CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Analysis of Zircon

The composition (%) of the zircon samples as analysed by instrumental neutron activation and X-ray fluorescence analyses are shown in Table 4.1

Table 4.1 Analysis of Zircon

Component	Sahasinrarethai		Lun-Seng		Thai-Nippon		Pungnga-Tin	
	INAA	XRF	INAA	XRF	INAA	XRF	INAA	XRF
ZrO_2	56.63	57.26	55.00	55.49	26.63	30.74	23.76	25.39
La_2O_3	1.30	1.11	0.42	0.32	0.61	0.87	2.91	3.68
CeO_2	1.90	1.69	0.90	0.79	0.85	1.28	3.35	6.32
TaO_2	1.61	*	1.68	*	0.10	*	0.38	*
UO_2	0.32	-	0.26	-	0.07	-	0.25	-
Pr_2O_3	0.36	-	*	0.88	*	0.92	*	1.44
Nd_2O_3	0.78	0.62	*	0.39	*	0.84	*	3.50

INAA = Instrumental neutron activation analysis

XRF = X-ray fluorescence analysis

* = not analysed

- = undetectable

In XRF the accuracy is governed by the similarity between the matrices of the sample and standard. As the compositions of the standard are quite different from those of the Thai-Nippon and Pungna-Tin sample, it is expected that the XRF results are not reliable and might be different from the INAA results.

As the purity of the Sahasinrarethai sample was highest, it was used for the fusion-study. The composition of the Sahasinrarethai sample is given in Table 4.2

Table 4.2 The composition of zircon from Sahasinrarethai

Component	% (by weight)	Method of Analysis
SiO_2	27.10	UV - Visible
Al_2O_3	0.64	INAA
Fe_2O_3	0.30	UV - Visible
TaO_2	1.61	INAA
TiO_2	1.43	INAA
UO_2	0.32	INAA
ThO_2	0.59	INAA
CeO_2	1.90	INAA
La_2O_3	1.30	INAA
Pr_2O_3	0.36	INAA
Nd_2O_3	0.78	INAA
HfO_2	1.99	INAA
ZrO_2	56.63	INAA

The Precision of X-ray Fluorescence for the Quantitative Analysis of Zirconium.

The precision of the method was checked by analysing seven samples taken from the same ground ore. The results are given in Table 4.3

Table 4.3 Analyses of zirconium in zircon

Sample	% ZrO_2 from analysis	Mean and Standard deviation	% Error
Sahasinrarethai	58.40 56.40 58.52 58.30 56.22 56.53 56.43	57.26 ± 1.46	2.55

It can be seen that the technique of X-ray fluorescence is very effective for the determination of zirconium in zircon if the matrices of the sample and the standard are closed to each other. The precision of the method was found to be excellent. The results agree with those obtained from instrumental neutron activation analysis. X-ray fluorescence was usually applied if rapid results were required.

4.2 Alkali Fusion of Zircon

The effects of sand to sodium hydroxide ratio, fusion
temperature, time of fusion and particle size were investigated.
The zirconium content in the ore prior to the fusion process
were determined as $ZrOCl_2.8H_2O$.

The percentage yield of fusion was evaluated as

$$\% \text{ yield} = \frac{100 \text{ x weight of } ZrOCl_2.8H_2O \text{ from digestion x MW.of } ZrO_2}{\text{weight of sample x } \%ZrO_2 \text{ in sample x MW.of } ZrOCl_2.8H_2O}$$

4.2.1 Effect of Sand to Alkali Ratio

In the study of the effect of the ratio of sand to sodium
hydroxide, the reaction temperature, time of reaction, particle size
were fixed and the ratio of sand to sodium hydroxide varied from
1:1.5 to 1:9 (wt/wt). A 50% sodium hydroxide solution was prepared
and the appropriate amount was used. The $ZrOCl_2.8H_2O$ precipitate
was weighed and the percentage yield was calculated. The results
of the experiment are shown in Table 4.4

Table 4.4   Effect of sand to alkali ratio

Conditions: weight of zircon   3 g

reaction temperature $650^{o}C$

time of reaction   1 hour

particle size   -100   mesh

Sand to alkali (wt/wt)	$ZrOCl_2.8H_2O$ yield (%)			
	I	II	III	average
1:1.5	23.60	24.89	23.01	23.83
1:3	47.77	45.95	47.01	46.91
1:4.5	64.05	66.89	64.92	65.28
1:6	76.31	76.38	76.08	76.26
1:7.5	75.21	77.29	74.99	75.83
1:9	77.99	73.22	73.67	74.96

The effect of the ratio of sodium hydroxide to sand is shown in Figure 4.1 by plotting the percentage yield as a function of sand to alkali ratio. The obtained results indicated that the fusion yield increases by increasing the amount of sodium hydroxide from 1.5 to 6 times the weight of the ore. Further increase of sodium hydroxide weight did not increase the yield.
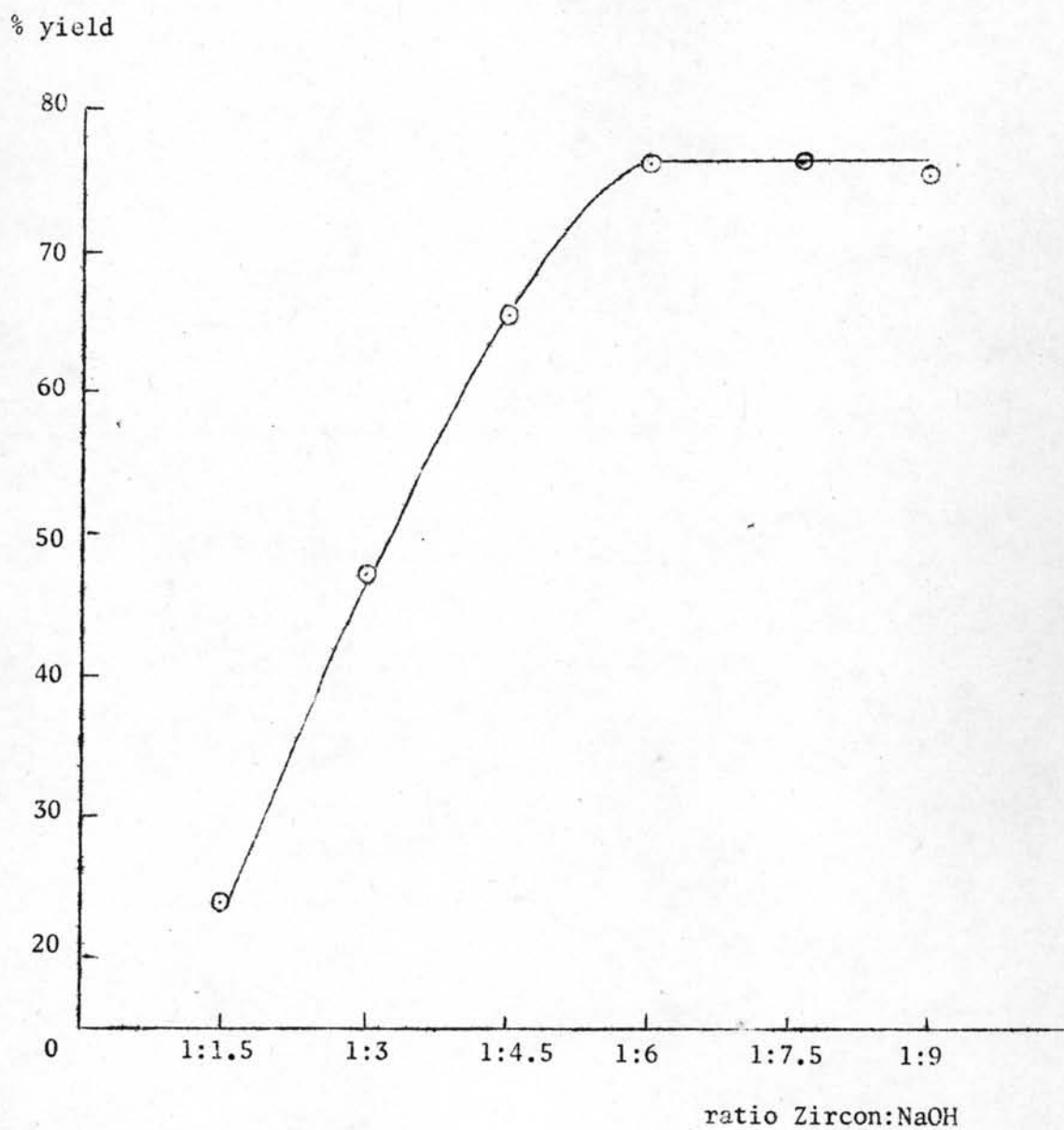
% yield

