CHAPTER IV

RESULTS AND DISCUSSIONS

4.1. Alkaline digestion of monazite

4.1.1. Effect of temperature and effect of alkaline-to-sand weight ratio on the decomposition of monazite.

In the investigation of the effect of temperature and effect of alkaline-to-sand ratio on the amount of monazite decomposed, the procedure described in 3.2 was followed. The temperature of the oven varied between 120°C to 180°C whereas the sodium hydroxide-to-sand ratio varied between 1 to 5. The amount of undigested monazite was obtained by weighing the residue ofter the dissolution of unchanged sodium hydroxide, trisodium phosphate and hydroxides of thorium, uranium and rare earths. The per cent digestion was evaluated as:

$$\text{Per cent digestion} = \frac{\text{weight of monazite} - \text{weight of undigested monazite}}{\text{weight of monazite}} \times 100$$

Actually, the residue should compose of two fractions, one with rutile, zircon and silica as main constituents and the other which is the actual fraction of undigested monazite. Attempts to separate the two fractions had been tried but without success. Based on the contents of thorium in monazite, S. Srisouta et al.(21)

calculated the content of the undigested monazite in the residue. They found that the amount of rutile, zircon and silica which are called gangue as a whole increases with increasing completeness of digestion. Under optimum conditions the per cent digestion which is based on the thorium content will be 20 per cent higher than the one which is based on the total weight of residue. This shows that the residue composes of 20 per cent gangue and 80 per cent undigested monazite. Since thorium is closely bound in the monazite crystal structure (22), the method of calculation of S. Srisouta et al. is justified. Consequently the per cent digestion that are reported here in the alkaline method must be higher since the contents of gangue in the residue were not corrected. The results on the study of the effect of temperature and the effect of alkaline-to-sand ratio are given in Table 4-1.

Table 4-1 Effect of temperature and effect of alkaline-to-sand weight ratio on the amount of sand decomposed.

Conditions:		
	Monazite	0.5 g
	Alkaline concentration	40 % (w/v)
	Alkaline : sand	1 : 1 - 5 : 1 (w/w)
	Oven temperature	120°C - 180°C
	Heating period	3 hours

Temperature ℃	NaOH ml	NaOH : Sand w/w	Digested Sand g	Digestion %
120	1.25	1 : 1	0.1811	23.34
140	1.25	1 : 1	0.3362	67.23
160	1.25	1 : 1	0.3861	77.24
180	1.25	1 : 1	0.4240	84.80
120	2.50	2 : 1	0.1663	33.26
140	2.50	2 : 1	0.3759	75.18
160	2.50	2 : 1	0.3927	78.56
180	2.50	2 : 1	0.4361	87.20
120	3.75	3 : 1	0.1167	36.21
140	3.75	3 : 1	0.3679	73.54
160	3.75	3 : 1	0.4000	79.97
180	3.75	3 : 1	0.4245	84.92
120	6.25	5 : 1	0.1134	22.68
140	6.25	5 : 1	0.3477	69.53
160	6.25	5 : 1	0.3479	69.57
180	6.25	5 : 1	0.4147	82.91

The per cent digestions as a function of temperature using various sodium hydroxide to sand ratios are plotted in Figure 4-1, from which it is obvious that the per cent of digestion increases

with the increase of temperature. Above 180°C, however, the reaction mass becomes too dry and thick to handle conveniently, and the high temperature adversely affects the solubility of the thorium cake when the cake is dissolved in a mineral acid in a later step. On the basis of handling considerations, Cuthbert (7) gave a maximum temperature of 220°C at which the reaction should be allowed to take place. Since the digestion was performed in an open vessel and the water lost by evaporation could not be compensated exactly though water was added in portions during the reaction time, it is difficult to distinguish between the effect of temperature and the effect of the concentration of the sodium hydroxide.

The per cent digestion as a function of soda-to-sand ratio is plotted in Figure 4-2. The ratio of the stoichiometric amount of sodium hydroxide to the sand is about 0.5 to 1 by weight. In practice, however, the stoichiometric amount is not sufficient to prevent complexes from forming which may occlude excessive amounts of phosphate within the precipitate(7); therefore, an excess of caustic soda must be used. Increasing the ratio of sodium hydroxide to monazite should increase the amount of sand decomposed. Bearse et al. (22) found that by increasing the soda-to-sand ratio from 2 to 1 to 3 to 1 and finally to 5 to 1, the amount of sand decomposed increased from 85 per cent to 92 per cent and finally to 97 per cent respectively. In the present investigation, little differences could be observed by changing the ratio from 2 to 1 to 3 to 1. The per cent digestion using 5 to 1 soda-to-sand ratio

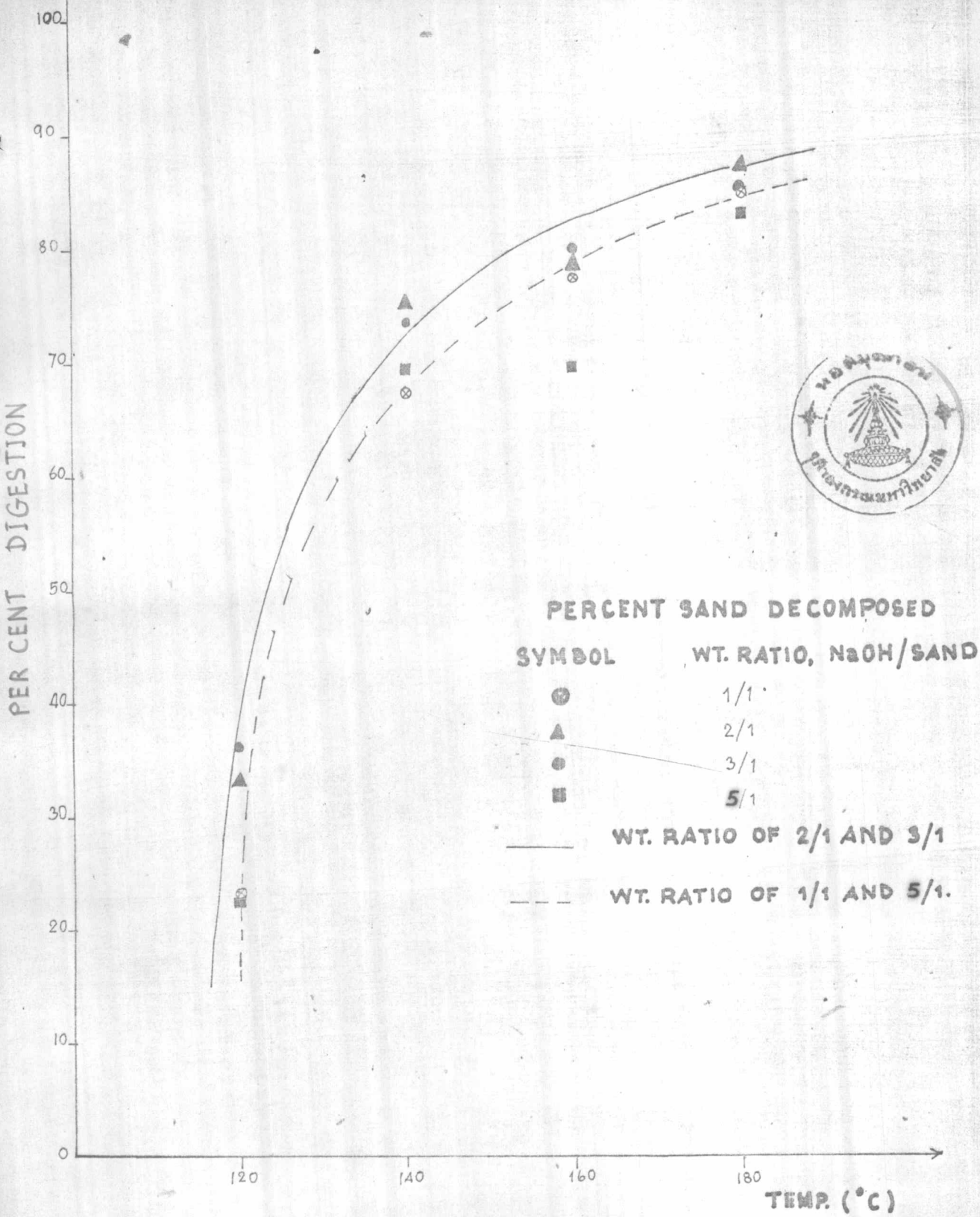

FIG. 4-1 EFFECT OF TEMPERATURE AND EFFECT OF SODIUM HYDROXIDE TO SAND WEIGHT RATIO ON THE DECOMPOSITION OF MONAZITE

CONDITIONS:		
	MONAZITE	0.5 G.
	ALKALINE CONCENTRATION	40 % (W/W)
	ALKALINE : SAND	1:1 – 5:1 (w/w).
	OVEN TEMPERATURE	120°C – 180°C
	HEATING PERIOD	3 HOURS.

