CHAPTER II

EXPERIMENTAL

Standards and samples

Monazite sand No. 7 A, containing 9.7% ThO_2 and 0.35% U_3O_8 as supplied by the New Brunswick Laboratory (NBL) was used as standard both in the radiometric and in the activation analyses for the determination of the contents of uranium and thorium. For the studies of the status of RE in the uranium family low grade uranium ore (U-ore) standards Nos. S_1 (torbernite), S_2 (torbernite), S_3 (Carnotite) and S_4 (Uraninite) supplied by the National Bureau of Standards (NBS) containing 0.471%, 0.313%, 0.418% and 0.375% U_3O_8, respectively were used. Two of them, Nos. S_1 and S_2 are guaranteed to be in RE. The contents of uranium and thorium in 12 monazite samples supplied by the Department of Mineral Resource, Ministry of Industries, Bangkok were analysed.

2.1 Radiometric method

2.1.1 Sample preparation

2.1.1.1 Preparation of samples for γ-ray measurements. All samples were separately ground into fine powders (-100 mesh). The

powders were filled into two kinds of containers. For measurements using a well-type NaI (Tl) detector, polyethylene vials, 1.6 cm. dia X 5.5 cm.height, were used, otherwise aluminium planchettes, 3 cm.dia X 0.7 cm.height, were used. In the first case the powders were filled into the vial to 1 cm.of height which corresponds to approximately 5 grams monazite. The covers of the vials were sealed by a heating sealer. In the latter case the powders were filled into the planchette with occasional tapping to avoid void volumes; then the surface of the planchette was covered by a thin film of mylar and finally the sample was sealed into a polyethylene bag. The weight of monazite in such containers varied from 12 to 16 grams. All standards used were prepared in the same way.

2.1.2 γ - detectors Detectors and their electronics which were used for the detection of γ - activities are shown in Table 2.1.

Table 2.1

Detectors used for the detection of γ-activities

Detector	Producer	Analyser (channel)	High voltage supply (Volt)	Active volume	FWHM	Peak / compton	Preamplifier	Linear amplifier	Type of sample container
A NaI (Tl)	Nuclear Chicago	single	2300 (Nuclear Chicago)	2.00 in.dia.X 1.75 in. height, dimension of the well: 0.65 in.dia X 1.50 in depth	–	–	Nuclear Chicago	Nuclear Chicago	1.6 cm. dia. X 5.5 cm. height polyethylene vials
B NaI (Tl)	Nuclear Data	128	1000 (Biard Atomic 312 A)	3 in.dia.X 3 in.height	–		Nuclear Data	Nuclear Data ND – 110	3.0 cm.dia.X 0.7 cm. height aluminum planchettes
C Ge (Li)	ORTEC 8001 – 0322	1024	2000 (ORTEC 459)	26.2 cc.	2.2 kev. at 1332 kev.	24	ORTEC 120	Nuclear Data 8001 – 0822	Same aluminum planchettes as above
D Si (Li)	ORTEC 7016 – 06215	1024	1500	6.3 mm.dia. X 3.0 mm. depth	5.9 kev. Mn K$_\alpha$	–	–	ORTEC 761A	0.8 cm.dia.(OD) X 1 cm. height polyethylene vials.