Figure 4.1 Effect of sand to alkali ratio

4.2.2 Effect of Temperature on Alkali Fusion

In the study of the effect of temperature, the reaction mass was dehydrated at $300^{o}C$ for 1 hour.and fused for 1 hour at temperature varied from 300 to $750^{o}C$.

The results of the experiment are shown in Table 4.5 and plotted in Figure 4.2

Table 4.5 Effect of temperature on fusion

Conditions: weight of zircon 3 g

ratio of sand to NaOH 1:6 (wt/wt)

reaction time 1 hour

particle size -100 mesh

Temperature (^{o}C)	$ZrOCl_2.8H_2O$ yield (%)			
	I	II	III	average
300	2.15	2.32	2.01	2.16
450	6.49	7.56	6.01	6.87
550	48.67	49.99	48.01	48.89
600	70.54	70.79	71.47	70.93
650	76.31	76.38	76.08	76.26
700	76.01	75.56	76.67	76.08
750	75.33	75.01	76.00	75.45

A maximum yield of 76 per cent was obtained between $650-750^{o}C$.
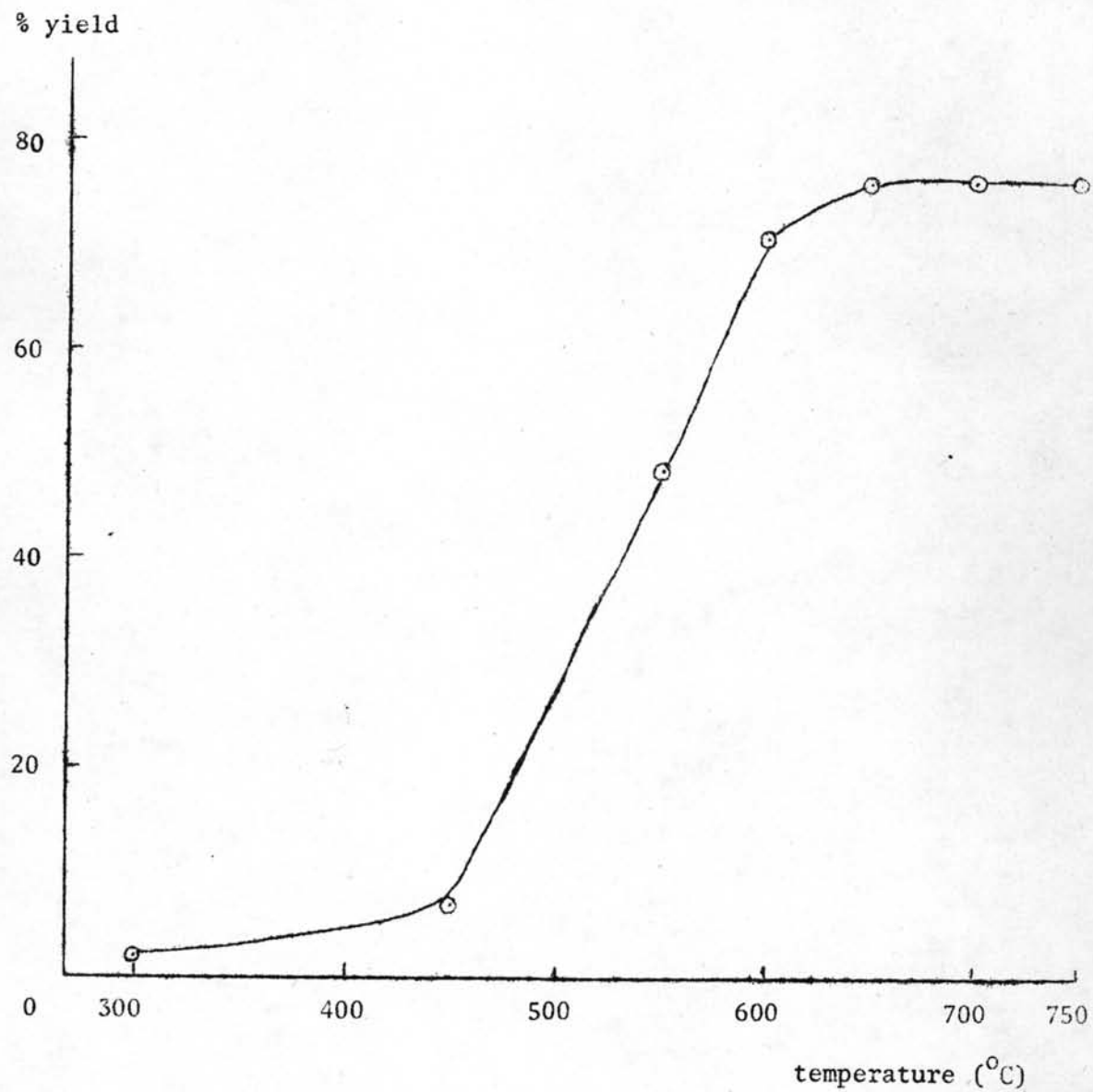
Figure 4.2 Effect of temperature on alkali fusion

4.2.3 Effect of Reaction Time on Alkali Fusion

In the investigation of the effect of reaction time, the time was varied between 20 to 180 minutes. The results are shown in Table 4.6 and plotted in Figure 4.3

Table 4.6 Effect of time on fusion

Conditions: weight of zircon 3 g

ratio of sand to NaOH 1:6 (wt/wt)

temperature 700°C

particle size -100 mesh

time (min)	$ZrOCl_2 \cdot 8H_2O$ yield (%)			
	I	II	III	average
20	76.51	76.99	78.87	77.46
40	75.45	75.36	75.01	75.27
60	76.51	-	-	76.51
90	75.30	76.05	76.59	75.98
120	75.45	76.12	76.97	76.18
150	77.98	76.87	75.22	76.69
180	75.06	75.12	75.43	75.20

