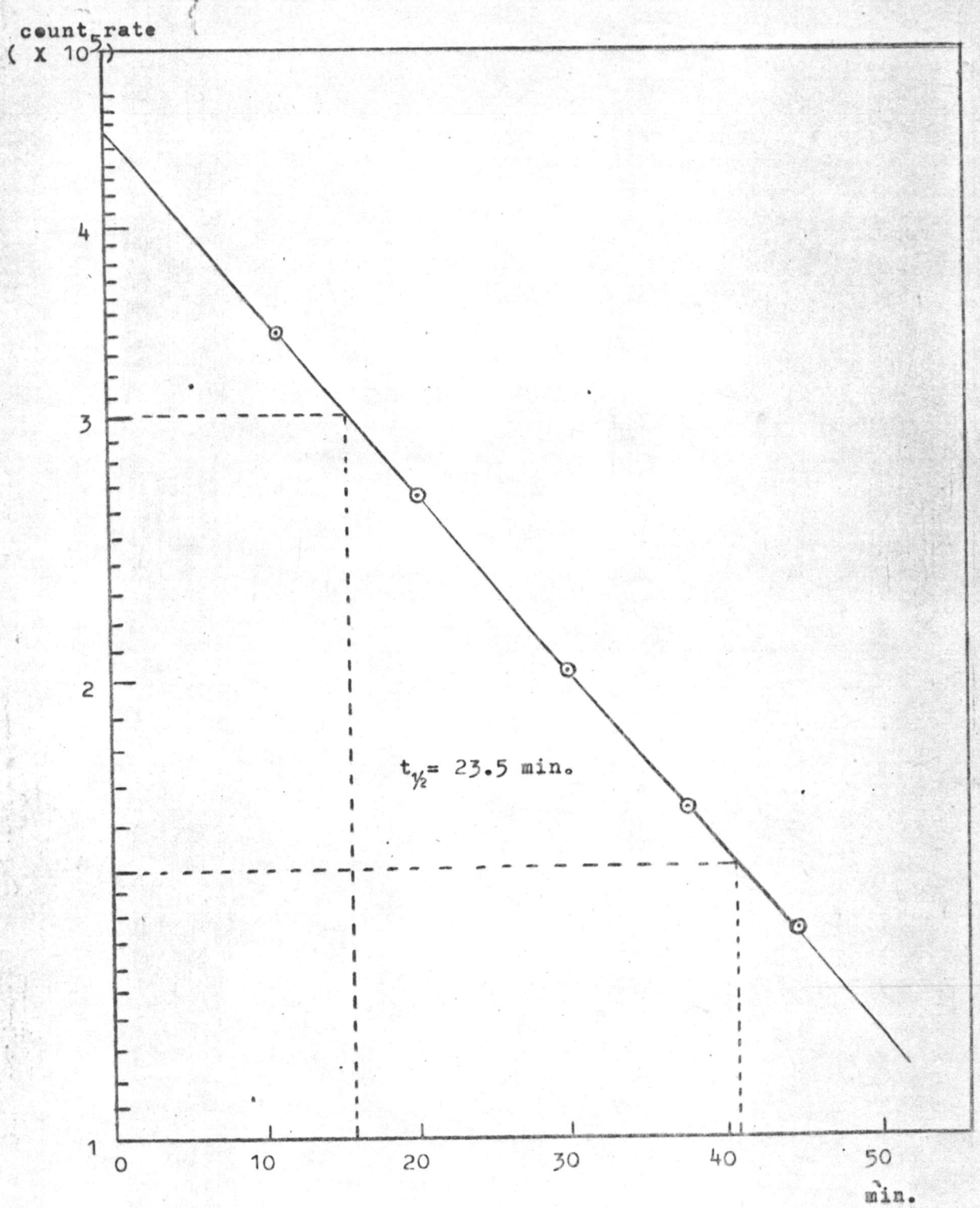


Figure 4.4 Decay curve of the 74.5 keV peak from the separated sample

Since the concentration of uranium in the samples of interest is generally in trace-level, 1.0 g of resin is considered sufficient.

Table 4.1 Effect of amounts of resin on the adsorption of uranium.

conditions : Weight of resin 0.5-3.0 g

Standard solution 100 $\mu g/cm^3$

Irradiated time 10 min

Counting time 200 sec.

Activity of 50 cm^3 100 $\mu g/dm^3$ standard solution

$$2402 \frac{\text{counts}}{200 \text{ sec.}}$$

Number of Test	Resin Weight (g)	Activities in effluent (counts/200sec)	Percentage adsorption
1	0.5	5240	99.78
2	0.8	376	99.98
3	1.0	26	99.99
4	1.2	-	100
5	1.5	-	100
6	2.0	-	100
7	2.5	-	100
8	3.0	-	100

4.1.3 Effect of Flow-Rate

The effect of flow-rate on the adsorption of uranium on resin is shown in Table 4.2 and plotted in Figure 4.6

No significant difference in the adsorption yield was observed if the flow-rate was varied between 2 to 15 cm^3/min. In the present study, 10 cm^3/min was used.

Table 4.2 Effect of flow-rate on the adsorption of uranium on resin

conditions: Weight of resin 1.0 g

Standard solution 100 $\mu g/cm^3$

Irradiated time 10 min.

Counting time 200 sec.

Activity of 50 cm^3 100 $\mu g/dm^3$ standard solution

$$2731 \frac{\text{counts}}{200 \text{ sec.}}$$

Number of test	Flow-rate (cm^3/min)	Activities in effluent	Percentage adsorption
1	3.0	-	100.0
2	9.0	-	100.0
3	12.0	-	100.0
4	16.5	125	99.99
5	25.0	1556	99.94
6	30.0	4503	99.83