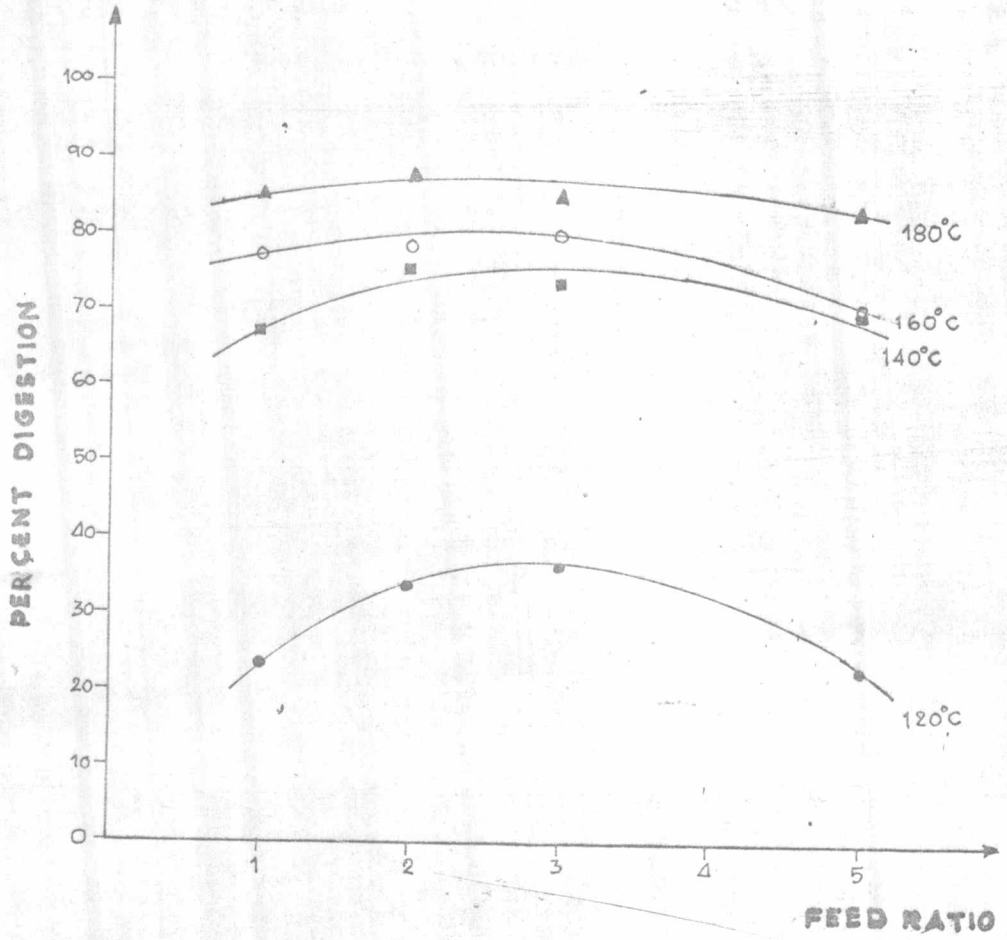

FIG. 4-2 EFFECT OF FEED RATIO AT VARIOUS TEMPERATURE ON THE DECOMPOSITION OF MONAZITE

CONDITIONS:

MONAZITE	0.5 G
ALKALINE CONCENTRATION	40 % (W/W)
ALKALINE : SAND	1:1 – 5:1 (W/W)
OVEN TEMPERATURE	120°C – 180°C
HEATING PERIOD	3 HOURS.

gave a slightly lower yield than expected. Since the mixture was not agitated continuously during the reaction, the lower yield may be caused by the formation of local concentrated or solidified sodium hydroxide, leaving smaller amount of caustic soda for the reaction.

Since a ratio greater than 2 to 1 may not recover more thorium to compensate for the additional cost of the caustic soda, a soda-to-sand ratio of 2 to 1 was chosen.

4.1.2. Effect of digestion time on the decomposition of monazite.

In the study of the effect of time of reaction 0.5 g monazite was mixed with 2.5 ml 40 per cent sodium hydroxide which corresponds to a sodium hydroxide-to-sand weight ratio of 2 to 1 and the reaction mass was heated at 160°C for times varied from 10 to 360 minutes. When the time was reached, the reaction was stopped immediately by dissolving the reaction mass in 40 ml water and the undigested monazite were separated as described in 3.2. The undigested monazite were weighed and the per cent digestion was evaluated as described in 4.1.1. The results are tabulated in Table 4-2.

Table 4-2 Effect of digestion time on the decomposition of monazite.

Conditions:

Monazite	0.5 g
Alkaline concentration	40 % (w/v)
Alkaline : sand	2 : 1 (w/w)
Oven temperature	160°C
Heating period	10 - 360 minutes

Digestion period min.	Digestion %
10	9.02
20	13.98
30	21.60
40	30.50
50	36.71
60	40.20
70	45.63
80	47.58
90	49.40
120	56.34
150	62.72
180	70.12
210	69.55
240	77.20
270	82.32
300	76.52
330	81.42
360	84.32

The per cent digestion as a function of time is plotted in Figure 4-3, from which it is obvious that the rate of reaction increases rapidly in the beginning and comes to saturation after 4 hours of reaction. Under severe reaction conditions, for example, higher temperature, the time required for the complete digestion may be shorter. Since slurry produced under mild reaction conditions is more reactive, severe conditions are avoided. For digestion at 160°C with a soda-to-sand ratio, 4 hours reaction time is needed.

4.1.3. Effect of sodium hydroxide concentration on the decomposition of monazite.

In the study of the effect of sodium hydroxide concentration, 0.5 g monazite was digested with sodium hydroxide which concentrations varied from 20 per cent (w/v) to 100 per cent (w/v). The amount of undigested monazite was weighed and the per cent digestion was calculated. The results are presented in Table 4-3.

Table 4-3 Effect of sodium hydroxide concentration on the decomposition of monazite.

Conditions:		
	Monazite	0.5 g
	Alkaline concentration	20 % (w/v) - 100 % (w/v)
	Alkaline : sand	2 : 1 (w/w)
	Oven temperature	160°C
	heating period	3 hours