No difference was observed by variation of reaction time between 20 to 180 minutes.
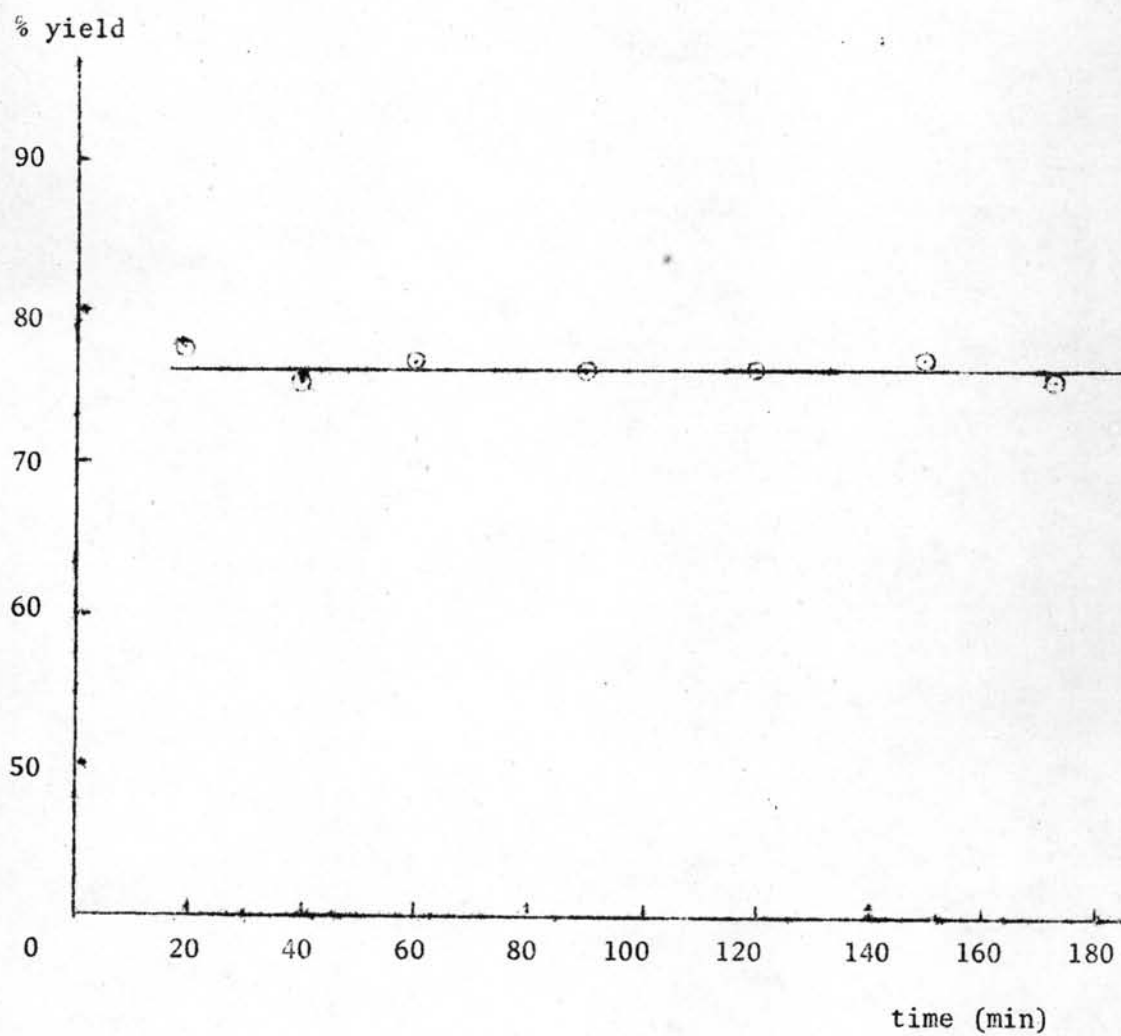
Figure 4.3 Effect of reaction time on fusion

4.2.4 Effect of Particle Size on Alkali Fusion

In the study of the effect of the mesh size of ore, particle size was varied between -60 to -200 mesh. The results are shown in Table 4.7 and plotted in Figure 4.4

Table 4.7 Effect of particle size

Conditions: weight of zircon 3 g

ratio of sand to NaOH 1:6 (wt/wt)

temperature $700^{o}C$

time 1 hour

particle size (mesh)	$ZrOCl_2 \cdot 8H_2O$ yield (%)			
	I	II	III	average
-60	81.01	80.09	76.77	79.29
-100	76.43	-	-	76.43
-200	76.01	75.53	75.45	75.69

It was found that particle size did not affect the yield of digestion. Since the reaction mass was not stirred, some ore may settle down at the bottom of the beaker. The reaction yield was therefore low and no effect of the particle size was observed.
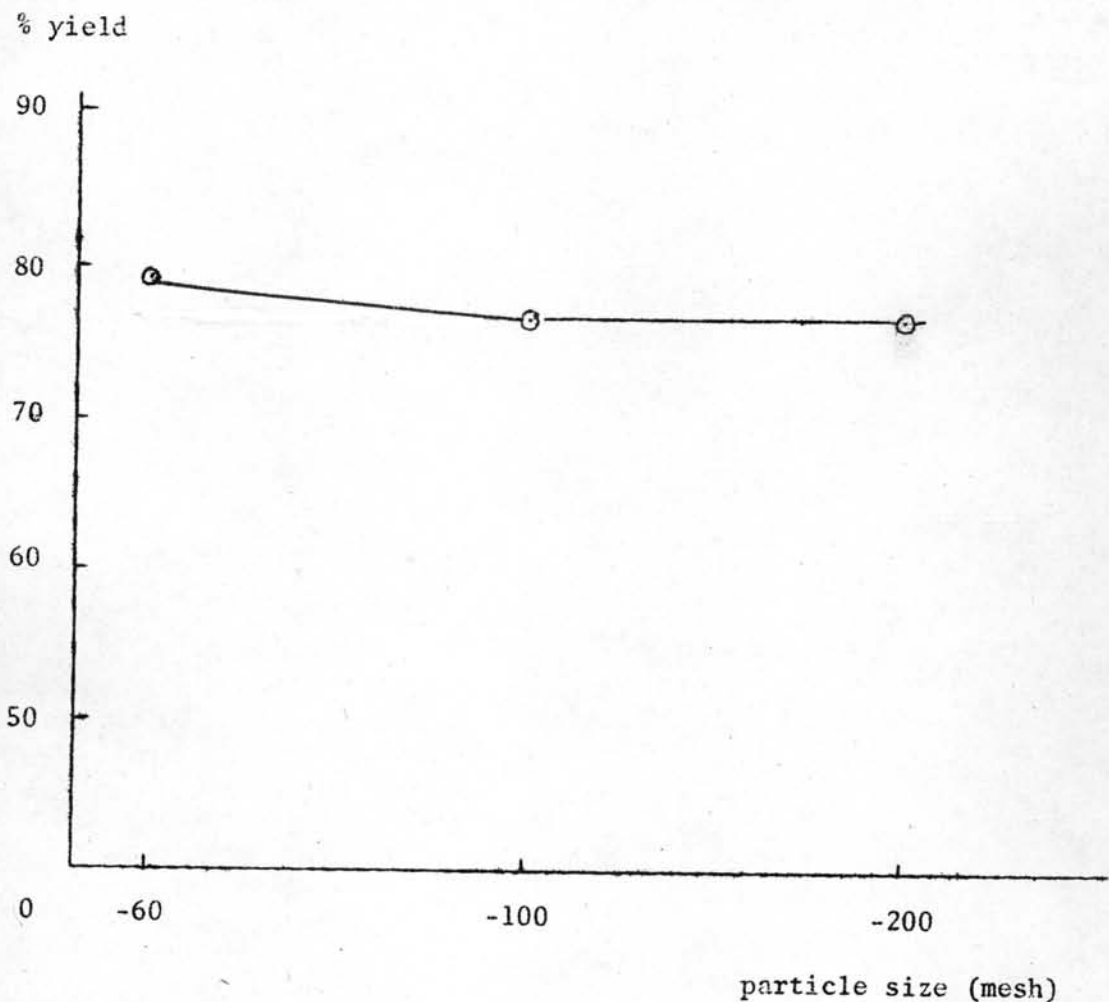
Figure 4.4 Effect of particle size on fusion

4.2.5 Repeatability Test

The repeatability of the process was determined by performing the experiment several times while all conditions were kept constant. The standard deviation was evaluated to determine the error of the experiments. The results are shown in Table 4.8