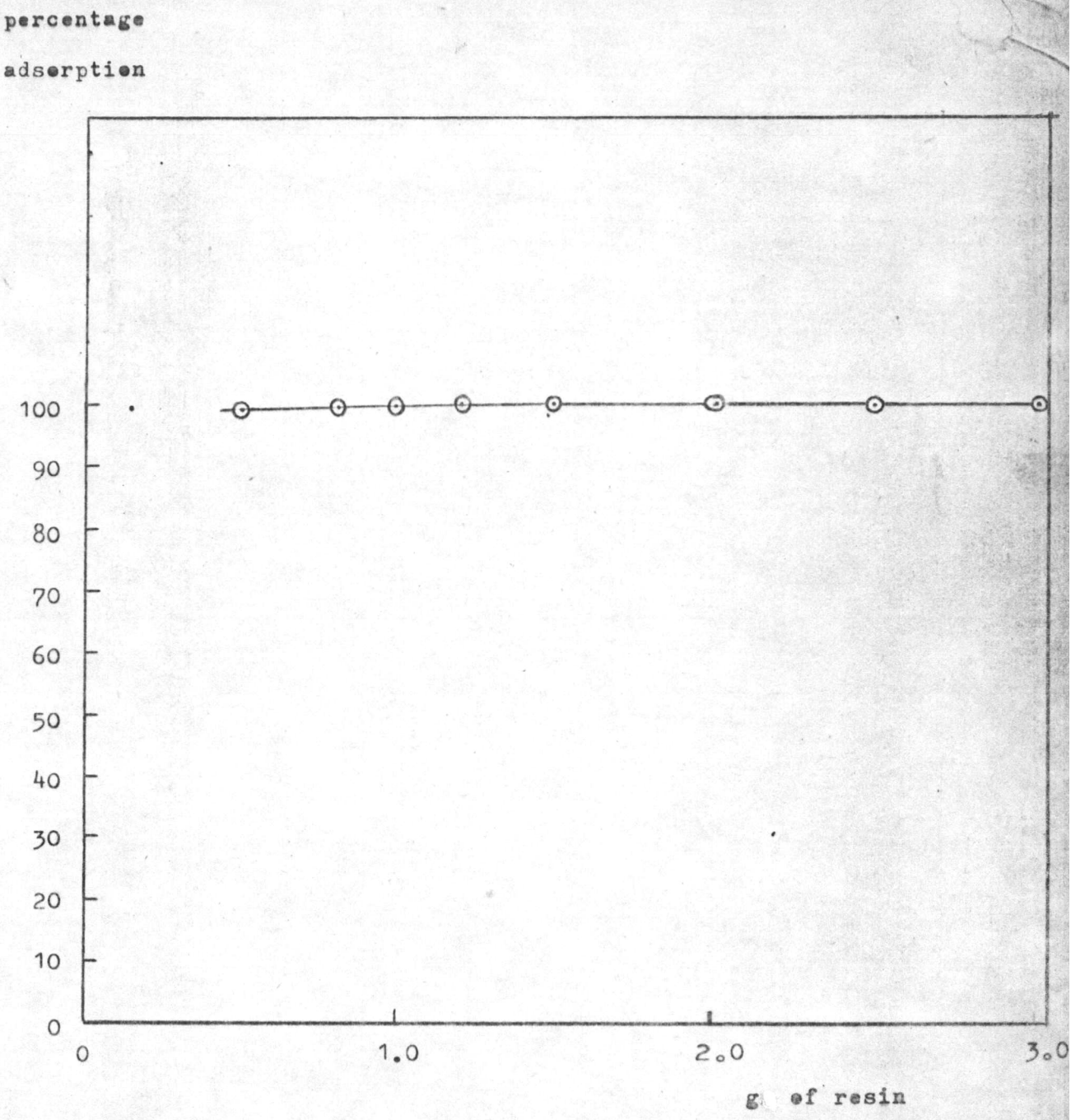


Figure 4.5 Effect of amounts of resin on the adsorption of uranium

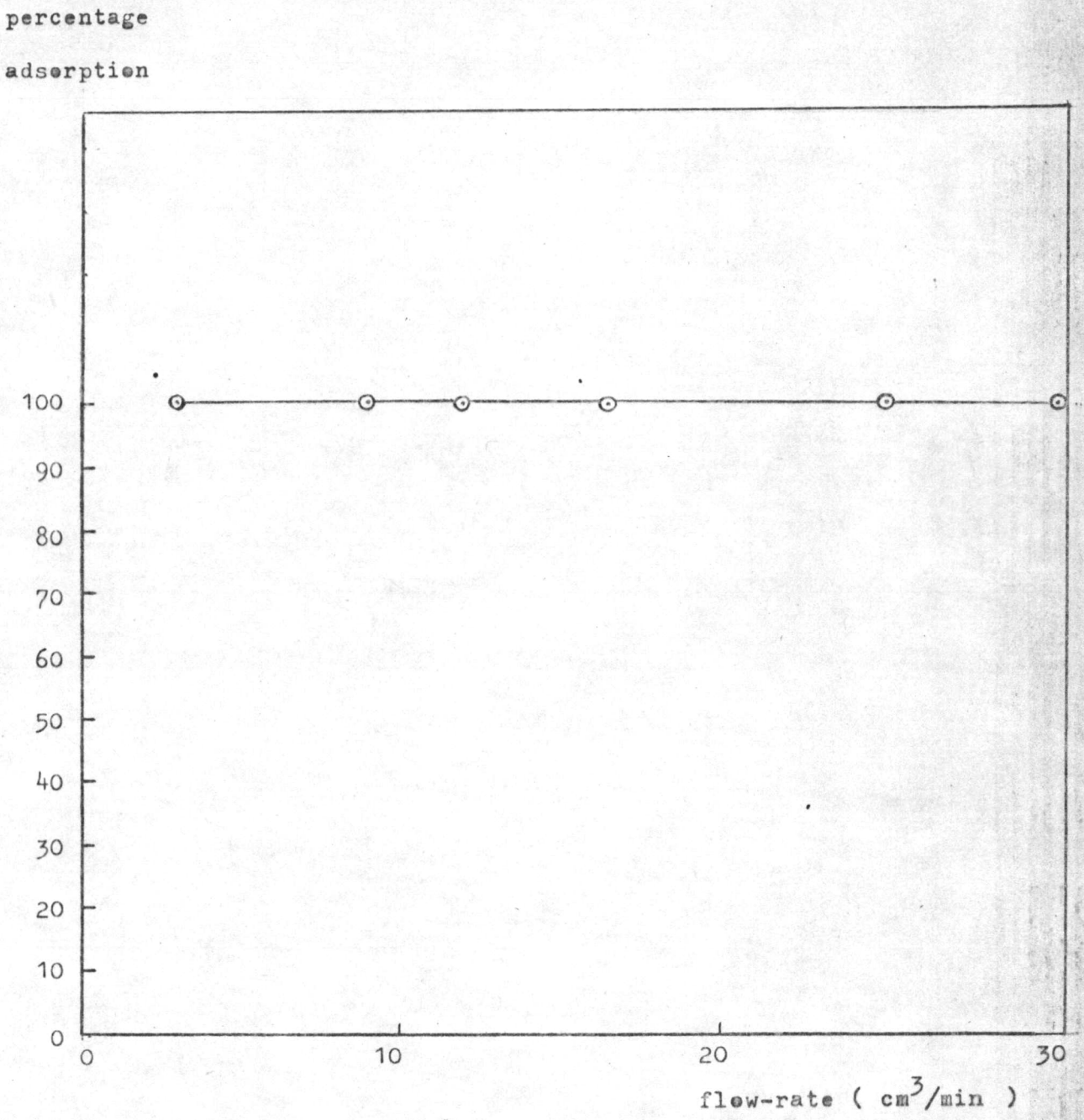


Figure 4.6 Effect of flow-rate on the adsorption of uranium

4.1.4 Limit of Detection

The relation between the concentration of U and the activity of the uranium peak after the separation procedure is given in Table 4.3

Table 4.3 Minimum determinable concentration of uranium

conditions : Weight of resin 1.0 g

Irradiated time 10 min.

Counting time 600 sec.

Number of test	concentration of uranium ($\mu g/dm^3$)	counts /600 sec.	
		counts	Background
1	0.05	27	2
2	0.10	37	3
3	0.50	79	5
4	1.0	132	6
5	3.0	232	10
6	5.0	310	20
7	8.0	639	50
8	10.0	1076	72

Since the activity increases linearly with increasing concentration, the concentration which begins to deviate from this general rule is considered as the limits of detection. From Figure 4.7 the minimum detectable concentration of uranium was 1.0 $\mu g/dm^3$.

The relation between the concentration of uranium and the activity of the uranium peak by non-destructive activation analysis are given in Table 4.4 and 4.5 and graphically in Figure 4.8, 4.9, 4.10 and 4.11

The limit of detection for destructive activation analysis and non-destructive activation analysis at different irradiated positions are compared in Table 4.6. It is obvious that separation process is necessary for the determination of trace analysis of uranium in water. As all elements which exist in the form of cation in dilute nitric acid medium are not removed by anion exchanger, the background in the stripped drill-hole water sample is considered to be similar to those of the matrix activities from general fresh water. Although the matrix activities are reduced by irradiation in the CA-2 position, the resonance neutron flux density in CA-2 is approximately much lower than the thermal neutron flux in the rotary specimen rack. An enrichment factor of 10^3-fold could be achieved by the present separation method. As the irradiation in CA-2 gives a much poorer detection limit, all samples were irradiated in the rotary specimen rack.