The relative efficiencies of the detector A at various energy ranges as measured by Bernard J. Snyder and Geza L. Gyorey (37) are given in Table 2.2. The relative efficiencies of the detector C as shown in Table 2.3 were measured after L.J. Jardine (38) using Tb^{160}. The efficiency curves obtained for the two detectors are shown in Figure 2.1.
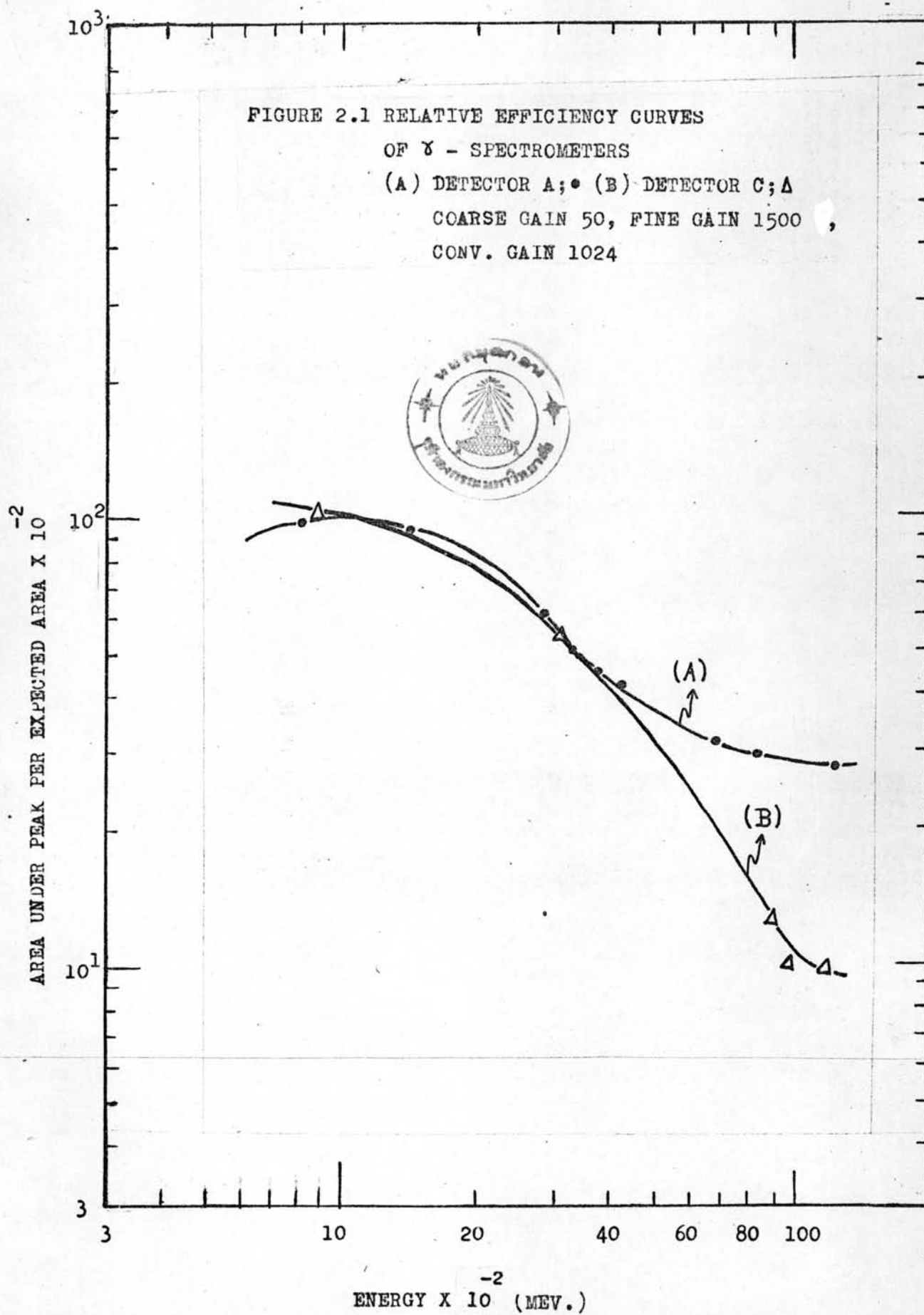
Table 2.2

The relative efficiencies of the detector A

at various energies (38)

Quantum energy Mev	Efficiency
0.080	0.97
0.142	0.94
0.279	0.61
0.321	0.51
0.364	0.46
0.411	0.43
0.662	0.32
0.835	0.30
1.114	0.28
1.332	0.25

Table 2.3

The relative efficiencies of the detector C

at various energies using Tb^{160}

Quantum energy (Mev)	Relative intensity (39)	Count under peak (c/20min)	Count relative to 0.087 Mev peak	Count under peak per expected count
0.087	12 (1)	3764	3764	1.00
0.299	30 (2.50)	5120	9410	0.54
0.879	31 (2.58)	1273	9711	0.13
0.966	22 (1.83)	703	6888	0.12
1.178	15 (1.25)	477	4705	0.10

FIGURE 2.1 RELATIVE EFFICIENCY CURVES OF γ - SPECTROMETERS (A) DETECTOR A; ● (B) DETECTOR C; Δ COARSE GAIN 50, FINE GAIN 1500, CONV. GAIN 1024

For the measurement of gross β -activity, a Geiger-Muller counter was used. It consisted of an end window G-M tube (Nuclear Chicago Corporation) of thickness 1.4 mg per cm^2 , and serial No. 014860 which is connected with a scaling unit from Nuclear Chicago, Model No. 161 A. High voltage supply was 900 volts.

2.1.3 Radiation measurements

2.1.3.1 Determination of the thorium content by γ -measurements. The contents of thorium in the samples were first determined by measuring the activities under the 0.91 and 2.61 Mev peaks. For evaluation, the activities of the samples after subtraction of background were compared to that of the standard which was measured under the same conditions. Detectors A, B and C were used; their sensitivities and feasibilities for the 0.91 and 2.61 Mev peaks were studied.