Table 4.8 Replicate yield at similar conditions

Conditions: weight of zircon 3 g

ratio of sand to NaOH 1:6 (wt/wt)

temperature $700^{o}C$

time 1 hour

particle size -60 mesh

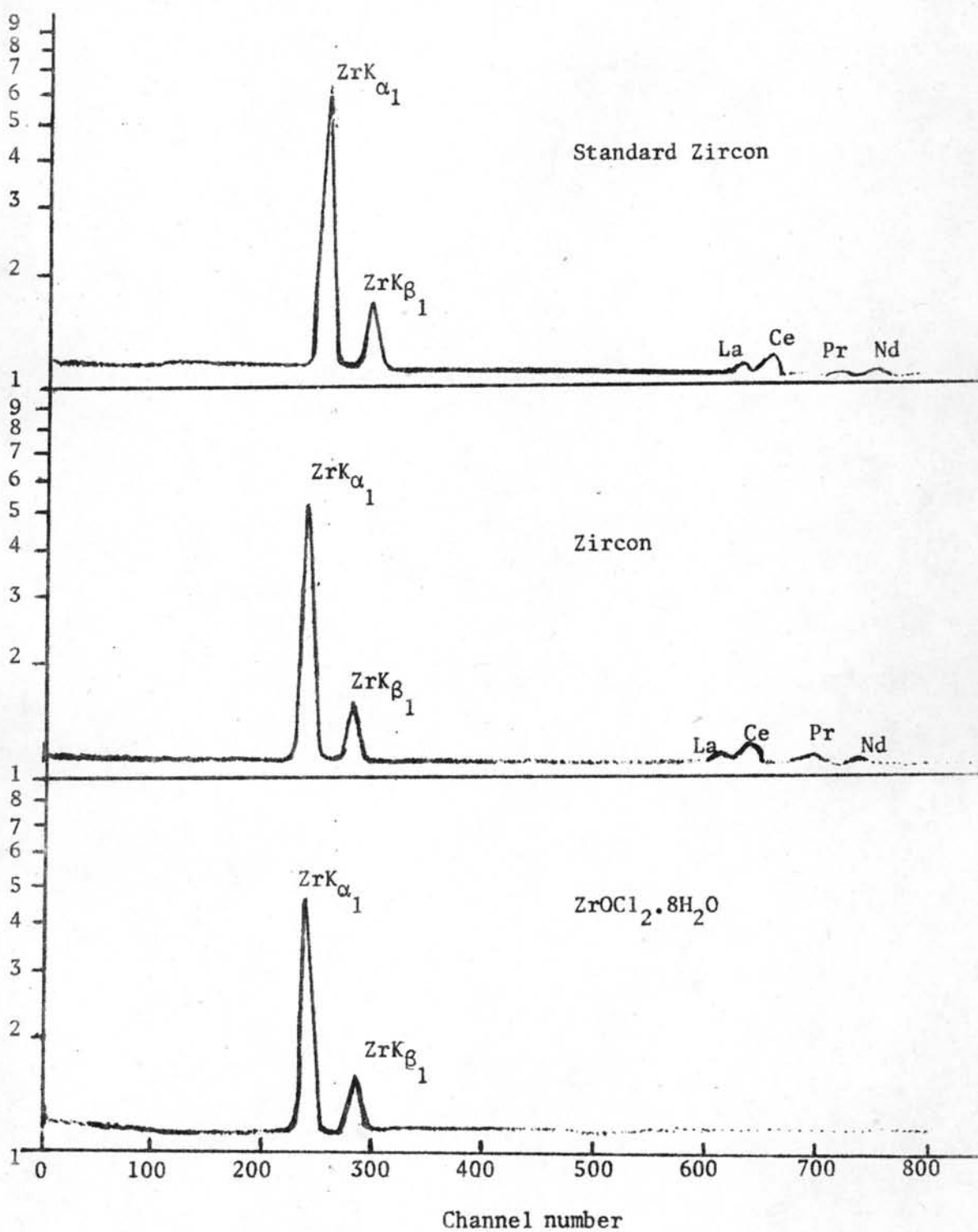| Number of the test	% yield
1	76.08
2	75.12
3	77.04
4	81.02
5	82.64
6	80.09
7	80.00
average	78.86
standard deviation	2.79
percentage error	3.54

Figure 4.5   X-ray fluorescence spectra of standard zircon, zircon

and zirconyl chloride octahydrate

The experimental error was found to be about 3%. The X-ray spectra of the standard ore, zircon, $ZrOCl_2 \cdot 8H_2O$ are given in Figure 4.5

4.3 Solvent Extraction

4.3.1 Effect of TBP Concentration

In the study of the effect of TBP concentration, the concentration of zirconium, extraction-time and nitric acid concentration were fixed and the concentration of TBP was varied between 5 and 100% in kerosene. The results are shown in Table 4.5 and plotted in Figure 4.6

Table 4.9 Effect of TBP concentration

Conditions: zirconium concentration 8.47 g/l

nitric acid 5.3 mol/l

extraction time 20 minutes

sodium nitrate nil.

% TBP in kerosene	Distribution coefficient				% Zr extracted
	I	II	III	average	
5	0.04	0.03	0.03	0.03	2.55
20	0.20	0.19	0.19	0.19	16.21
40	0.76	0.76	0.76	0.76	43.19
50	1.37	1.32	1.27	1.32	56.99

Table 4.9 Effect of TBP concentration

Conditions: zirconium concentration 8.47 g/l

nitric acid 5.3 mol/l

extraction time 20 minutes

sodium nitrate nil.

% TBP in kerosene	Distribution coefficient				% Zr extracted
	I	II	III	average	
50	1.37	1.32	1.27	1.32	56.99
60	1.64	1.65	1.69	1.67	62.42
70	2.78	2.55	2.84	2.72	73.13
80	4.02	4.02	4.08	4.04	80.16
100	6.80	6.61	6.87	6.76	87.29