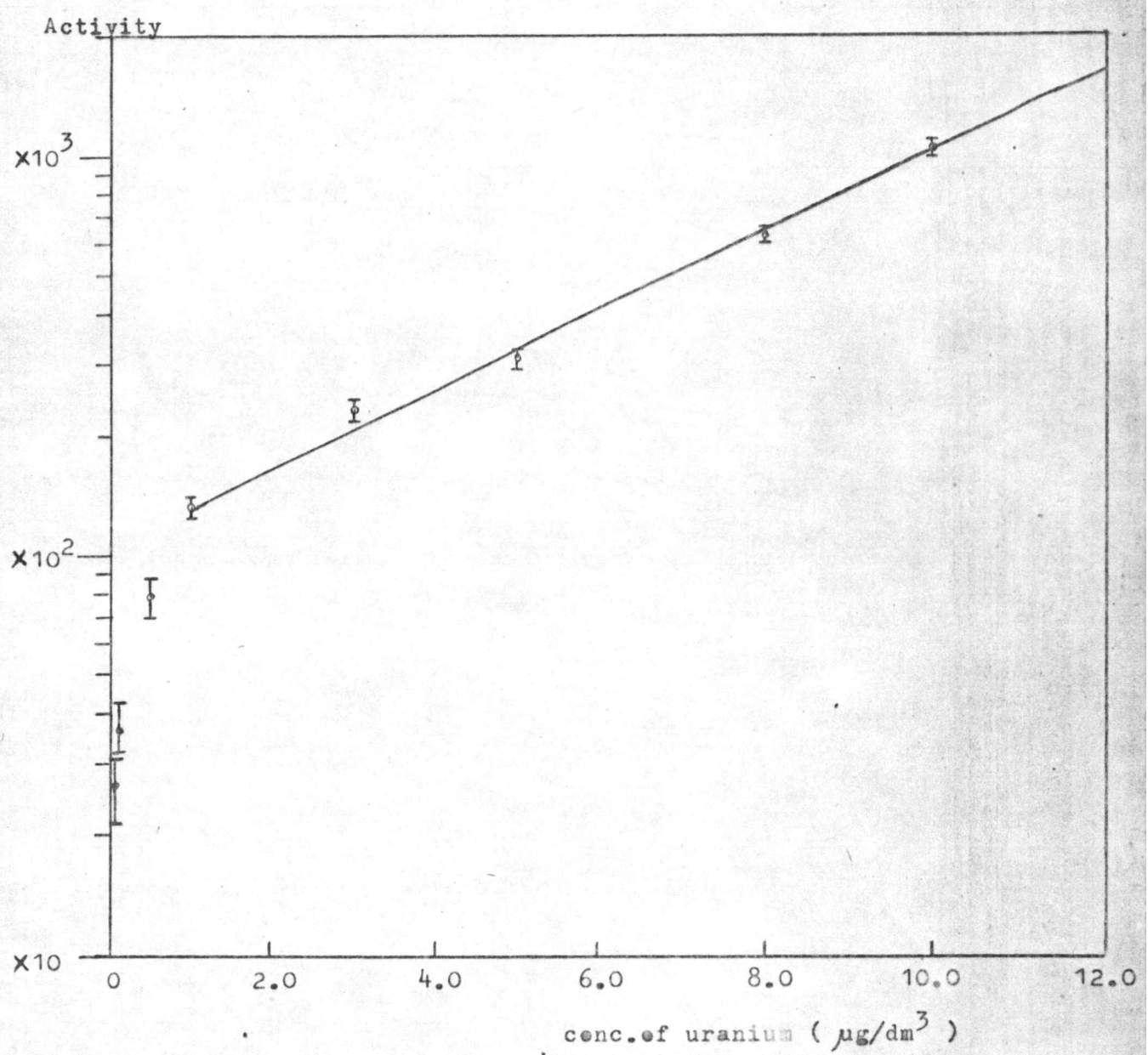


Figure 4.7 Relation between the concentration and the activity of uranium after the separation procedure

Table 4.4 Detection limit for the non-destructive neutron activation analysis of uranium in tri-distrilled water.

conditions :

	Rotary Specimen Rack	CA-2
Irradiation time (min)	10	20
Counting time (sec.)	200	200

conc. ($\mu g/dm^3$)	counts/200 sec		conc. ($\mu g/cm^3$)	counts/200 sec	
	Rotary Specimen Rack			CA-2	
	Peak	Bdg		Peak	Bdg
1	49	40	0.1	74	6
3	47	30	0.3	252	10
5	95	25	0.5	535	25
10	112	20	1.0	925	30
30	221	30	1.5	2311	40
50	480	30	3.0	2854	55
			5.0	4020	60
			7.0	5012	74

Table 4.5 Detection limit for the non-destructive neutron activation analysis of uranium in stripped drill-hole water.

conditions :

	Rotary Specimen Rack	CA-2
Irradiation time (min.)	10	20
Counting time (sec)	200	200

conc. ($\mu g/cm^3$)	counts/200 sec		conc. ($\mu g/cm^3$)	counts/200 sec	
	Rotary Specimen Rack			CA-2	
	Peak	Bdg		Peak	Bdg
0.1	205	230	1.0	31	10
0.3	365	250	3.0	103	10
0.5	541	245	5.0	153	10
1.0	790	235	8.0	205	10
3.0	1356	230	10.0	237	15
5.0	2218	275	14.0	360	15
7.0	3759	275	20.0	678	20

Table 4.6 Comparison of the limit of detection of uranium in water at different irradiated position

Irradiated position	Destructive Determination ($\mu g/cm^3$)	Non-destructive Determination ($\mu g/cm^3$)	
		in Tridistilled water	in Stripped drill-hole water.
Rotary Specimen Rack	0.001	0.005	1.0
CA-2	-	1.5	3.0

4.1.5 Results of the Quantitative Analysis

The results of the analysis of 35 samples are given in Table 4.7. The results are from two separate determinations. In each determination, two samples and one standard uranium solution were irradiated at the same time in the Rotary Specimen Rack. The uncertainties of the method (high value of standard deviation) is mainly caused by the errors involved in the counting statistics on account of the low gamma counting rate.

The fresh water sample from Phuvieng was collected from a stream that flows through the uranium outcrop. The day the sample was collected was a day after heavy raining.

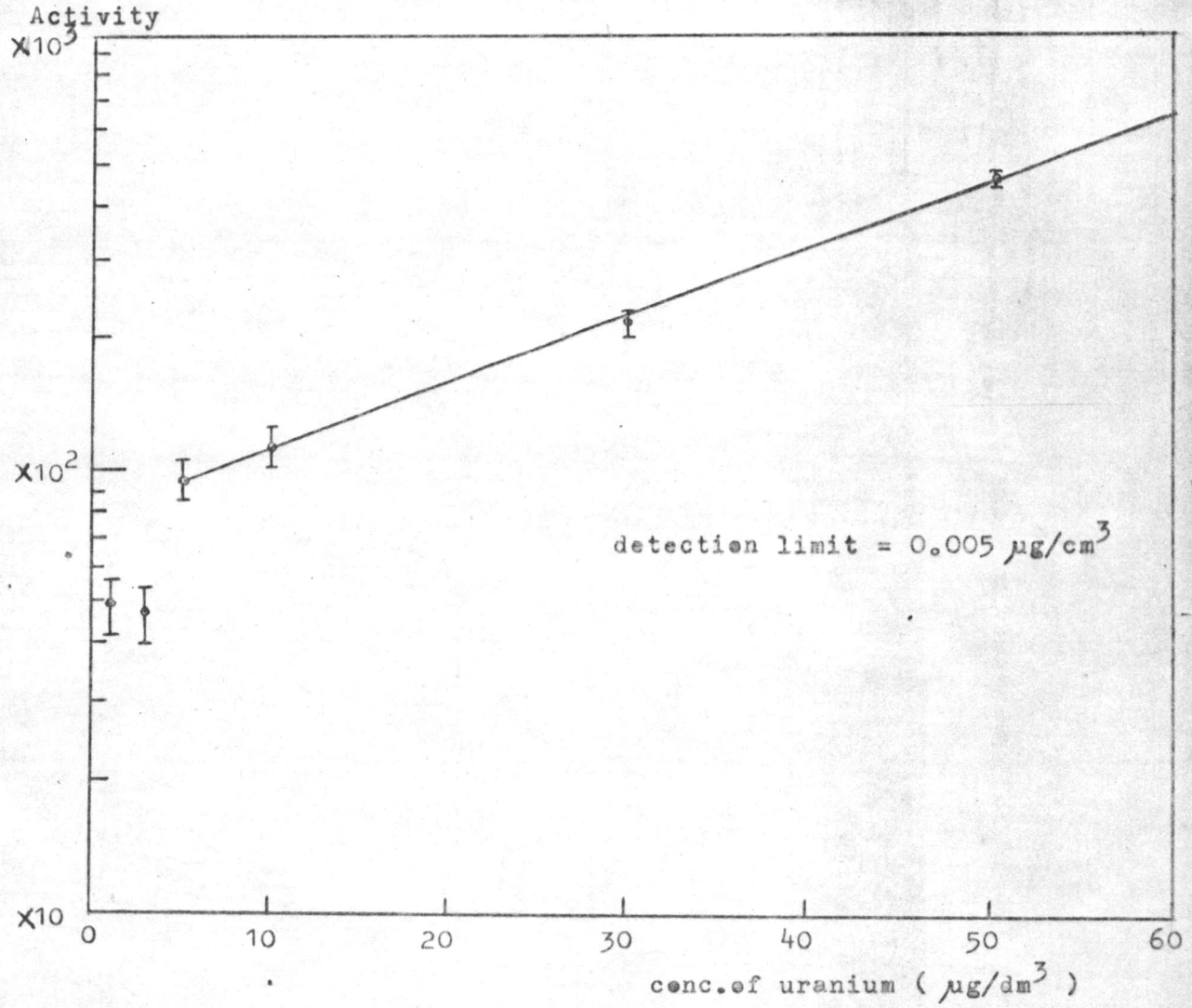


Figure 4.8 Uranium in tri-distilled water by the non-destructive activation analysis at Retary Specimen Rack position