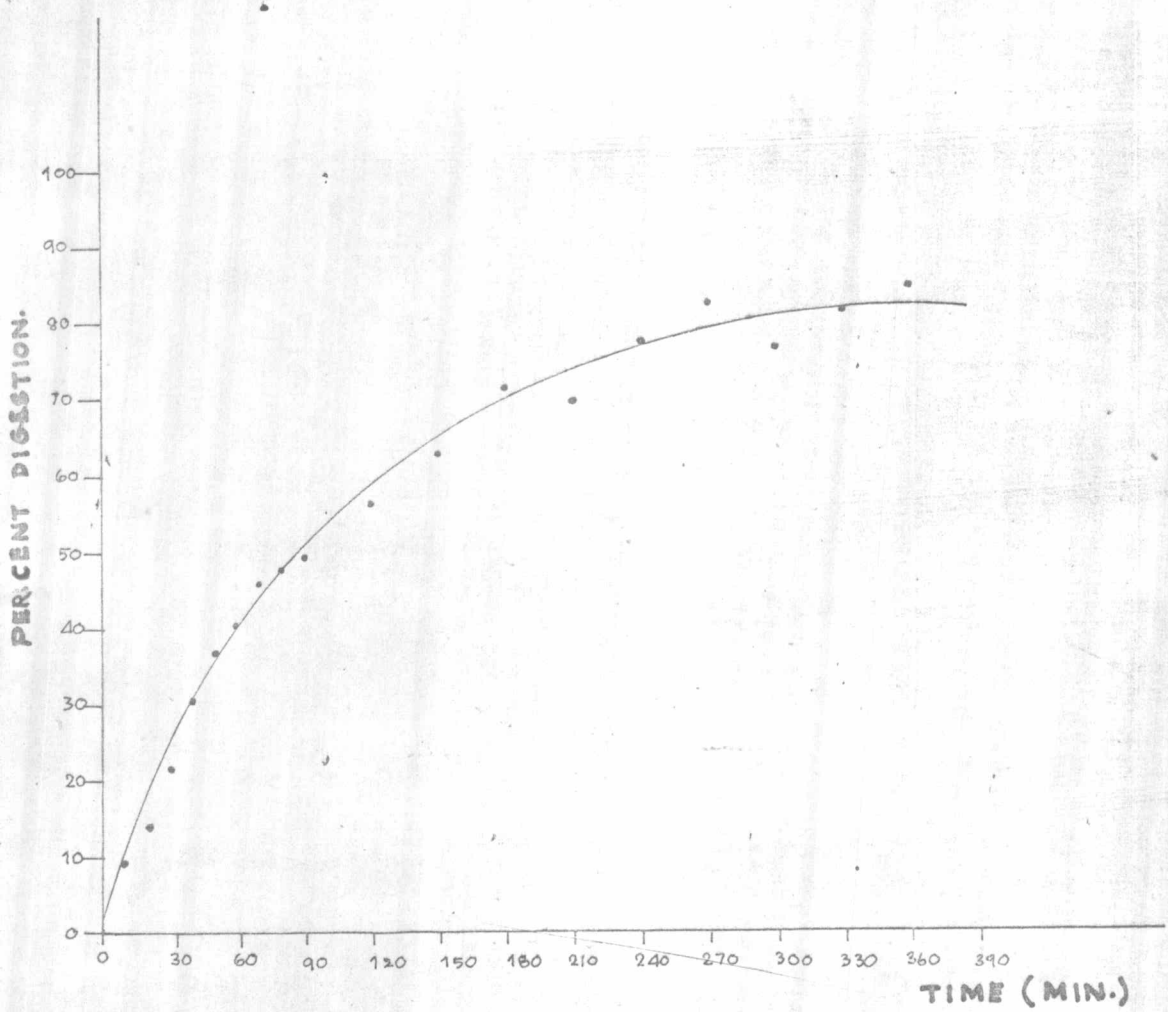

FIG. 4-3 EFFECT OF TIME OF REACTION UPON THE DECOMPOSITION OF MONAZITE

CONDITIONS:

MONAZITE	0.5 G
ALKALINE CONCENTRATION	40 % (W/W)
ALKALINE : SAND	2 : 1 (W/W)
OVEN TEMPERATURE	160° C
HEATING PERIOD	10 - 360 MINUTES.

Alkaline concentration % (w/v)	NaOH ml	NaOH : Sand. w/w	Digestion %
20	5.00	2 : 1	75.52
30	3.33	2 : 1	76.70
40	2.50	2 : 1	70.84
50	2.00	2 : 1	76.48
70	1.43	2 : 1	73.50
80	1.25	2 : 1	70.74
100	1.00	2 : 1	72.08

The effect of alkaline concentration on the decomposition of monazite with sodium hydroxide is shown in Figure 4-4. The alkaline concentration is expressed in per cent by weight of soda to the total volume of the solution. No distinguish effect of the concentration of sodium hydroxide on the decomposition of monazite could be observed. The slight decrease in per cent digestion by increasing the concentration of the sodium hydroxide might be caused by experimental error, since the concentration of the sodium hydroxide solution could not be controlled exactly.

In the case of a larger scale digestion in which the reaction mixture could be stirred continuously and the concentration of the solution could be controlled . S. Srisouta (21) found that the concentration of sodium hydroxide used should correspond to its

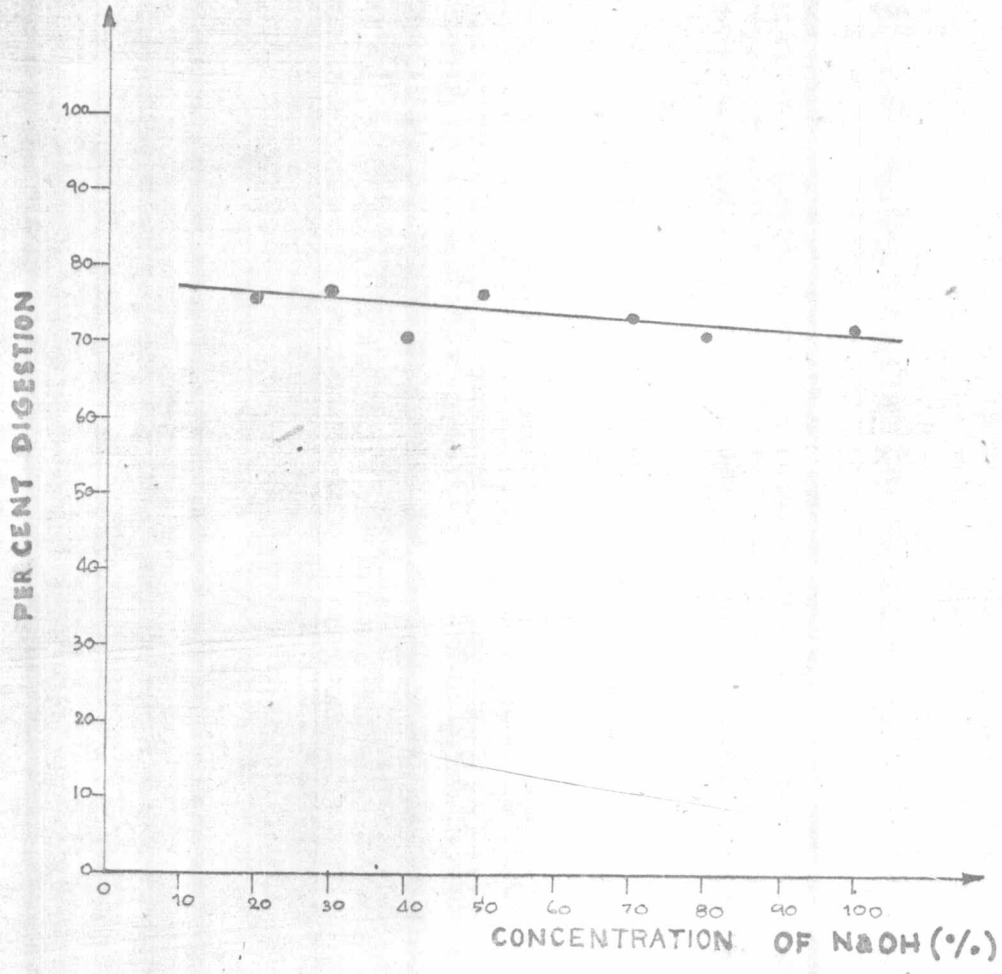

FIG. 4-4 EFFECT OF THE CONCENTRATION OF SODIUM HYDROXIDE ON THE DECOMPOSITION OF MONAZITE.

CONDITIONS:

MONAZITE	0.5 G
ALKALINE CONCENTRATION	20 % (W/V) – 100 % (W/V)
ALKALINE : SAND	2 : 1 (W/V)
OVEN TEMPERATURE	160° C
HEATING PERIOD	3 HOURS.

boiling point, since the efficiency of mixing at the temperature of the boiling point of the sodium hydroxide solution will be highest.

The preparation of sodium hydroxide solution as was performed in this investigation caused a large experimental error. In a large scale operation the sodium hydroxide solution should be prepared at its boiling piont and to prevent the crystallization of the sodium hydroxide crystal, the solution at high concentration should be warmed at 70°C before using. The Dühring lines for the sodium hydroxide-water system in which the boiling point of the sodium hydroxide solution as a function of concentration are plotted is given in Figure 4-5.

4.1.4. Effect of particle size on the decomposition of monazite.

In the study of the effect of particle size, monazite with the grain size ranging from minus 100 to minus 250 mesh were investigated. Sodium hydroxide of 40 per cent was mixed with 0.5 g monazite at a weight-by-weight ratio of 2 to 1 and heated at 180°C. After the reaction, the per cent digestion was calculated.