At a constant composition of the feed solution, the distribution coefficient of zirconium increases with the increase of TBP concentration. For the TBP concentration of 60 and 70 per cent in kerosene, the percentage extraction of zirconium are 62.42 and 73.13 respectively. Moreover TBP is also very viscous and rather expensive. For these reasons including the economical point of view, the 60 per cent mixture is therefore chosen and employed in the subsequent experiments.
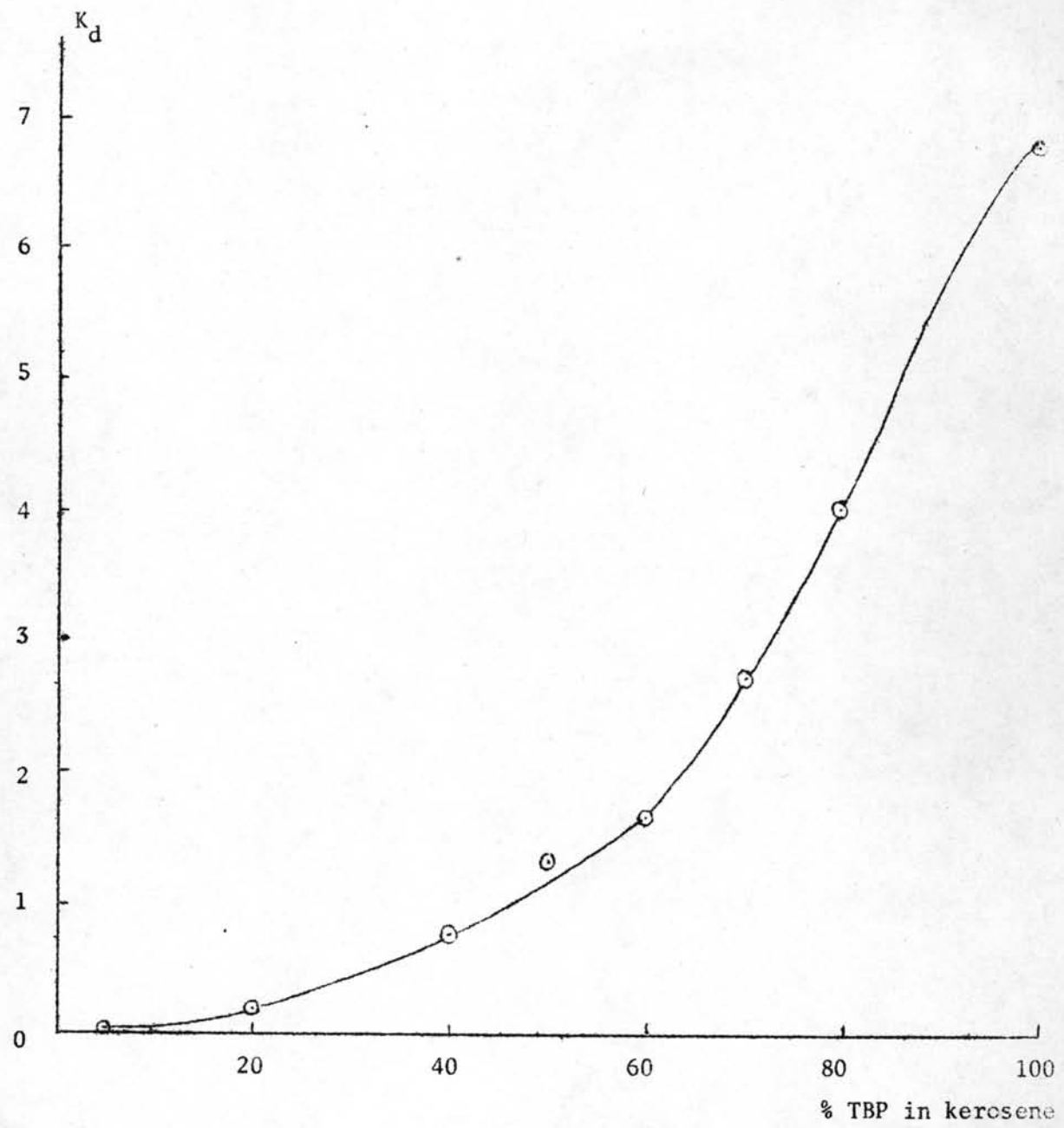
Figure 4.6 Effect of TBP concentration on the extraction

of zirconium

4.3.2 Effect of Zirconium Concentration

The concentration of zirconium was varied from 1.41 to 14.12 g/1. Other conditions were kept constant. The results in Table 4.10 and Figure 4.7 indicated that the distribution coefficient decreases with the increase of zirconium concentration. A very dilute solution requires large extraction vessels, a concentration of 8.47 g/1 was normally used.

Table 4.10   Effect of zirconium concentration on
the extraction of zirconium

Conditions: TBP concentration   60%   in kerosene

nitric acid   5.3   mol/1

extraction time   20 minutes

sodium nitrate   nil.

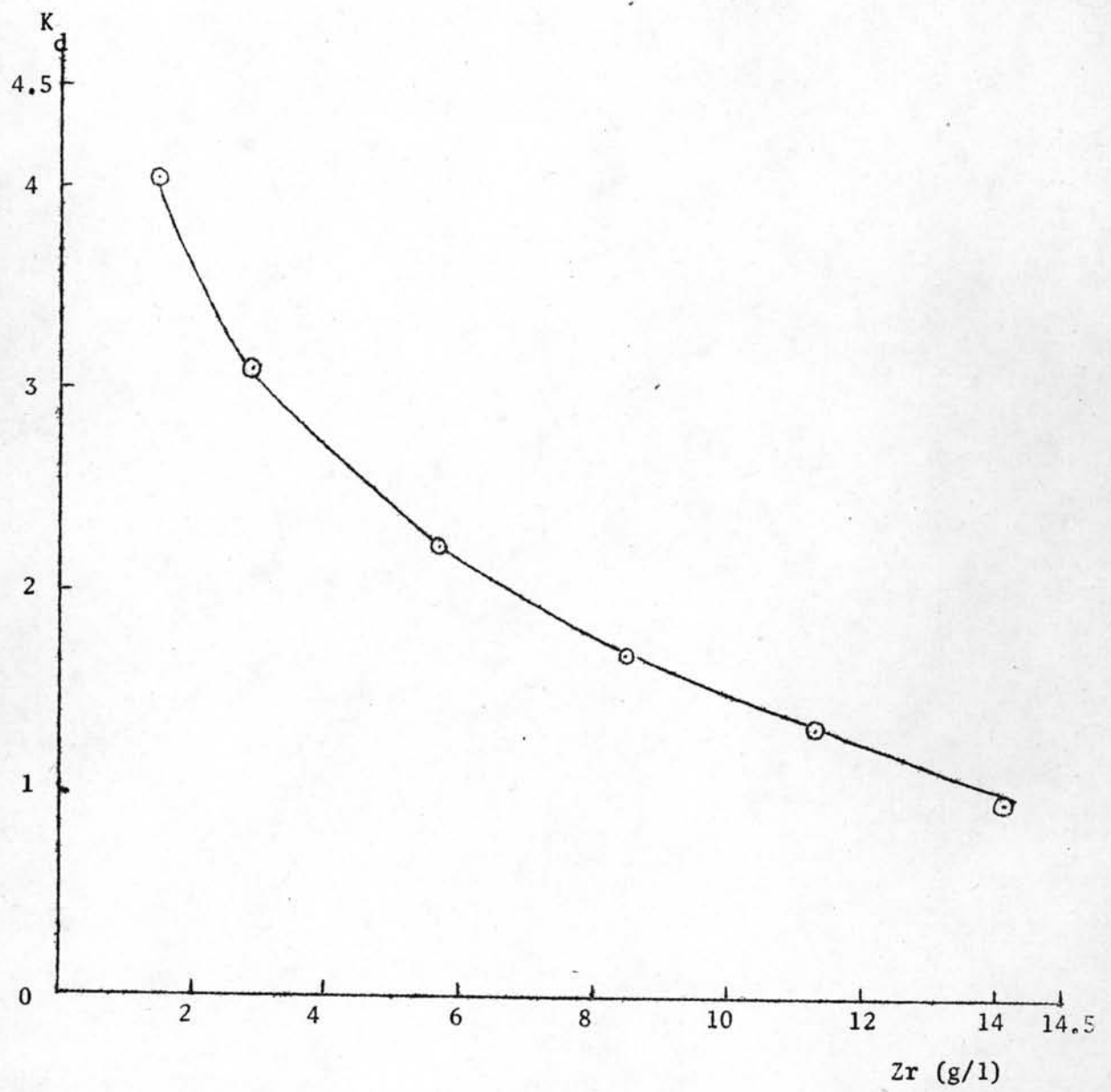| Zirconium	Distribution Coefficient			
(g/1)	I	II	III	average
1.41	3.84	4.00	4.29	4.04
2.82	3.16	3.01	3.11	3.09
5.64	2.24	2.24	2.23	2.24
8.47	1.71	1.71	1.67	1.70
11.30	1.27	1.42	1.36	1.35
14.12	1.01	0.97	0.90	0.96

Figure 4.7 Effect of zirconium concentration

4.3.3 Effect of Extraction Time on the Extraction of Zirconium

The concentration of TBP, zirconium and nitric acid were fixed and the time varied from 5 to 80 minutes. The results in Table 4.11 and Figure 4.8 show that 5 minutes was sufficient to attain the extraction equilibrium.