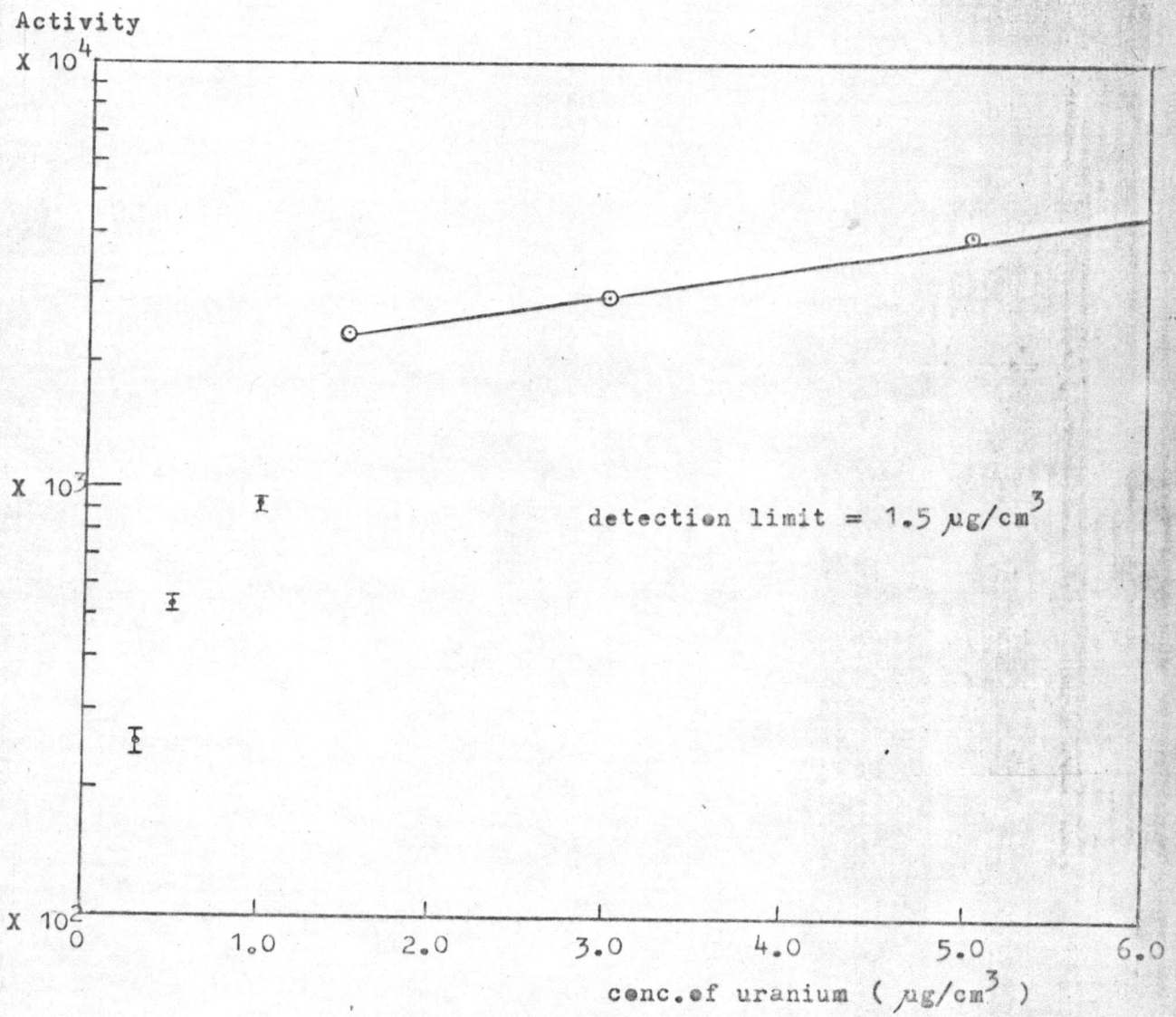


Figure 4.9 Uranium in tri-distilled water by the non-destructive activation analysis at CA-2 position

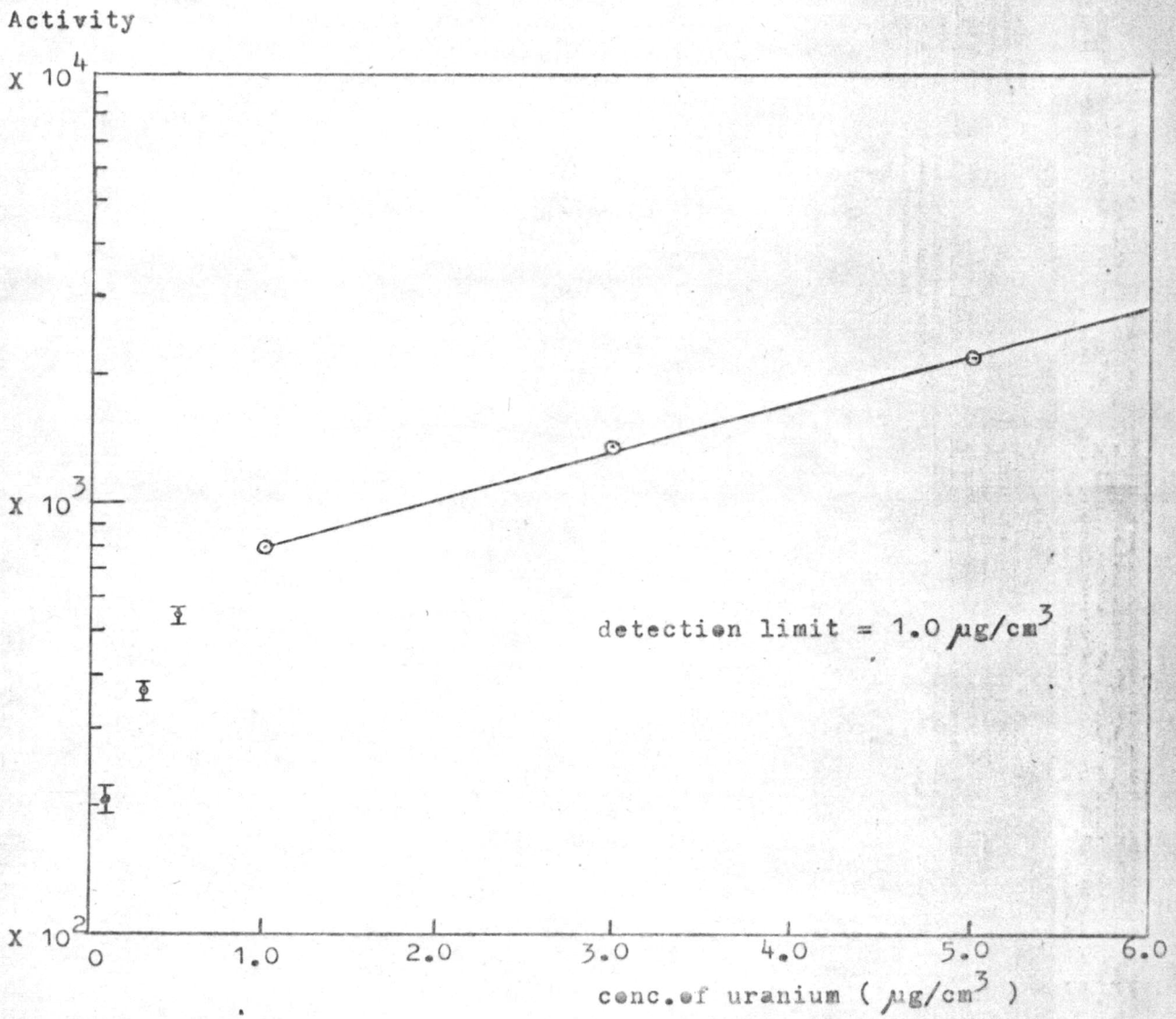


Figure 4.10 Uranium in stripped drill-hole water by non-destructive activation analysis at Retary Specimen Rack position