BOILING POINT CHART OF NaOH SOLUTION

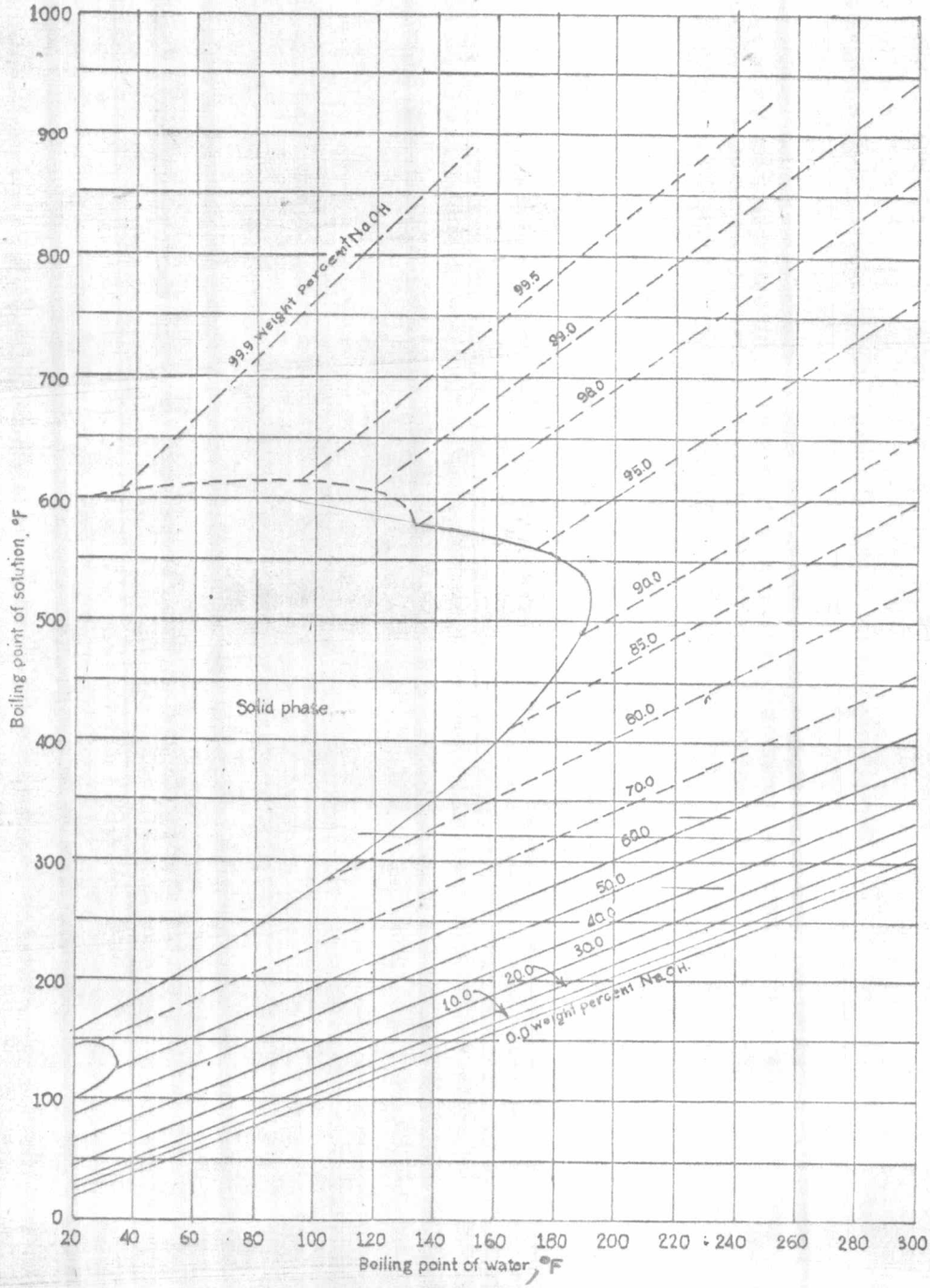

FIG. 4-5 DÜHRING LINES FOR THE NaOH-H_2O SYSTEM

Table 4-4 Effect of particle size on the decomposition of monazite

Conditions:

Monazite	0.5 g
Grain size	- 100 to -250 mesh
Alkaline concentration	40 % (w/v)
Alkaline : sand	2 : 1 (w/w)
Oven temperature	180°C
Heating period	3 hours

Particle size mesh	Digestion %
- 100	73.26
-150 to -200	78.87
- 250	92.87

The per cent digestion as a function of particle size is plotted in Figure 4-6. Reducing particle size to as small a value as possible may increase the per cent digestion. However, decreasing particle size of the monazite may not recover more thorium to compensate for the additional cost of grinding.

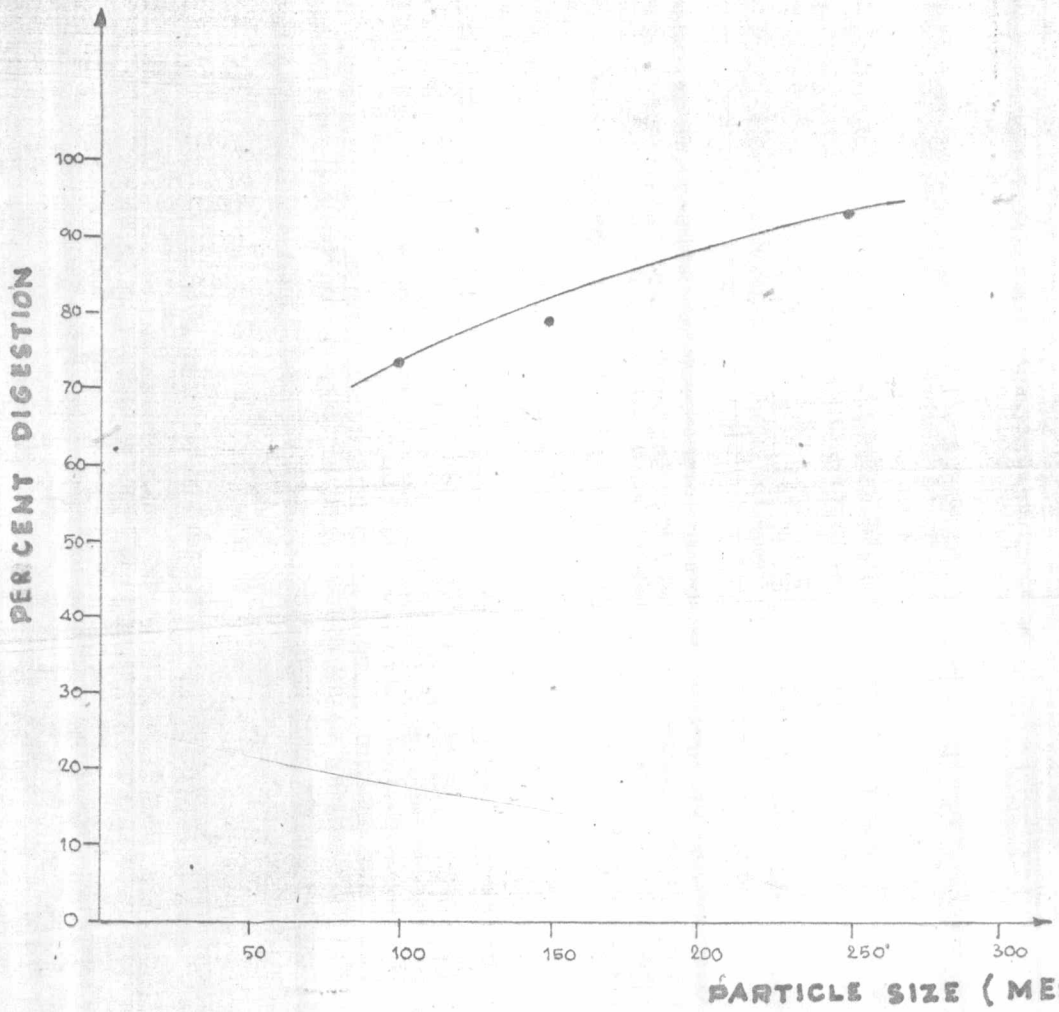

FIG. 4-6 EFFECT OF PARTICLE SIZE OF MONAZITE ON THE COMPLETENESS OF THE REACTION WITH SODIUM HYDROXIDE

CONDITIONS:

MONAZITE	0.5 G.
GRAIN SIZE	- 100 to -250 MESH
ALKALINE CONCENTRATION	40 % (W/W)
ALKALINE : SAND	2 : 1 (W/W)
OVEN TEMPERATURE	180° C
HEATING PERIOD	3 HOURS.

4.2. Acid digestion of monazite

4.2.1. Effect of temperature and effect of acid-to-sand ratio on the decomposition of monazite.

In the study of the effects of temperature and acid-to-sand ratio, monazite in 0.5 g per batch was treated with 96.5 per cent sulphuric acid for 3 hours. The volumes of sulphuric acid varied between 0.5 and 1.4 ml whereas the temperature of the reaction was allowed to vary between 86°C to 210°C. It should be mentioned that, throughout the small scale acid digestion of monazite, it was not possible to measure the temperature of the reaction mixture directly. After mixing sulphuric acid with sand at room temperature, the mass was placed on the hot-stirred plate which was previously set at the approximate temperature of the experiment. When the reaction started, the temperature of the reaction mixture might rise considerably higher than the bath temperature. The temperatures reported here were the temperatures at the end of the reaction which were believed to be stable for over an hour. When the reaction time was over, the mass was cooled to 70°C and 9 ml cold water was added into the mixture. The resulting monazite sulphate solution was filtered through a Whatman number 42 filter paper and the residue after washing with a small amount of water was dried in an oven at 100°C for 1 hour, and the per cent digestion evaluated.