Table 4.11 Effect of time on extraction

Conditions: zirconium concentration 8.47 g/l

TBP concentration 60% in kerosene

nitric acid 5.3 mol/l

sodium nitrate nil.

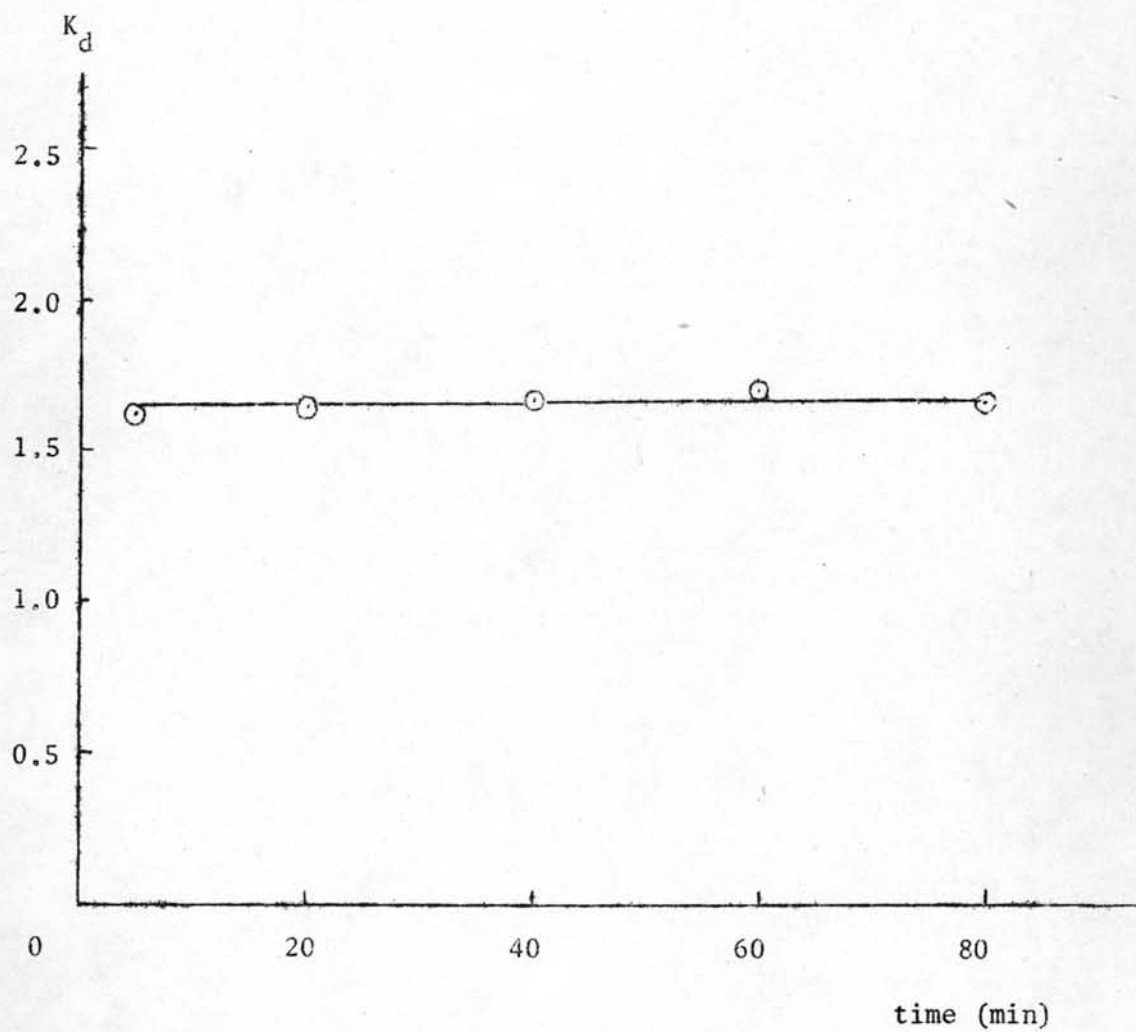| time	Distribution coefficient			
(minute)	I	II	III	average
5	1.62	1.62	1.61	1.62
20	1.67	1.66	1.63	1.65
40	1.64	1.65	1.69	1.66
60	1.69	1.71	1.70	1.70
80	1.65	1.65	1.66	1.65

Figure 4.8 Effect of extraction time on the extraction

of zirconium

4.3.4 Effect of Salting out Agent

Inorganic nitrates may be employed as salting out agent in TBP extraction. The sodium nitrate concentration was varied between 0 to 4.0 mol/l. The results are given in Table 4.12 and plotted in Figure 4.9

Table 4.12 Effect of sodium nitrate concentration

Conditions: zirconium concentration 8.47 g/l

TBP concentration 60 % in kerosene

nitric acid 5.3 mol/l

extraction time 20 minutes

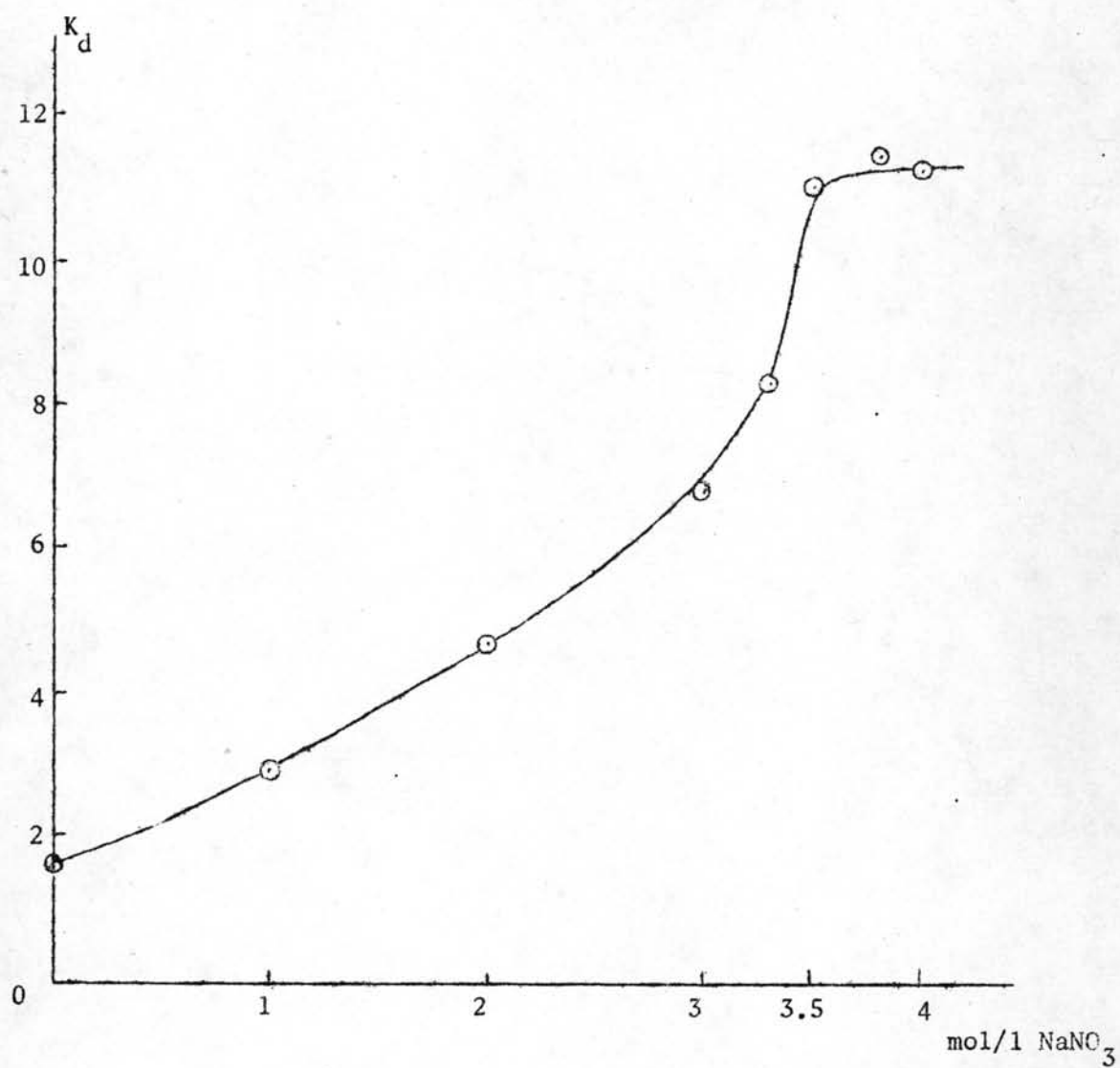| NaNO$_3$ (mol/l)	Distribution coefficient			
	I	II	III	average
0	1.65	1.65	1.65	1.65
1	2.88	2.95	2.98	2.94
2	4.70	4.71	4.84	4.75
3	6.80	6.89	6.89	6.86
3.3	8.28	8.20	8.38	8.28
3.5	10.68	10.95	11.33	10.97
3.8	11.01	11.94	11.55	11.47
4.0	11.19	11.17	11.41	11.26