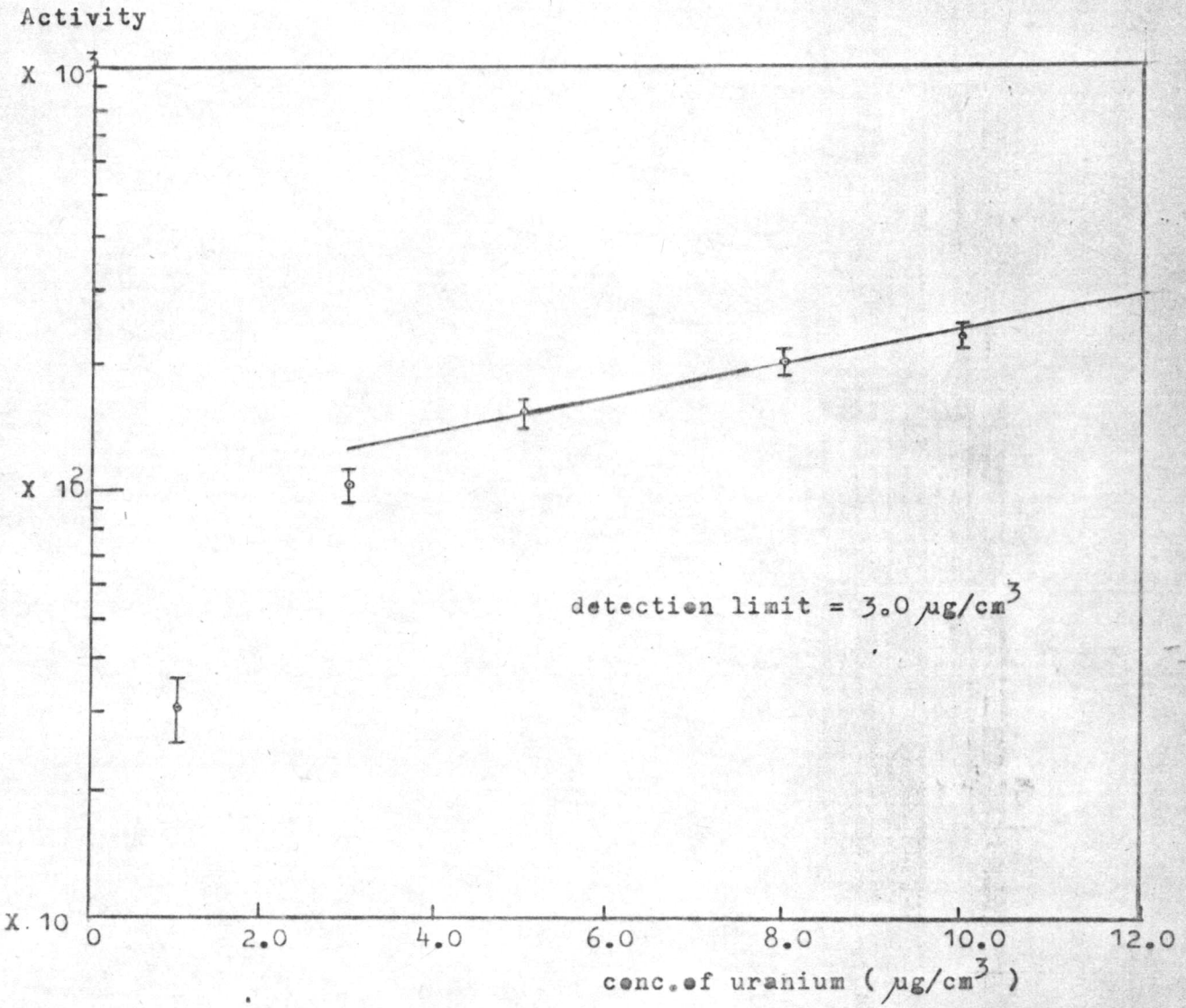


Figure 4.11 Uranium in stripped drill-hole water by non-destructive activation analysis at CA-2 position

It is noteworthy that the uranium content in fresh water from various rivers was under the detection limit. A sample of sea water was analyzed. It is found that the separation method was not sufficient to remove all the salt from the sample so that the gamma peak of uranium was overwhelmed by the high counting rate of the background.

Table 4.7 Results of the quantitative analysis of uranium in water samples by NAA,

Samples	Uranium Content ($\mu g/dm^3$)				average ($\mu g/dm^3$)
	1	2	3	4	
DDH1 NO.1	27.33±2.04	29.06±2.13	26.52±2.01	27.83±2.10	27.69±2.07
DDH2 NO.2	126.46±7.01	125.83±6.92	129.17±7.19	123.13±6.44	126.15±6.89
DDH3 NO.3	20.58±1.41	22.31±1.95	21.31±1.91	21.58±2.01	21.45±1.82
DDH4 NO.4	11.28±1.77	14.43±1.06	13.56±1.41	17.25±2.11	14.12±1.52
DDH5 NO.5	18.97±1.65	20.57±1.84	19.48±1.34	20.23±1.73	19.81±1.64
DDH8 NO.6	262.18±12.44	267.09±15.01	257.26±14.92	260.89±11.75	261.86±13.53
DDH9 NO.7-1	32.22±2.10	34.17±3.05	33.49±3.52	33.14±2.85	33.20±2.88
DDH9 No.7-2	23.44±2.03	26.46±2.54	24.57±2.30	26.65±1.97	25.28±2.21
DDH10 NO.8-1	5.06±0.94	4.17±0.61	4.73±0.69	4.50±0.68	4.61±0.73
DDH10 NO.8-2	7.30±1.05	8.62±0.73	8.18±0.94	7.74±0.88	7.96±0.90
DDH11 NO.9-1	18.95±2.14	20.11±1.42	19.15±1.68	19.22±1.60	19.36±1.71
DDH11 NO.9-2	23.81±2.05	20.93±2.51	22.62±2.07	21.13±1.93	22.12±2.14

continue :

samples	1	2	3	4	average
DDH12 NO.10	7.0±1.17	7.98±1.03	7.69±0.86	7.42±0.90	7.52±0.99
DDH13 NO.11	37.36±3.27	38.87±3.42	32.26±3.12	43.77±2.71	38.07±3.13
DDH14 NO.12-1	21.37±2.96	20.54±3.72	20.74±3.18	21.16±3.22	20.95±3.27
DDH14 NO.12-2	221.39±11.42	226.09±11.91	236.13±9.98	222.42±10.01	224.26±10.83
DDH17 NO.13-1	44.95±2.16	41.73±3.31	42.81±2.55	39.59±2.98	42.27±2.75
DDH17 NO.13-2	43.96±3.63	43.07±4.25	45.16±4.08	42.98±3.92	43.79±3.97
DDH19 NO.14	27.99±2.48	26.65±2.92	28.82±2.27	27.27±2.65	27.69±2.58
DDH20 NO.15-1	121.68±7.14	133.19±6.88	128.73±7.01	127.18±6.89	127.69±6.98
DDH20 NO.15-2	73.11±4.26	74.67±3.87	74.12±4.21	72.36±4.50	73.57±4.21
DDH21 NO.16-1	601.02±28.96	592.36±27.63	590.32±29.11	593.69±28.02	594.36±28.43
DDH21 NO.16-2	233.43±20.89	238.46±20.49	236.09±19.34	231.65±21.12	234.91±20.46

continue :

samples	1	2	3	4	average
DDH22 NO.17-1	6.59±1.74	6.41±1.92	6.77±2.38	6.22±1.04	6.50±1.77
DDH22 NO.17-2	4.39±0.75	4.25±0.89	4.28±0.91	4.36±0.73	4.32±0.82
DDH24 NO.19-1	384.09±16.18	378.22±11.75	372.35±14.92	382.89±15.39	379.39±14.56
DDH24 NO.19-2	477.82±20.10	450.69±16.51	442.90±16.05	443.28±16.66	453.67±17.33
DDH30 NO.21	9.16±1.12	8.53±1.40	8.97±1.53	8.89±0.99	8.89±1.26
Phuvieng, Khonkhan	1.61±0.17	1.54±0.14	1.57±0.15	1.63±0.21	1.59±0.17
Bangpakong, Prachinburi	N	N	N	N	N
Chaophaya, Nondthaburi	N	N	N	N	N
Bangphra, Cholburi	N	N	N	N	N
Klongprapha, Prachachoen	N	N	N	N	N

continue :

samples	1	2	3	4	average
Kwae, Khanchanaburi	N	N	N	N	N
Sea Water, Angsila	M	M	M	M	M