It was observed that the residue could be separated into two fractions with different densities. The color of the lighter fraction

was greyish white and contained only 0.8 per cent thorium. It was assumed that this fraction should compose mainly of zircon, rutile, silica etc. and was represented as a whole as gangue, whereas the heavier fraction was identified according to its density and thorium content to be undigested monazite. Experiments were also performed to separate the two fractions in order to find out the exact per cent of monazite decomposed. The results which are presented in Table 4-5 show that the amount of gangue in the residue increases with the completeness of digestion and under optimum conditions the residue contains upto 75 per cent gangue. When the thorium content in the fraction of undigested monazite was analysed and the amount of extracted thorium evaluated, it was observed, as can be seen in Table 4-6, that the percentage of thorium extracted nearly equals the percentage of sand dissolved. This confirms the theory of Bearse et al. (22) that thorium is closely bound in the monazite crystal structure and is not present as a separate entity.

The effect of temperature and the effect of acid-to-sand ratio on the per cent digestion are plotted in Figure 4-7. The per cent digestion based on the amount of total residue, curve a, and the per cent digestion based on the amount of real undigested monazite, curve b, are plotted separately. The two curves show the same general form that the per cent digestion increases with increasing temperature and acid-to-sand ratio. It is apparent that fairly complete decomposition was obtained at 140°C to 210°C for a weight ratio of 5 to 1 and 3 to 1, and at 170°C for a weight ratio of 2 to 1.

Table 4-5 Effect of temperature and effect of acid-to-sand ratio on the decomposition of monazite.

Conditions:

Monazite	0.5 g
Acid concentration	96.5 % (w/w)
Acid : sand	2 : 1 - 5 : 1 (w/w)
Temperature	86°C - 210°C
Heating period	3 hours

Temperature °C	H_2SO_4 ml	H_2SO_4:sand w/w	Digestion (gangue not separated) %			Digestion (After separation of gangue) %	Gangue Content in the residue %	Thorium extracted %
			1	2	Average			
86	0.54	2:1	75.56	75.86	75.71			
140	0.54	2:1	87.36	88.40	87.88			
166	0.54	2:1	84.42	91.78	88.10			
210	0.54	2:1	89.30	91.12	90.21			
86	0.54	2:1	73.40			78.98	21.00	
140	0.54	2:1	87.70			90.92	26.54	
166	0.54	2:1	88.50			97.06	76.56	
210	0.54	2:1	92.00			98.00	75.00	
86	0.81	3:1	72.00	64.06	68.03			
140	0.81	3:1	89.14	88.48	88.62			
186	0.81	3:1	91.80	91.70	91.75			
210	0.81	3:1	92.34	91.42	91.88			
86	0.81	3:1	76.63			80.88	18.14	85.85
140	0.81	3:1	93.00			96.86	55.14	99.10
166	0.81	3:1	92.75			98.02	72.65	99.70
210	0.81	3:1	92.82			98.62	80.63	99.90
86	1.35	5:1	68.96	71.32	70.14			
140	1.35	5:1	92.06	89.08	90.57			
166	1.35	5:1	91.80	90.40	91.10			
210	1.35	5:1	90.98	88.90	89.94			
86	1.35	5:1	89.00			92.98	35.24	
140	1.35	5:1	93.76			97.08	53.21	
166	1.35	5:1	92.35			98.30	77.75	
210	1.35	5:1	91.95			98.88	86.10	

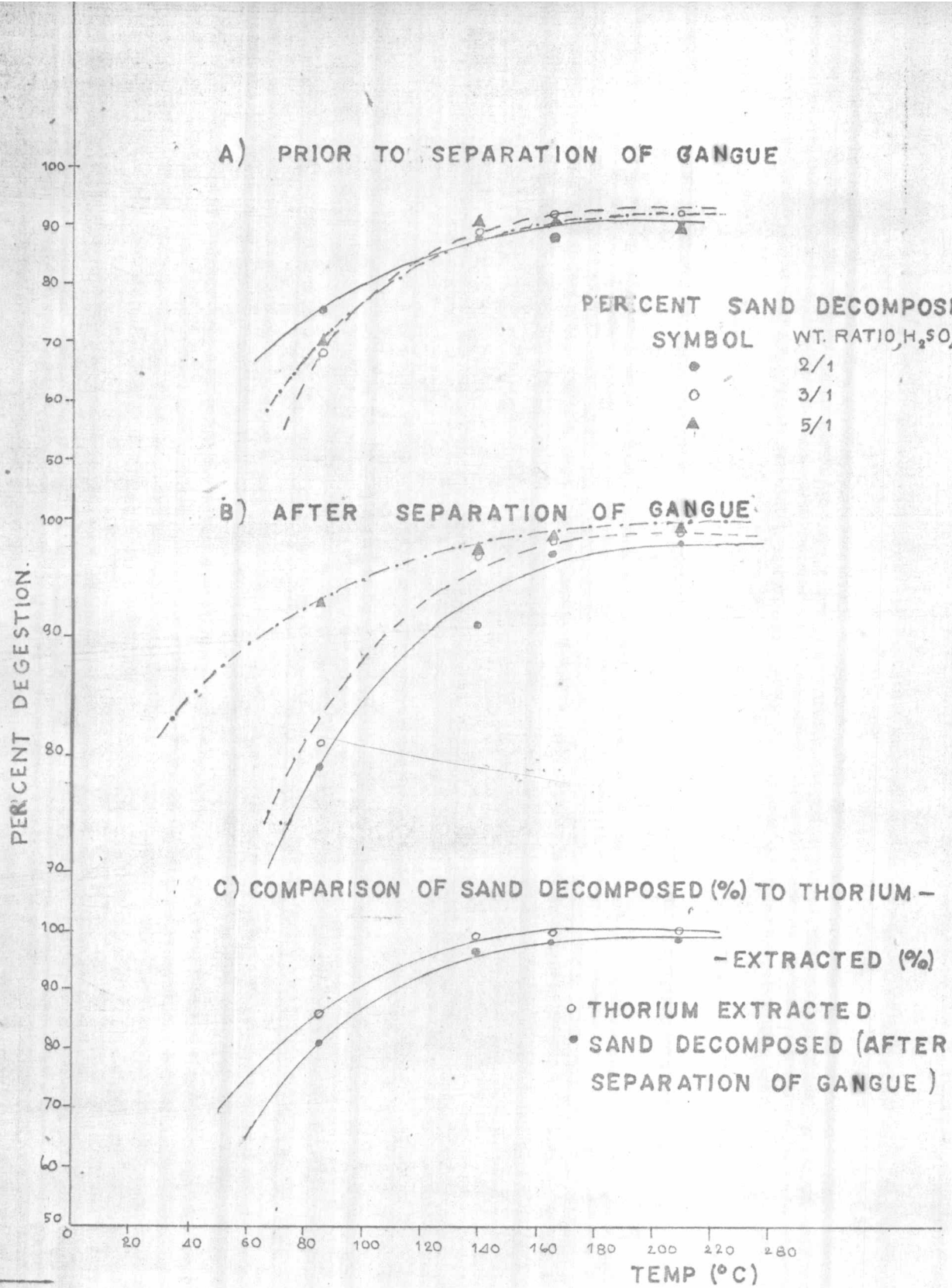

FIG. 4-7 EFFECT OF TEMPERATURE AND ACID TO SAND WEIGHT RATIO IN THE DIGESTION OF MONAZITE

CONDITIONS:

MONAZITE	0.5 G
ACID CONCENTRATION	96.5 %
ACID : SAND	2:1 TO 5:1 (W/W)
TEMPERATURE	86°C – 210°C
HEATING PERIOD	3 HOURS

4.2.2 Effect of acid concentration on the decomposition of monazite.

Monazite, in 0.5 g per batch, was heated at a constant acid-to-sand ratio of 3 : 1 with various concentrations of sulphuric acid ranging from 10 to 96.5 percent. The temperature of the heater was kept contant at 210°C and the procedure described in 4.2.1. was followed. After digestion and separation of the gangue, the residue was dried, weighed and the per cent digestion evaluated. The results of the experiment are shown in Table 4-6 and the per cent digestion as a function of acid concentration is plotted in Figure 4-8.

Table 4-6 Effect of acid concentration on the decomposition of monazite.

Test conditions:	Monazite	0.5 g
	Acid concentration	10% - 96.5% (w/w)
	Acid : sand	3 : 1 (w/w)
	Temperature	210°C
	Heating period	3 hours

Acid concentration %	Acid ml	Digestion (After separation of gangue) %
10	13.60	47.26
30	3.84	49.98
50	2.00	51.94
70	1.25	91.16
90	0.93	98.70
92	0.91	98.85
94	0.88	98.92
95	0.87	98.60
96.5	0.84	98.62

Diluting concentrated sulphuric acid with water has two effects: the reactivity of the acid is decreased, and the fluidity of the reaction mixture is increased, providing better agitation. The first effect decreases and the second increases the over all rate of reaction. Sulphuric acid with concentration higher than 90 per cent gave fairly complete digestion at 210°C.