2.1.3.2 The equilibrium condition of the uranium series in samples was checked by two different methods:

a) Method based on the measurement of gross β - and gross γ - activity. Since thorium is present in all local monazite samples and the content could be easily analysed by γ - ray spectrometry at 2.61 Mev, the activity contributed by thorium could be corrected using monazite NBL-7A which U_3O_8 content (0.35%) was previously corrected using the U-ore S_1 data. The G.M. counter was used for the gross β - and the detector A was used for the gross γ - measurement.

b) Method based on γ - measurements at the regions of
80 - 100 Kev and 610 Kev. The γ -activity in the region of
80 - 100 Kev arises from the decay of Th^{234} whereas the high
intensity peak at 610 Kev is due to RaC (Bi^{214}), the daughter
product of Ra^{226}. The ratio of the activities at the two energy
peaks after correction of the detector efficiencies is evaluated.
An agreement in the ratio of the activities at 80 - 100 Kev and
610 Kev with that obtained from the standard U-ore S_1 shows that
the U-family in the sample is in RE. Detector A and C were used
for this measurement.

2.1.3.3 Determination of the U_3O_8 contents in samples in
which the uranium family is in RE. In case that the uranium in
the sample is in RE, as evident from either (i) the agreement
between e $(U_3O_8)_\beta$ and e $(U_3O_8)_\gamma$ measurements, or (ii) the agree-
ment in the ratio of the activities at 80 - 100 Kev and 610 Kev,
with that obtained from the standard U-ore S_1; the U_3O_8 content
is determined from the gross activity measurement or intensity
measurements at any of the major γ -ray bands. For gross β -
activity, the G.M. counter was used whereas for gross γ -activity
detector A was used. The U_3O_8 content was also checked by the
intensity measurement under the 1.76 Mev peak via detector A.

2.1.3.4 Determination of the U_3O_8 contents in samples in which
the uranium family is out of RE. In case where the uranium in the
sample is out of RE, the U_3O_8 in RE and the U_3O_8 out of RE can be
calculated with some confidence from the intensity measurements
in the 80 - 100 Kev and the 610 Kev regions. For this purpose,

pure U_3O_8 out of equilibrium was prepared by dissolving uranyl nitrate in water and successive precipitate of ammonium diuranate by addition of concentrated ammonium hydroxide. The precipitate was ignited in air at the temperature of 1000°C for about three hours. The U_3O_8 obtained was diluted with standard sand from BDH chemicals Ltd., which is known to contain negligible radioactivities to give a 16.47% U_3O_8 standard. From the specific activities per gram per percent uranium oxide of the standard U-ore S_1, of the uranium oxide powder and of the sample, at 80 - 100 Kev and 610 Kev, simple algebraic equations could be derived from which the percent of U_3O_8 in RE and out of RE could be solved. Detector A was used for the measurements of activities in the two regions.

2.1.3.5 Simultaneous determination of ThO_2 and U_3O_8 contents in samples. For the simultaneous determination of thorium and uranium using equations 1 and 2 described in section 1.3.2.1, the constants K_{UE_1}, K_{UE_2}, K_{ThE_1} and K_{ThE_2} were first determined using standard U-ore S_1 and monazite NBL-7A. The contents of uranium and thorium could be solved by substitution of the constants in the two equations. Detector A was also used for this purpose.

2.2 Non-destructive neutron activation analysis for the assay of the uranium and the thorium contents in monazite samples

2.2.1 Sample preparation Monazite samples prepared as described in section 1.1 were weighed, 0.05 gram each, into polyethylene vials with 0.8 cm. dia X 1 cm. height which were previously cleaned

with alcohol and dried. The monazite NBL-7A. was prepared in the same way and used as the standard for comparison.

2.2.2 Sample irradiation and measurement Two samples and one standard were subjected to irradiation at the same time for a period of two minutes. The neutron flux in the pneumatic tube of the Thai Research Reactor 1 at the position where irradiations were performed was approximately $7.6 \times 10^{10} n/cm^2 sec$. Gamma-ray spectrometry was performed using detector D. The block diagram of the whole counting system is shown in Figure 2.2.

The standard and the samples were counted for 2 minutes each. The areas under the 29.2 Kev and the 74.5 Kev peaks were used for the determination of the contents of thorium and uranium respectively.