N = undetectable

M = very high count rate from background

4.2 Fluorometry

4.2.1 Effect of the Amounts of Flux Mixture at very low Uranium Concentration (part per billion region)

The fluorometric readings of 50 $\mu g/dm^3$ uranium after extraction together with blanks at different weight of flux mixture are listed in Table 4.8 and graphically in Figure 4.12

Table 4.8 Fluorometric readings of 50 $\mu g/dm^3$ uranium at different amount of flux mixture

weight of flux (gm)	Fluorometric Reading (μA)					
	blank (a)	50 $\mu g/dm^3$ uranium				
		1	2	3	average (b)	average-blank (c)
0.02	0.720	1.0	0.95	1.05	1.00	0.280
0.04	0.725	1.1	1.1	1.0	1.07	0.345
0.06	0.730	1.2	1.2	1.1	1.17	0.440
0.08	0.735	1.25	1.3	1.2	1.25	0.515
0.10	0.740	1.3	1.4	1.3	1.33	0.590
0.14	0.755	1.4	1.6	1.4	1.47	0.715
0.18	0.765	1.5	1.75	1.55	1.60	0.835
0.22	0.770	1.6	1.85	1.7	1.72	0.950
0.26	0.780	1.65	1.9	1.8	1.78	0.995
0.30	0.785	1.7	1.93	1.85	1.83	1.045
0.40	0.80	1.8	1.95	1.90	1.88	1.080

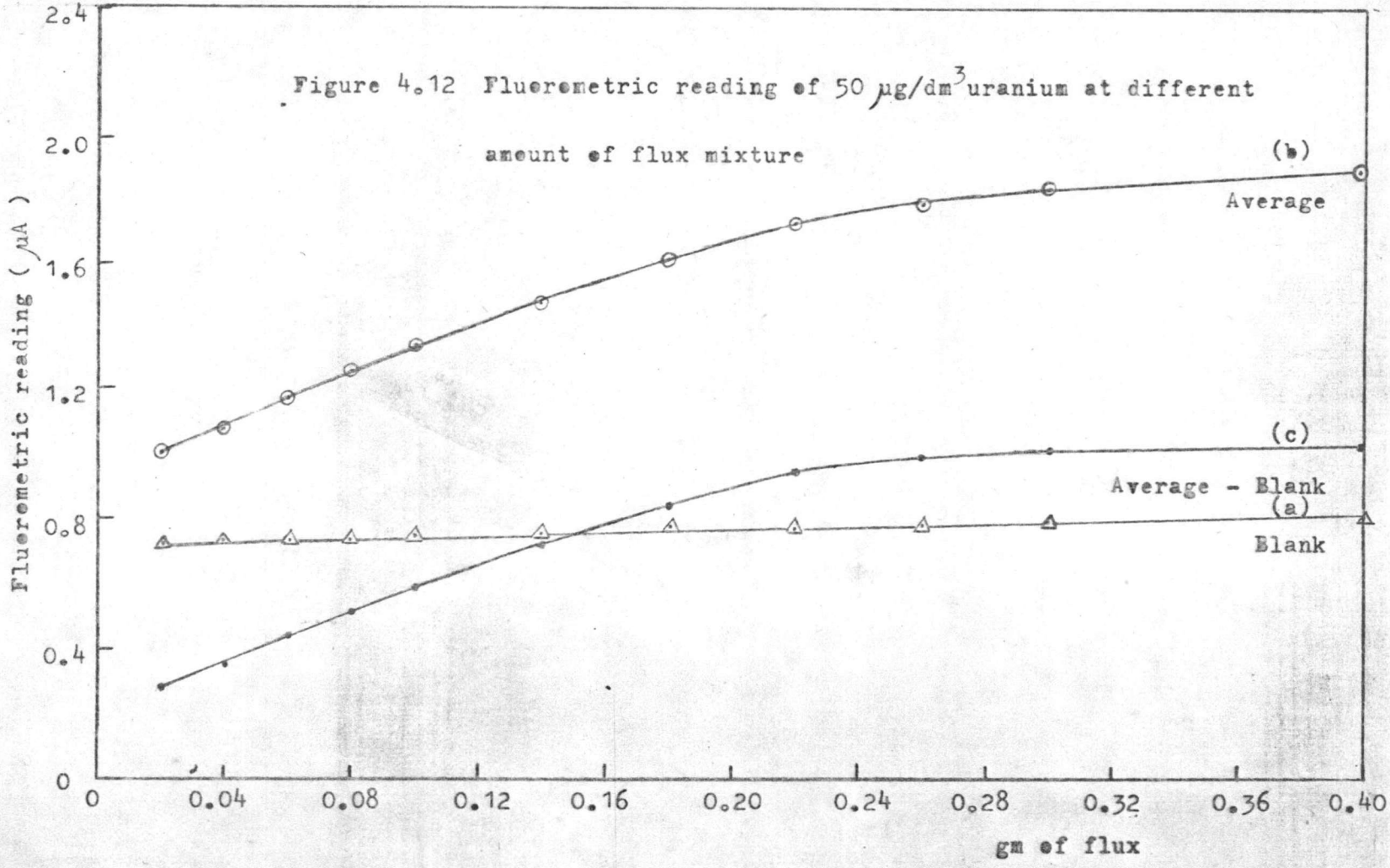


Figure 4.12 Fluorometric reading of 50 µg/dm³ uranium at different amount of flux mixture
Fluorometric reading (µA)
2.4
2.0
1.6
1.2
0.8
0.4
0
0
0.04
0.08
0.12
0.16
0.20
0.24
0.28
0.32
0.36
0.40
gm of flux
(b)
Average
(c)
Average - Blank
(a)
Blank

It is obivous that at very low uranium concentration (part per billion region) the fluorometric reading increases with the increase of the weight of flux. This increase becomes less drastic when the weight of the flux is larger than 0.22 g . In the present study, 0.3 g flux mixture was used to avoid the fluctuation of fluorescence due to the change in flux weight.

From trial experiments it was observed that in part per million region (or μg uranium perdish), the shape of the curve (see figure 4.13) was different. Generally, the fluorometric analysis of uranium is applied to the analysis of samples with an uranium content in parts per billion region.

4.2.2 Relation between Fluorometric Reading and Uranium Concentration

The relation between the fluorometric reading and the corresponding uranium concentration is given in Table 4.9. The graphical presentation in Figure 4.14 shows that a linear relation is obtained.

Table 4.9 Relation between fluorometric reading and uranium concentration

conditions :	weight of flux mixture	0.3 g
	time of fusion	10 min
	temperature of fusion	700°C