4.2.3. Effect of time of reaction on the decomposition of monazite.

In the investigation of the effect of time of reaction, 0.5 g monazite were treated with 96.5 per cent sulphuric acid with an

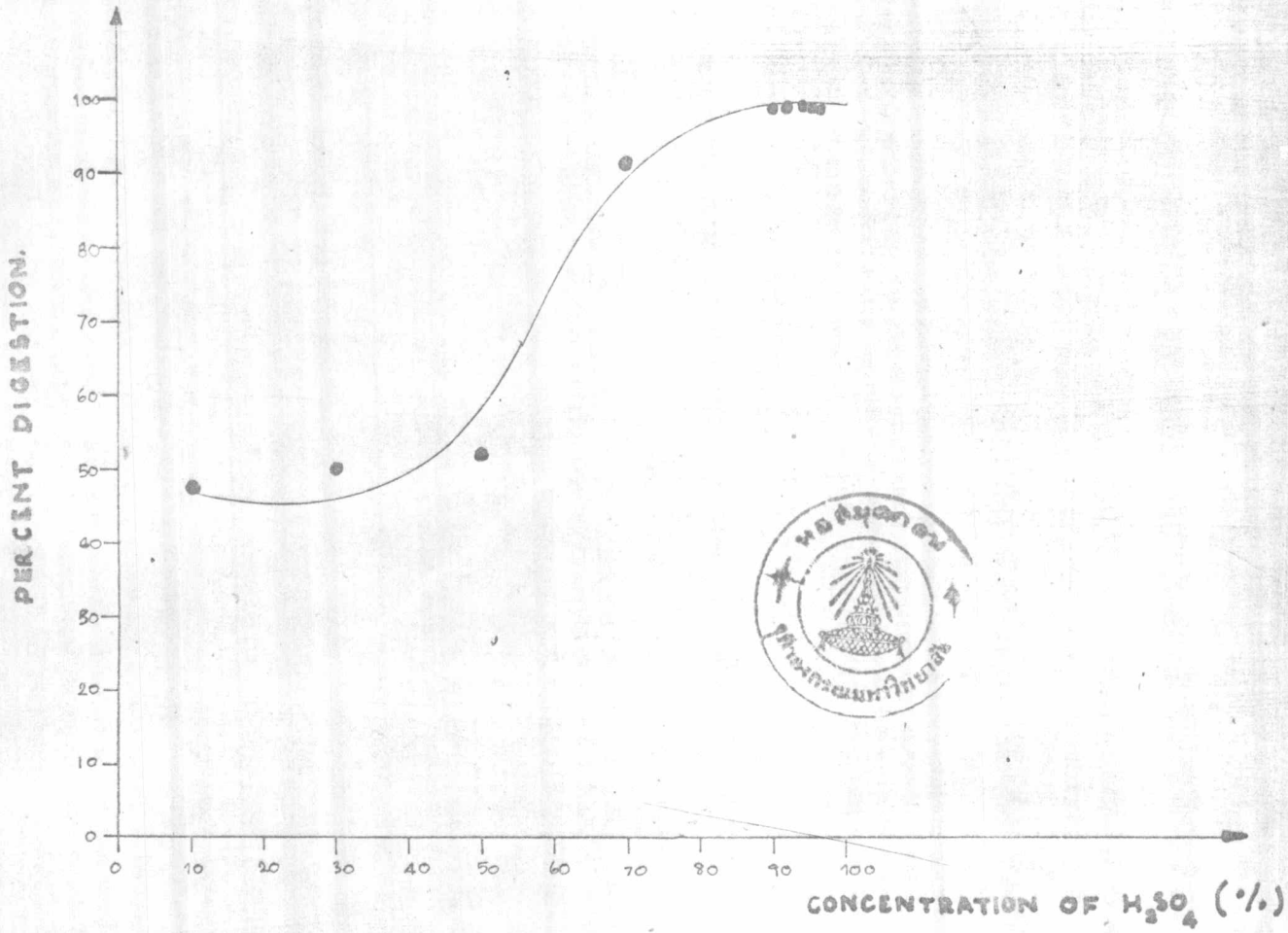

FIG. 4-8 EFFECT OF ACID CONCENTRATION ON THE DECOMPOSITION OF MONAZITE

CONDITIONS:		
MONAZITE	0.5 G.	
ACID CONCENTRATION	10-96.5	% (W/W)
ACID : SAND	3: 1	(W/W)
TEMPERATURE	210	°C
HEATING PERIOD	3	HOURS.

acid-to-sand ratio of 3 to 1 and the temperature of the heater was set at 210°C. The reaction was allowed to take place for a period varying from 10 to 330 minutes. When the reaction time was reached, the reaction was stopped immediately by adding cold water into the reaction mass. After the gangue was separated, the undigested monazite was dried and weighed. The results of this experiment are shown in Table 4-7.

Table 4-7 Effect of time of reaction on the decomposition of monazite.

Conditions:

Monazite	0.5 g
Acid concentration	96.5 % (w/w)
Acid : sand	3 : 1 (w/w)
Temperature	210°C
Heating period	10 - 330 minutes

Digestion period min.	Digestion (After separation of gangue) %
10	92.53
20	97.46
30	96.73
40	97.74
50	96.72
60	98.04
70	98.45
80	98.56
90	98.38
120	98.34
150	98.46
180	98.71
210	98.25
240	98.41
270	98.16
300	98.12
330	98.47

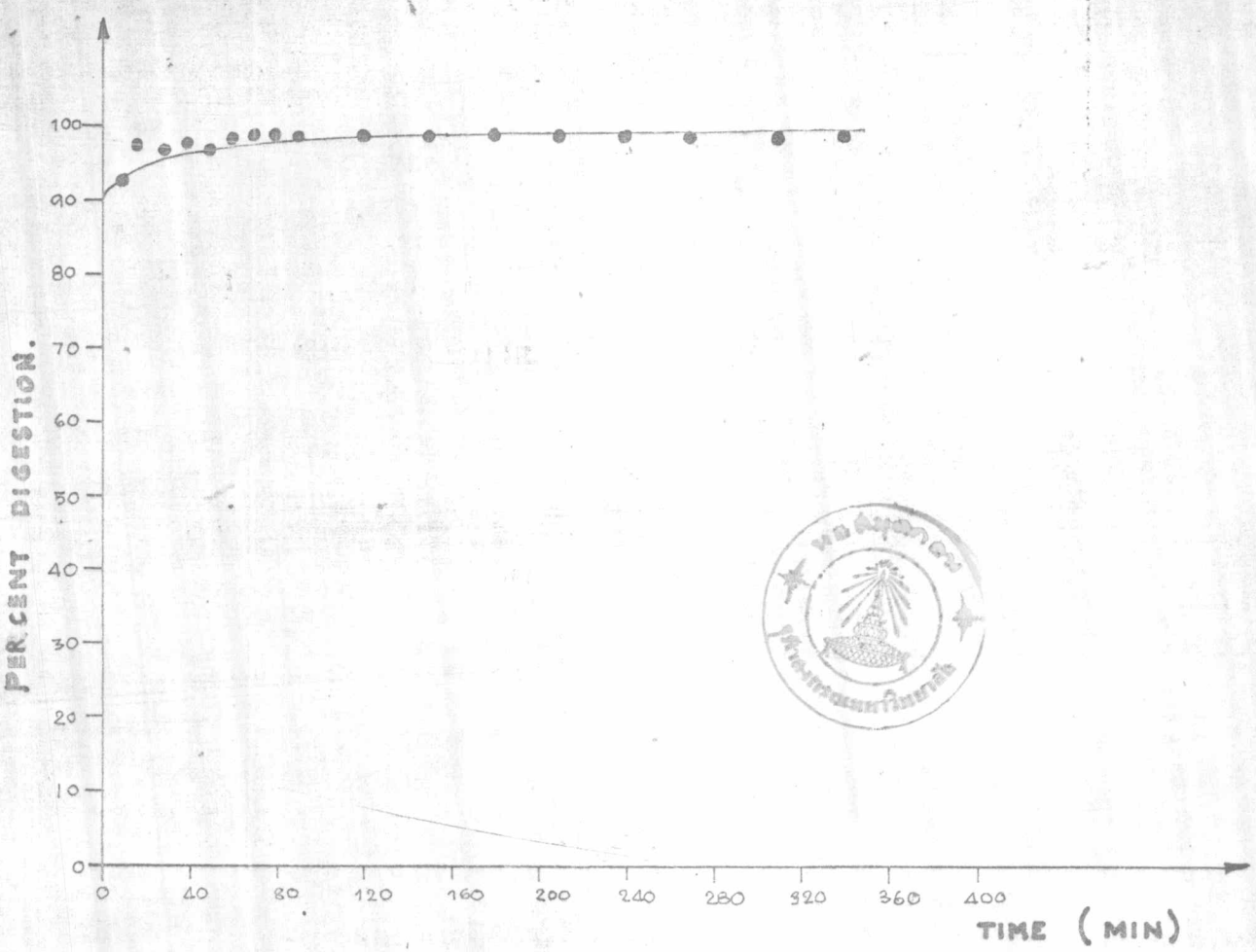

FIG. 4-9 EFFECT OF DIGESTION TIME ON THE DECOMPOSITION OF MONAZITE

CONDITIONS:

MONAZITE	0.5 G.
ACID CONCENTRATION	96.5 % (W/W)
ACID : SAND	3 : 1 (W/W)
TEMPERATURE	210 °C
HEATING PERIOD	10-330 MINUTES.