Figure 4.9 Effect of salting out agent

The presence of 3.5 mol/l sodium nitrate solution causes a
sevenfold increase in the zirconium extraction. Further addition
of sodium nitrate does not result in any increase of the distribution
coefficient.

4.3.5 Extraction of Hafnium

The optimum conditions for the zirconium extraction was
applied in the extraction of hafnium in order to study the content of
hafnium contamination. The hafnium concentration was fixed at 0.3
per cent and the sodium nitrate concentration varied from zero to
4 mol/l. The result was shown in Table 4.13 and Figure 4.10

Table 4.13   Effect of sodium nitrate on hafnium extraction

Conditions: zirconium concentration   nil

hafnium concentration   3   g/l

TBP concentration   60% in kerosene

extraction time   20   minutes

nitric acid   5.3   mol/l

NaNO$_3$ (mol/l)	Distribution coefficient of hafnium			Distribution coefficient of zirconium[*] from Table 4.12
	I	II	average	
0	0.04	0.04	0.04	1.65
1	-	-	-	2.94
1.5	0.07	0.07	0.07	4.75
3.0	0.12	0.10	0.11	6.86
3.2	-	-	-	8.28
3.5	0.14	0.14	0.14	10.97
3.8	-	-	-	11.47
4.0	0.28	0.28	0.28	11.26

[*]Conditions: hafnium concentration   nil

zirconium concentration   8.47   g/l

TBP concentration   60% in kerosene

extraction time   20 minutes
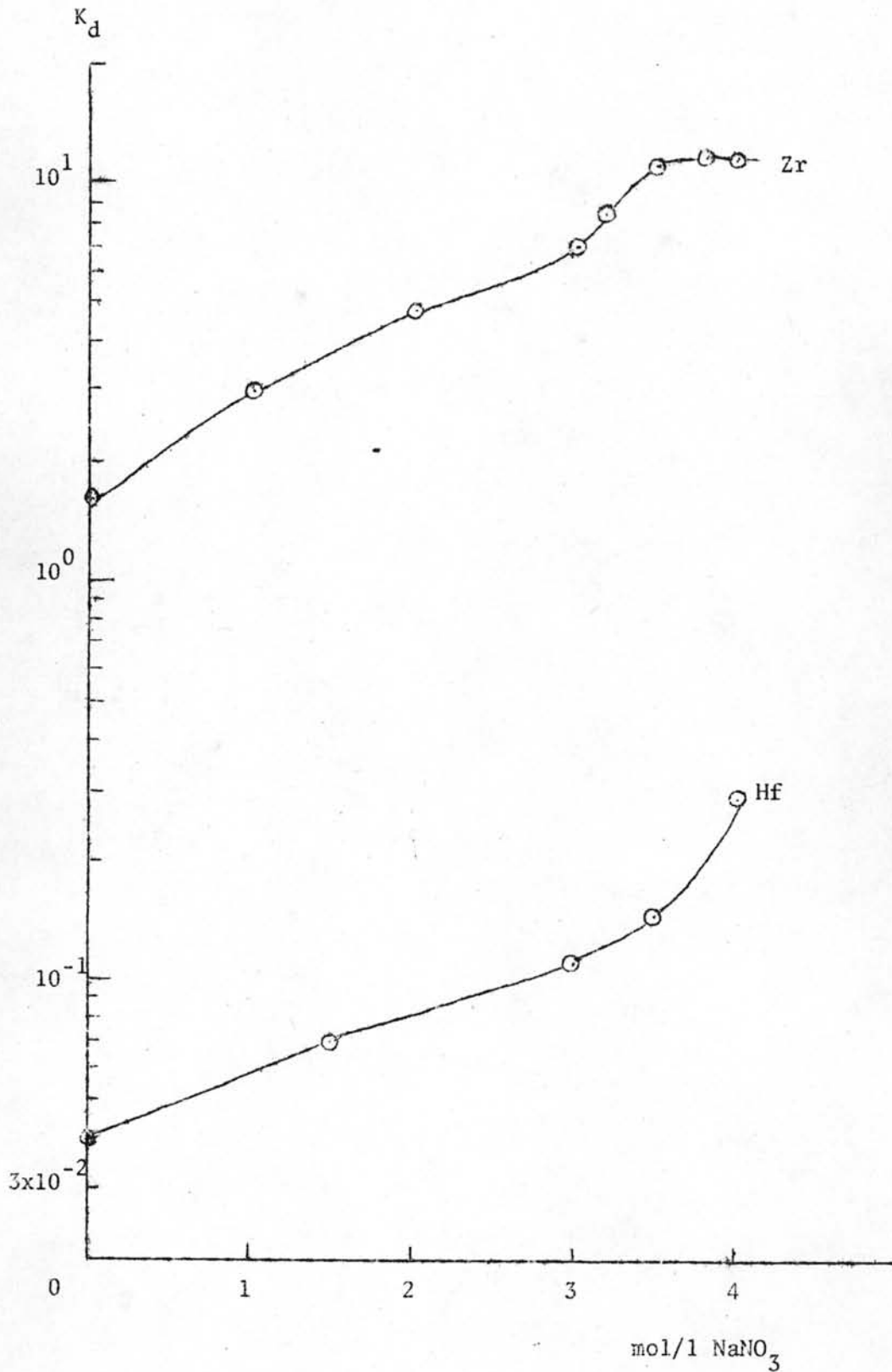
nitric acid   5.3   mol/l

Figure 4.10   Effect of sodium nitrate concentration on the
extraction of zirconium and hafnium

It is noteworthy that the extraction of hafnium follows the same pattern as that of zirconium. The hafnium distribution coefficient increases with the increase in sodium nitrate concentration. In the presence of 3.5 mol/1 $NaNO_3$ which is the optimum condition for zirconium extraction, hafnium will be extracted up to 10 per cent. After 2 scrubbing stages with 3.5 mol/1 $NaNO_3$, the organic phase contains about 0.0003% hafnium.