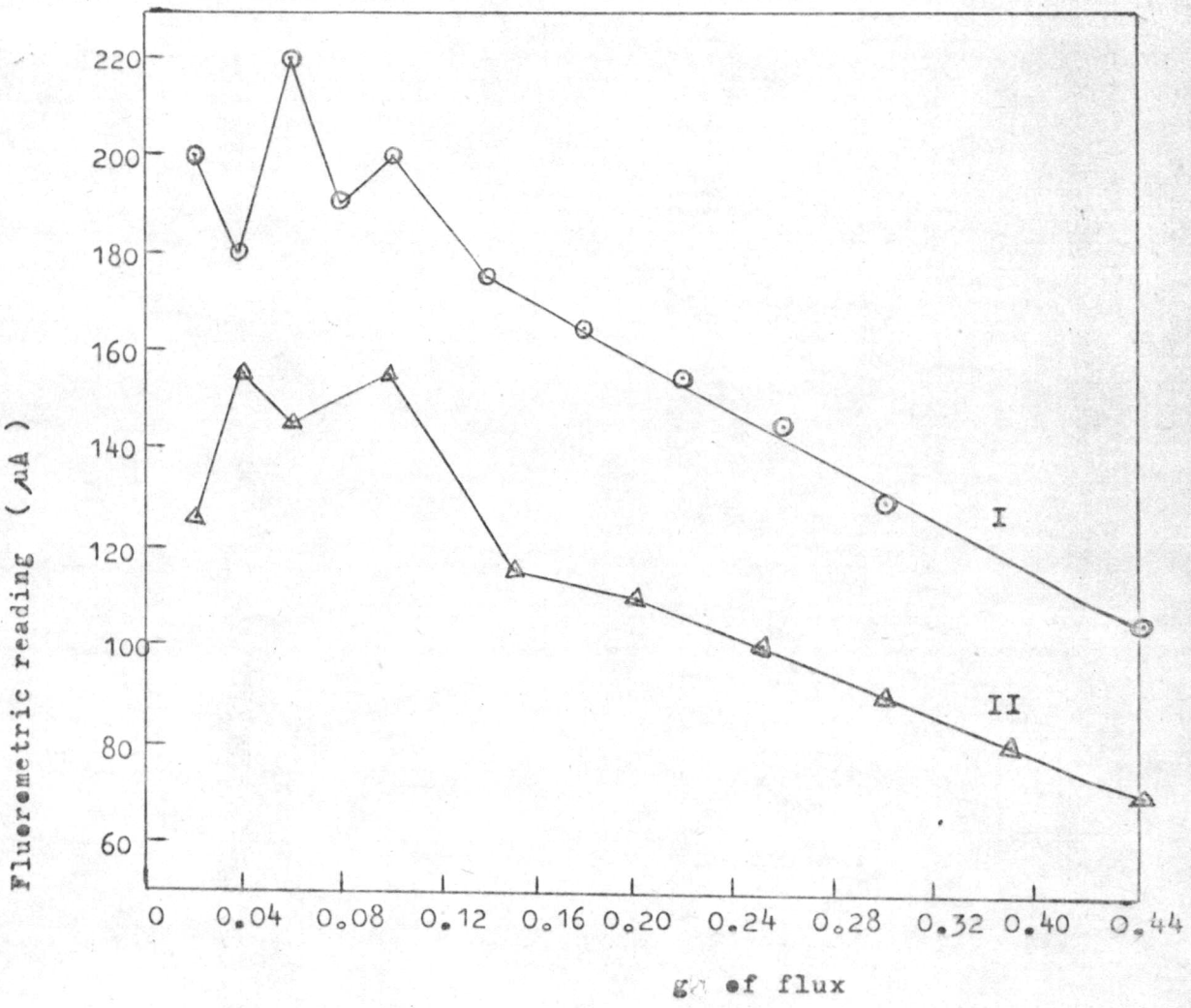


Figure 4.13 Fluorometric reading of 10 $\mu g/cm^3$ uranium at different amount of flux mixture

number of dishes	conc. of standard uranium sol^{n} ($\mu g/dm^3$)	fluorometric reading (μA)	FR-Blank (μA)	FR from least square test
1	10	1.0	0.3	0.267
2	30	1.2	0.5	0.621
3	50	1.7	1.0	0.975
4	100	2.6	1.9	1.860
5	200	4.1	3.4	3.63
6	300	5.6	4.9	5.40
7	500	9.7	9.0	8.94
8	800	15.2	14.5	14.25
9	1000	19.0	18.3	17.79
10	blank	0.7	-	-

4.2.3 Extraction Yield of Uranium by Ethyl acetate

The results of a single stage extraction are tabulated in Table 4.10

Table 4.10 Results of ethyl acetate extraction in the recovery of uranium from water.

conditions : weight of flux mixture 0.3 g

time of fusion 10 min.

temperature of fusion 700°C

volume of salting-agent 15 cm^3

volume of ethyl acetate 10 cm^3

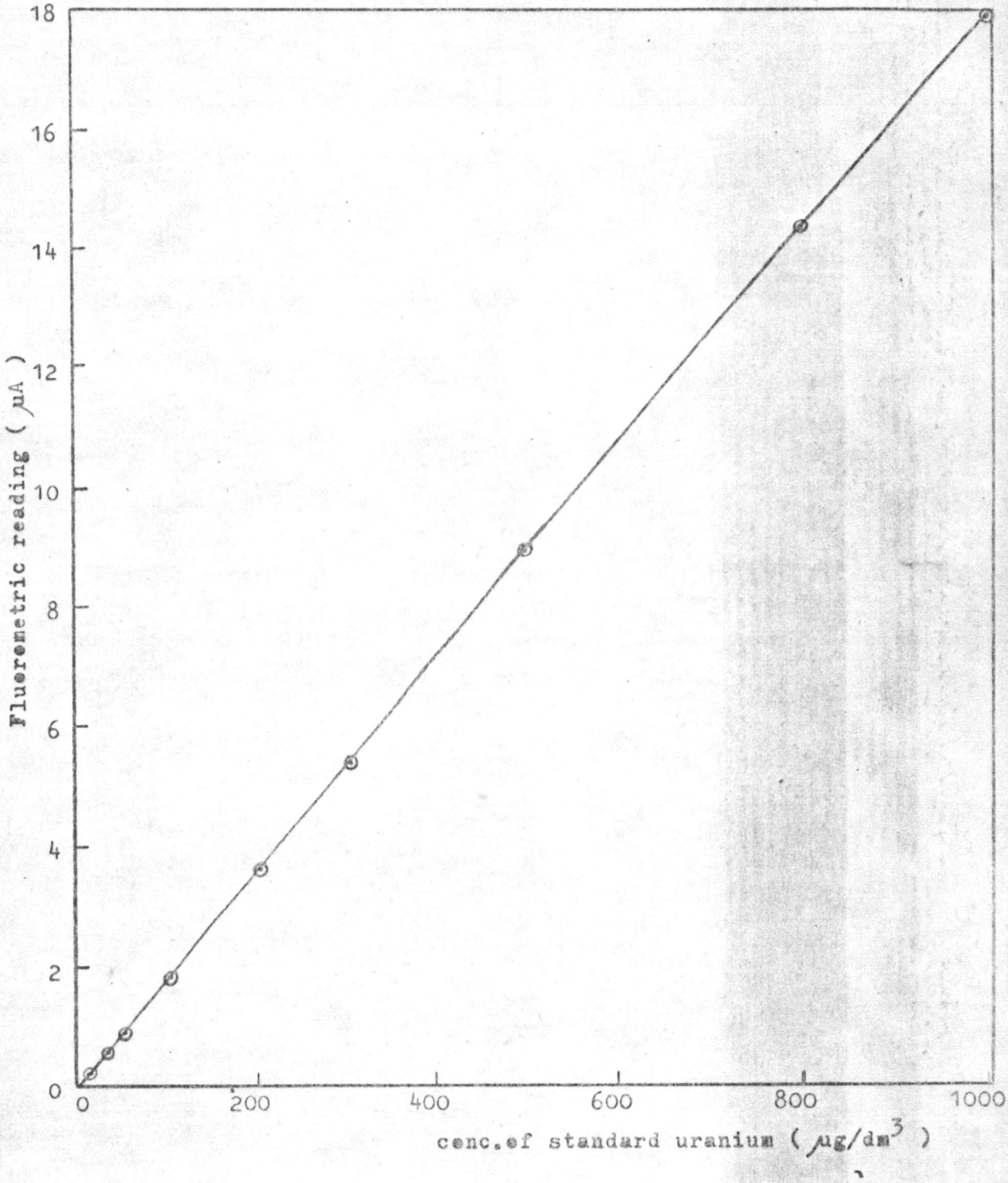


Figure 4.14 Relation between uranium concentration and fluorometric reading

no.of test	fluorometric reading (μA) (1st extraction	average (μA)	(FR-B) μA	W calculated weight ($\mu g/dm^3$)	% Recovery
1	20.0				
2	20.0				
3	20.0				
4	20.0	19.83	18.03	933.91	
5	18.5				
6	20.5				
Standard (non-extracted) uranium reading					93.39
1	100.0				
2	100.0	98.33	96.53	1000	
3	95.0				
Blank reading					
1	1.8	1.8	-	-	
2	1.8				

It is obvious that ethyl acetate is a specific solvent for uranium. Higher extraction yield could be achieved by increasing the number of extraction stage, as one could observe from Table 4.11

Table 4.11 Percent recovery of uranium from water at various sequential extraction stages (Blank = 0.71 μA, uranium concentration = 1000 μg/dm^3, fluorometric reading of standard uranium = 18.58 μA)

Extraction Stage	FR-Blank (μA)				extracted uranium	
	1	2	3	average	μg/dm^3	yield (%)
1	16.79	16.29	17.46	16.84	906.35	90.64
2	0.79	1.19	0.71	0.897	48.28	4.83
3	0.08	0.08	0.05	0.07	3.77	0.38
Total extracted uranium					958.4	95.84

The data above show that high extraction yield of uranium could be obtained from single stage extraction with ethyl [illegible].