From Figure 4-9 in which the per cent of monazite decomposed is plotted as a function of reaction time, it would be seen that the reaction between monazite and sulphuric acid takes place very rapidly. Under the given conditions, the reaction was completed within 20 minutes.

4.3. Chemical yield and purity of the extracted thorium.

The standard monazite, NBL-7A, was used for the investigation of the yield of each chemical processing step. The general digestion procedure described in 3.2. with the optimum conditions which are summarized in Table 4-8, were followed. The crude thorium precipitate was dissolved in 4 N nitric acid and then subjected to purification by solvent extraction with conditions, sequences and number of stages tabulated in Table 3-2. The amount of thorium lost in each processing step was checked by analysing the thorium content in the discarding fraction. Thorium was precipitated from the stripped solution in the form of thorium oxalate, after which was converted to thorium oxide by ignition at 1000°C. The results of the experiment are presented in Table 4-9.

Table 4-8 Optimum conditions for the decomposition of monazite

Method	Temperature* C°	Acid or Alkaline concentration %	Acid or Alkaline -to-sand ratio (w/w)	Heating period hr.
Acid	220	96.5	3 : 1	2
Alkaline	140	40.0	2 : 1	4

*The oven temperature used in 4.3 for alkaline digestion was 160°C.

TABLE 4-9 CHEMICAL YIELD AND PURITY OF THORIUM FROM EACH PROCESSING STEP

CONDITIONS: MONAZITE NBL-7A (8.5 PER CENT THORIUM.)

GRAIN SIZE - 250 MESH

DIGESTION CONDITION SEE TABLE 4-8

SOLVENT EXTRACTION SEE TABLE 3-2

MONAZITE	UNDIGESTED MONAZITE		CRUDE PRECIPITATION								SOLVENT EXTRACTION			RECOVERY OF TRISODIUM PHOSPHATE
			OXALATE PRECIPITATION		THORIUM IN FILTRATE		HYDROXIDE PRECIPITATION		THORIUM IN FILTRATE		THORIUM OXIDE OBTAINED			
											YIELD		PURITY	
g	WEIGHT g	PER CENT	WEIGHT g	THORIUM IN TOTAL PRECIPITATE %	g/l	TOTAL g	WEIGHT g	THORIUM IN TOTAL PRECIPITATE %	g/l	TOTAL g	WEIGHT g	PER CENT	THORIUM OXIDE IN TOTAL OXIDE %	g
ALKALINE DIGESTION														
0.50	0.0244	4.8	0.5899	9.18	Nil	Nil	0.3614	33.75	Nil	Nil	0.0192	40.0	81.01	0.27
1.00	0.0729	7.3	1.2740	12.89	Nil	Nil	0.7372	27.00	Nil	Nil	0.0493	51.0	85.10	0.60
ACID DIGESTION														
0.50	0.0043	0.86	—	—	—	—	0.4110	22.89	0.04	<0.0024 *	0.0276	57.0	91.00	—

— Not analysed

* Approximate total volume of solution

4.4. Monazite processing for thorium in scale of 50 g per batch.

In order to obtain more reliable data on the yield of each chemical processing step and also to investigate the problems one would face in the large scale processing, experiments as described in 4.3 were repeated using 50 g monazite per batch. The condition for digestion and for solvent extraction presented in Table 4-8 and 3-2 were applied. It should bementioned that, the number of extraction stages was larger here than in the small scale investigation. Since it was found that the filtration of crude thorium hydroxide from the alkaline digestion was very time-consuming, so in the experiment which was marked with a, in Table 4-10, the hydroxide was dissolved in dilute sulphuric acid and thorium was precipitated at sulphate. Consequently the weight of the crude thorium precipitate waslarger in this case. From the results which are shown in Table 4-10, the detrimental effect of the sulphate ion to the extraction of thorium is obvious. The thorium in the raffinate rises from 1.9 per cent for the extraction in the absence of sulphate ion to 20.6 per cent for the extraction in the precence of sulphate ion.

Using minus 200 mesh monazite, sulphuric acid gives under optimum condition a higher yield of digestion than caustic soda. However, as is shown in section 4.1.4. the per cent digestion can be increased to 90 per cent by decreasing the particle size to about minus 250 mesh.

TABLE 4-10 CHEMICAL YIELD AND PURITY OF THORIUM FROM EACH PROCESSING STEP

CONDITIONS: MONAZITE CONTAINING 8.5 PER CENT THORIUM WITH A GRAIN SIZE OF -200 MESH.
DIGESTION CONDITIONS SEE TABLE 4-8
SOLVENT EXTRACTION SEE TABLE 3-2

MONAZITE	UNDIGESTED MONAZITE		CRUDE PRECIPITATION.					SOLVENT EXTRACTION.						THORIUM OXIDE OBTAINED			IMPURITIES IN THORIUM. OXIDE		RECOVERY OF TRI SODIUM. PHOSPHATE
			CRUDE THORIUM [a]		THORIUM IN FILTRATE.			THORIUM CONTENT IN SCRUBBED SOLUTION.			THORIUM CONTENT IN RAFFINATE.			YIELD.		PURITY			
					AMOUNT	TOTAL		AMOUNT	TOTAL		AMOUNT	TOTAL							
g	WEIGHT g	PER CENT	WEIGHT g	THORIUM IN TOTAL PRECIPITATE %	g/l	WEIGHT g	PER CENT	g/l	WEIGHT g	PER CENT.	g/l	WEIGHT g	PER CENT	WEIGHT g	PER CENT	THORIUM OXIDE IN TOTAL OXIDE %	CERIUM OXIDE (CeO_2) g	LANTANUM OXIDE (La_2O_3) g	g
ALKALINE DIGESTION																			
50	8.5	17.0	8.4	—	0.154	0.15	3.6	—	—	—	0.28	0.08	1.9	2.5	60	~100	Nil	0.2	53.31
50	9.8	19.5	56.0 [a1]	8.5	0.128	0.13	3.1	0.1885	<0.38 [b]	<9.1 [b]	0.47	0.59	13.9	2.1	50	~100	1.3	2.8	54.29
ACID DIGESTION																			
50	0.93	1.8	76.6	—	Nil	Nil	Nil	—	— [b]	— [b]	0.26	0.77	18.2	5.6	116	~100	Nil	0.9	—
50	1.04	2.1	70.7	15.1	Nil	Nil	Nil	0.0736	<0.22 [b]	<5.2 [b]	0.24	0.54	12.6	4.3	90	~92	5.6	2.9	—
50	0.76	1.5	78.2	14.7	Nil	Nil	Nil	0.0633	<0.19 [b]	<4.5 [b]	0.31	0.87	20.6	4.5	94	~96	1.8	0.6	—

Remarks a) The crude thorium precipitate in the acid digestion is believed to be in the form of phosphate and sulphate complexes. The crude thorium precipitate in the alkaline digestion is normally in the form of hydroxide. In the case marked with a, the hydroxide precipitate was converted to sulphate by the addition of dilute sulphuric acid, (see text).

b) Approximate percent of thorium content in scrubbed solution is given since the total volume of solution was not accurately measured.

\- Not analysed

The gamma spectrum of the final thorium oxide powder from alkaline processing is shown in Figure 4-10 in comparison to the spectra of monazite sample prior to processing, the crude thorium nitrate solution and spec pure grade thorium oxide. The contamination by cerium oxide and lanthanum oxide was determined using the Ge (Li) detector. Since Pa^{233} which is built up by the decay of Th^{233} gives strong gamma-lines in the region of 200-400 KeV, the determination of the rare earths contents are difficult and the results might not be accurated. The spectra of the thorium oxide powder from alkaline digestion measured by Ge (Li) detector at one and seven days after irradiation are shown in Figure 4-11 compared to the spectrum of spect pure grade thorium oxide

Comparing the results of alkaline digestion from Table 4-9 and Table 4-10, it is apparent that it is not essential to precipitate

thorium as oxalate and then convert the oxalate to hydroxide prior to solvent extraction. The purity of the final products can be increased by increasing the number of scrubbing stages.