4.4 Counter Current Extraction of Zirconium

Continuous extraction is normally achieved by allowing the two liquid phases flow counter currently in mixer settlers or columns. The number of stages required can be experimentally determined by the construction of a Mc-Cabe Thiele diagram. A series of extraction was performed by which the concentration of TBP, nitric acid and sodium nitrate were fixed and the zirconium concentration varied between 1.16 to 14.12 g/1. The results are given in Table 4.14 and the Mc-Cabe Thiele diagram is constructed in Figure 4.14.

Table 4.14 Extraction of zirconium

Conditions: TBP concentration 60% in kerosene

nitric acid 5.3 mol/1

extraction time 20 minutes

sodium nitrate 3.5 mol/1

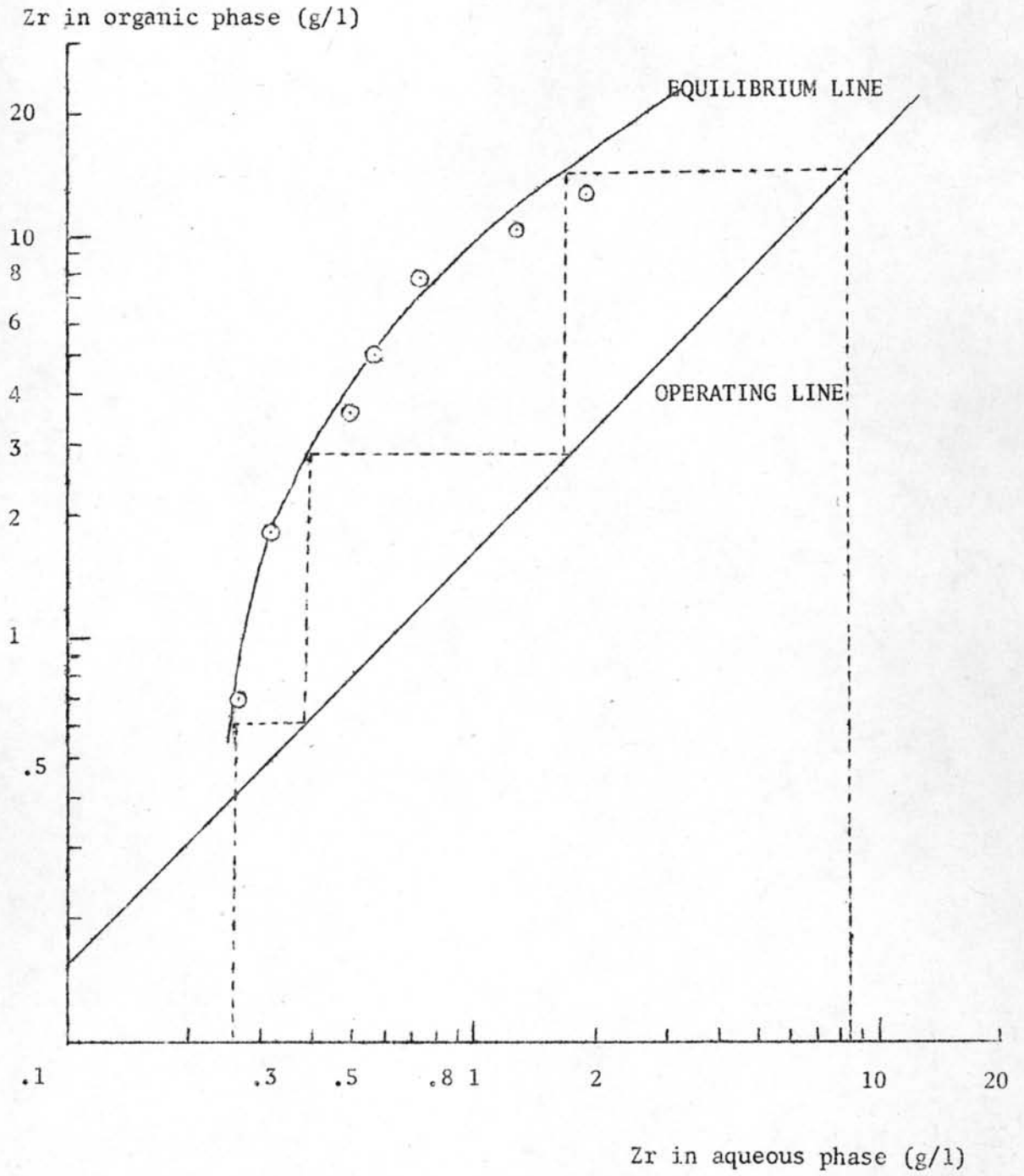| feed (g/1)	aqueous (g/1)	organic (g/1)	K_d
1.16	0.28	0.88	3.11
2.12	0.31	1.81	5.89
4.24	0.50	3.74	7.48
5.65	0.56	5.09	9.09
8.47	0.74	7.73	10.41
11.30	1.23	10.07	8.20
14.12	1.66	12.46	7.51

Figure 4.11 Mc-Cabe Thiele diagram for the extraction of

zirconium

The equilibrium line in Figure 4.11 was obtained by plotting the concentration of zirconium in the aqueous phase against the concentration in organic phase. The operating line was obtained from the equation.[27] Y_n is the concentration of solute in organic phase.

$$Y_n = \frac{A}{Q} (x_n - x_w) + y_0$$

where

A = rate of flow of solute in aqueous phase

Q = rate of flow of solute in organic phase

x_n = concentration of solute in feed solution

x_w = concentration of raffinate (waste)

y_0 = initial concentration of solvent

The flow rate of the organic and the aqueous phases are assumed to be equal. The feed concentration was set at 8.47 g/l and the organic load 14.57 g/l. If the zirconium concentration in raffinate is 0.02 g/l, 3 stages are required for a purification process with a 97 per cent zirconium recovery yield.

4.5 Processing for Zirconium of 50 g/batch

In order to obtain more reliable data on the chemical yield and also to investigate the problems one might encounter in the larger scale, experiments were repeated using 50 g zircon per batch. The optimum conditions for fusion and solvent extraction were applied as found out from the previos experiments. After 2 stages scrubbing found to the zirconium extract was contained 0.03% hafnium.

Zirconium in the solution was precipitated as zirconium hydroxide and ignited to oxide at 400°C.[11] The impurities in the product were determined by neutron activation and spectrophotometric analysis. The results are shown in Table 4.15

Table 4.15 Composition of zirconium oxide from
the processing of 50 g/batch zircon

Component	Concentration (%)	Method of Analysis
SiO_2	0.0800	UV- Visible
Al_2O_3	0.0589	INAA
Fe_2O_3	0.0200	UV- Visible
TaO_2	0.1973	INAA
TiO_2	0.1640	INAA
UO_2	0.0011	INAA
ThO_2	0.0065	INAA
CeO_2	0.0416	INAA
La_2O_3	0.1154	INAA
Pr_2O_3	0.0133	INAA
Nd_2O_3	0.0444	INAA
HfO_2	0.0295	INAA
ZrO_2	94.9600	INAA

The chemical yield and purity of the product from each processing step is shown in Table 4.16

Table 4.16 The chemical yield and purity of zirconium from each processing step

Zircon	ZrO_2 in Zircon (by INAA)		ALKALI FUSION ZrO_2		FUSION, SOLVENT EXTRACTION and precipitation of ZrO_2		
(g)	weight (g)	per cent	weight (g)	per cent	yield		Purity
					weight (g)	per cent	ZrO_2 in total oxide (%)
3	1.69	56.63	1.33	78.86			
50	28.31	56.63	23.59	83.35	15.28	54.00	94.34
50	28.31	56.63	25.87	91.40	17.01	60.08	95.57

It is obvious and logical that the chemical yield from the larger scale is higher. More loss is expected in transferring small amount of samples.

It is apparent that the alkali fusion followed by the TBP extraction is a specific method for the preparation of pure zirconium oxide.