4.2.4 Limit of Detection

The fluorometric readings of various uranium solution, concentration ranging from 0.05 to 20 μg/dm^3, are given in Table 4.12. The correlation is graphically shown in Figure 4.15

Table 4.12 Minimum determinable concentration of uranium in water by fluorometry.

conditions : weight of flux 0.3 g
time of fusion 10 min.
temp. of fusion 700°C
blank reading 1.8 μA

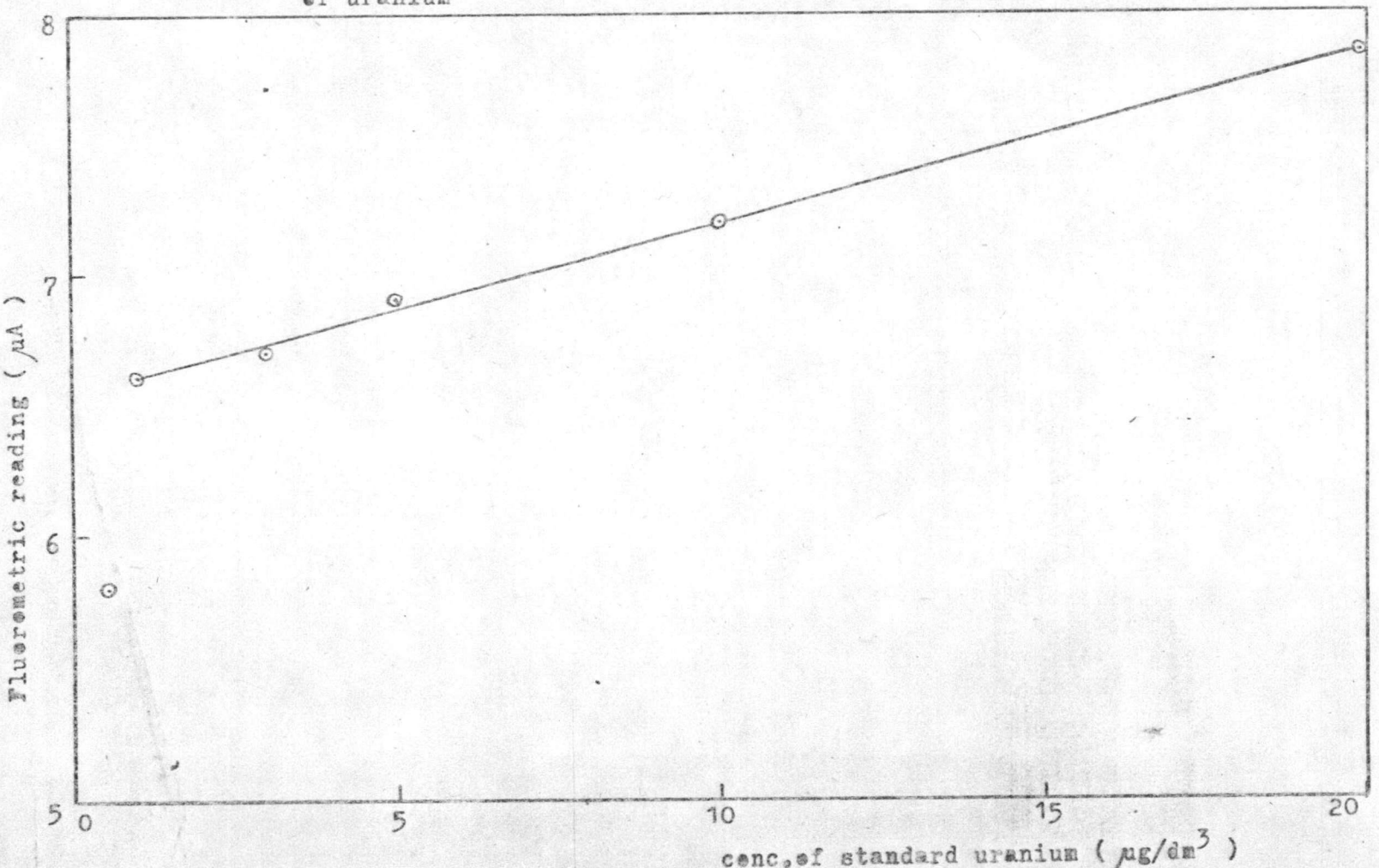
number of dish.	cone. of std. uranium ($\mu g/dm^3$)	fluorometric reading-blank (μA)
1	0.05	2.2
2	0.10	2.3
3	0.50	5.8
4	1.0	6.6
5	3.0	6.70
6	5.0	6.90
7	10.0	7.20
8	20.0	7.85

The experimental results indicated that the detection limit in the fluorometric method is 1.0 $\mu gU/dm^3$.

4.2.5 Results of the Quantitative Analysis

The results of the analysis of the 28 samples are given in Table 4.13. The results are obtained from five

Figure 4.15 The relation between the concentration and the fluorescence intensity of uranium



separated determination. The sample number 2, 8-1, 10 and those collected from rivers, canals and sea were subjected to pre-concentration prior to extraction with ethyl acetate For the analysis of uranium in river and canal waters, larger volume of water sample is required. When the uranium concentration in the sample is higher than the detection limit, no significant increase of the precision is obtained by the preconcentration technique.

Table 4.13 Results of the quantitative analysis of uranium in water samples by fluorometry.

samples	uranium content ($\mu g/dm^3$)					Mean and standard deviation (σ)
	1	2	3	4	5	
DDH-1, 1	32.89	29.60	38.18	23.03	26.32	30.00 ± 5.86
DDH-2, 2	131.34	122.39	128.36	120.21	128.30	126.12 ± 4.63
DDH-3, 3	18.64	16.95	16.95	29.66	21.19	20.68 ± 5.31
DDH-5, 5	17.14	11.43	28.57	17.14	22.86	19.43 ± 6.52
DDH-8, 6	268.66	253.73	259.44	271.64	274.88	265.67 ± 8.81
DDH-9, 7-1	33.73	36.14	32.77	33.73	31.33	33.54 ± 1.75
DDH-9, 7-2	34.66	27.44	20.22	27.44	20.22	25.99 ± 6.04
DDH-10, 8-1	6.06	3.46	4.33	2.16	6.93	4.59 ± 1.93
DDH-10, 8-2	13.64	4.55	9.09	6.82	9.09	8.64 ± 3.37
DDH-11, 9-2	19.23	21.15	24.04	20.19	27.88	22.49 ± 3.51
DDH-12, 10	8.80	5.60	4.00	8.00	12.00	7.68 ± 3.08

continue :

DDH-13, 11	38.64	36.36	40.91	45.45	38.64	40.00 ± 3.45
DDH-14, 12-1	18.18	15.91	20.45	18.18	22.73	19.09 ± 2.59
DDH-14 12-2	181.82	186.36	190.91	200.00	204.55	192.73 ± 9.43
DDH-17, 13-1	50.00	45.24	47.62	46.19	47.62	47.33 ± 1.80
DDH-17, 13-2	35.71	40.48	40.48	50.0	45.24	42.38 ± 5.43
DDH-19, 14	26.19	26.19	28.57	19.05	30.95	26.19 ± 4.45
DDH-20, 15-1	121.43	121.43	130.95	135.71	133.33	128.57 ± 6.73
DDH-20, 15-2	107.14	88.09	97.61	97.61	88.09	95.71 ± 7.97
DDH-21, 16-1	597.62	588.09	621.43	569.05	573.81	590.0 ± 20.92
DDH-21, 16-2	221.43	230.95	223.81	223.81	230.95	226.19 ± 4.45
Bangpakong, Prachinburi	N	N	N	N	N	N
Chaophaya, Nondthburi	N	N	N	N	N	N
Bangphra, Cholburi	N	N	N	N	N	N

continue :

Klongprapha, Prachachoen	N	N	N	N	N	N
Kwae river Khanchanaburi	N	N	N	N	N	N
Sea water Angsila	0.42	0.48	0.41	0.32	0.39	0.40 ± 0.06
Phurieng, KnonKhan	1.52	1.09	1.66	1.63	1.44	1.47 ± 0.23

N = undetectable