The difference in the yields of thorium from the two processes is insignificant. It should be mentioned that experiments onalarger scale must be performed to obtain more reliable data on chemical yields. From the present investigation it is obvious that the number of scrubbing performed in this experiment is not sufficient to produce high purity thorium oxide.

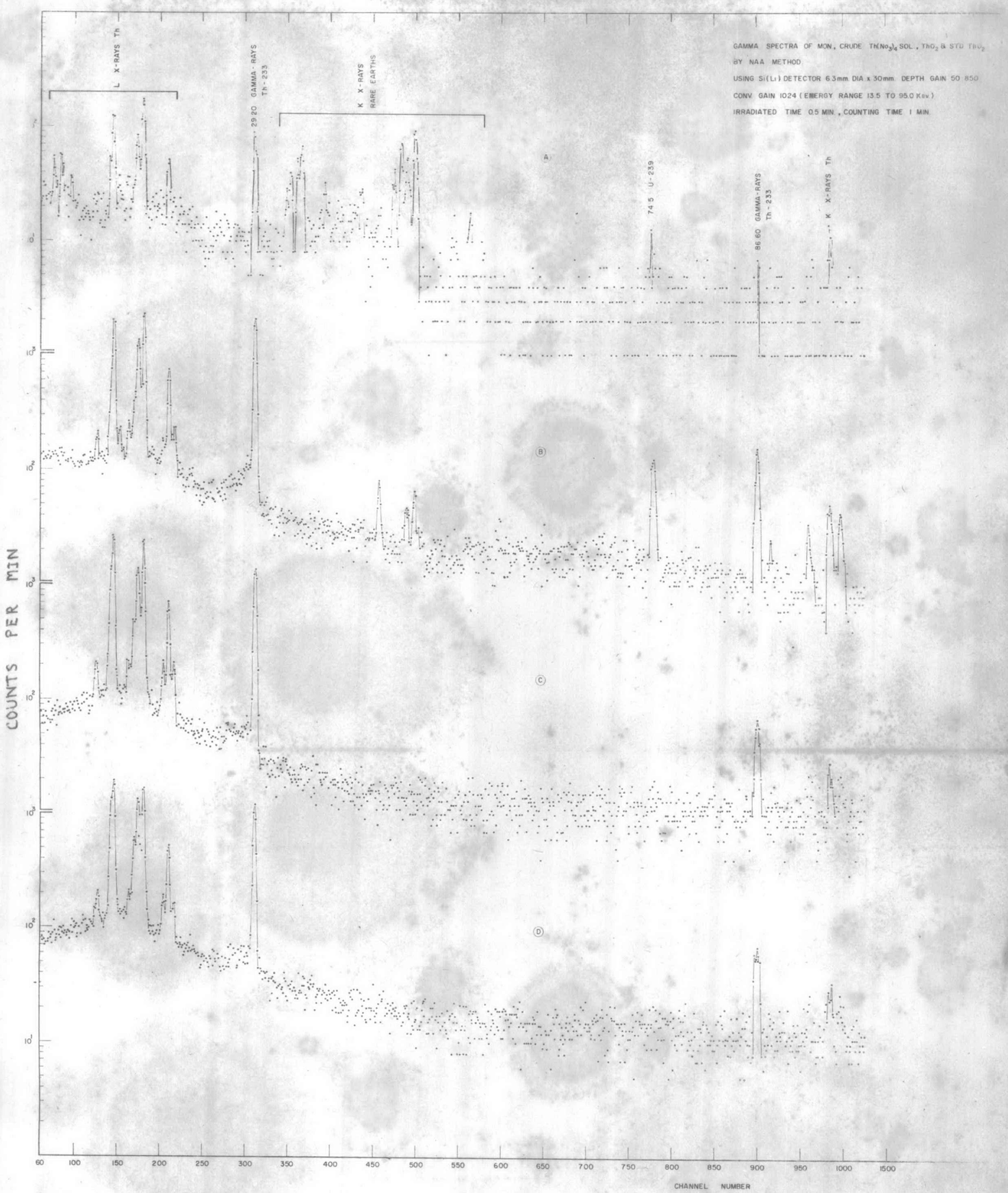

Fig. 4 - 10 Gamma spectra of monazite, crude thorium nitrate solution, extracted thorium oxide and standard thorium oxide by neutron activation analysis.

Ⓐ: Monazite
Ⓑ: Crude thorium nitrate solution
Ⓒ: Extracted thorium oxide
Ⓓ: Standard thorium oxide

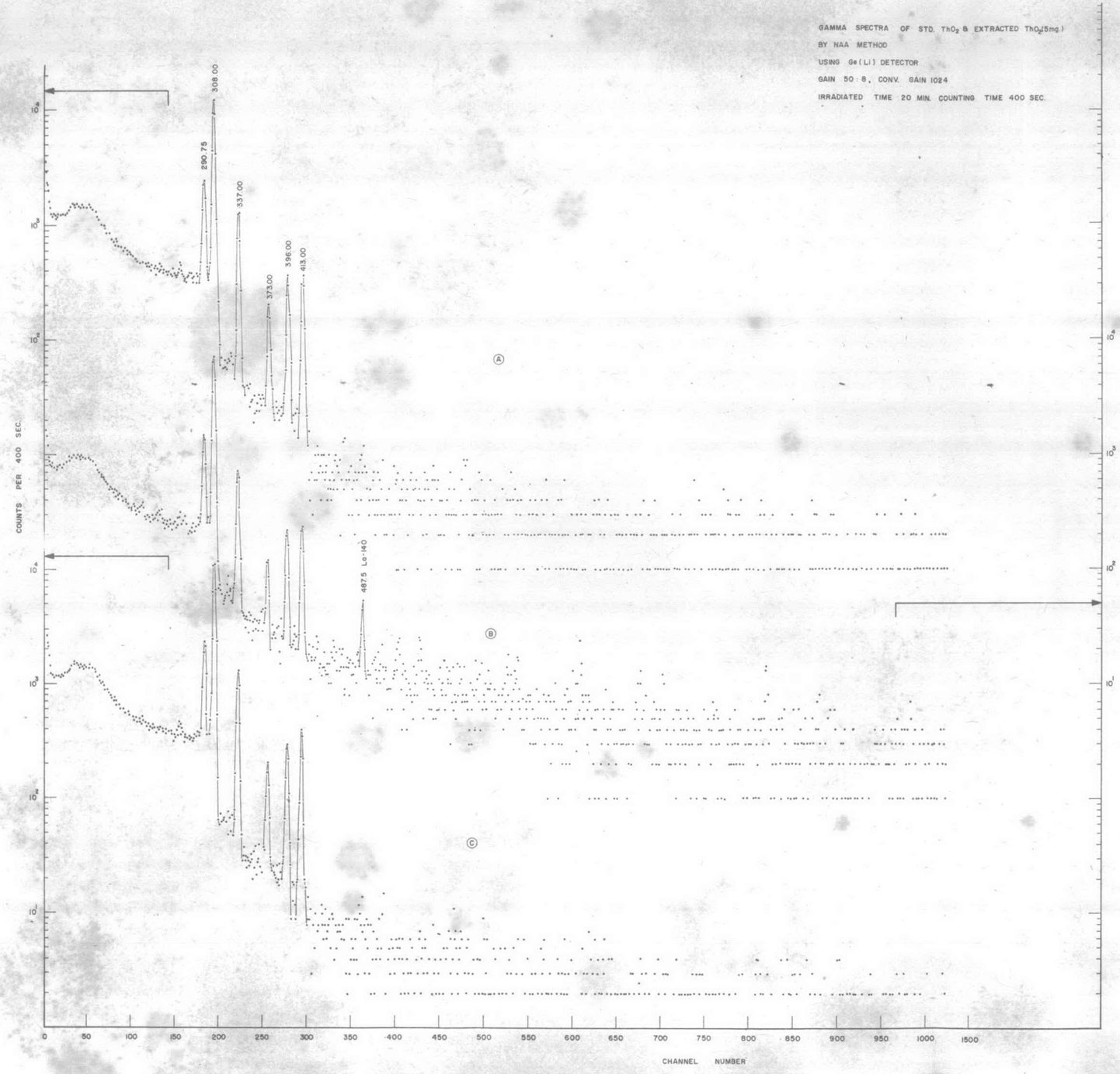

Fig.4-11 Gamma spectra of standard thorium oxide and extracted thorium oxide by neutron activation analysis

Ⓐ: Standard thorium oxide

Ⓑ: Extracted thorium oxide (one day after irradiation)

Ⓒ: Extracted thorium oxide (seven days after irradiation)