Figure 2.2

The block diagram of the counting system
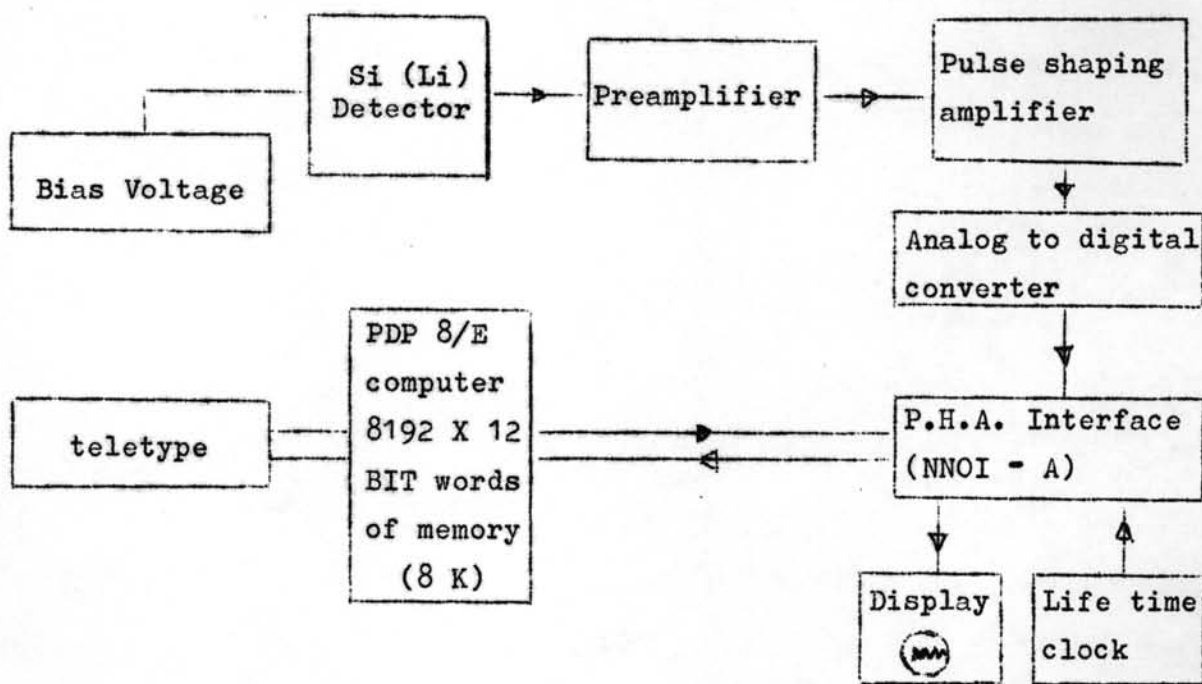
2.3 Spectrophotometric determination of thorium in monazite

The method described by W.J. Ross and J.C. White (40) for the determination of thorium in samples resulting from the leaching of monazite and other raw materials with sulphuric acid and from subsequent stages in the extraction of thorium by tri-n-octyl-phosphine oxide (TOPO) was applied by N. Sridaranop (41) to the determination of thorium in some local monazites. To be able to compare the accuracy and the rapidity between the chemical and the physical methods in the analysis of the thorium content, the mon. NBL-7A was analysed via the mentioned spectrophotometric method.

2.3.1 Instrument The grating double beam spectrophotometer, Perkin Elmer, Model 124, containing a pair of matching silica cells of 1 cm. light path was used.

2.3.2 Reagents All reagents were from A.R. grade. Thorium nitrate stock solution, containing 1000μg thorium per ml, was prepared by dissolving 0.59484 gram thorium nitrate tetrahydrate in 250 ml water. Thorium solutions with different concentrations were prepared by appropriate dilution of the stock solution.

Tri-n-octylphosphine oxide, 0.1 M, was prepared by dissolving 3.86 grams of tri-n-octylphosphine oxide in 100 ml cyclohexane.

Thorin, 0.1% solution, was prepared by dissolving 0.1 gram O-(2-Hydroxy-3, 6-disulfo-1-naphthylazo) benzenearsonic acid in 100 ml water.

2.3.3 <u>Procedure</u> The digestion of monazite was performed by heating 500 mg. monazite with 1.5 ml concentrated sulphuric acid for 2 hours on a hot stirred-plate. The temperature of the digestion was approximately 200°C. After completion, the reaction mass was allowed to cool for 30 minutes and then diluted with 90 ml distilled water. The undigested monazite was separated by filtration using Whatman filter paper No.42. The solution was transfer into a 100 ml volumetric flask and water was added to bring the volume to 100 ml. The resulting solution was called solution A.

25 ml of solution A was pipetted into a 100 ml separating funnel containing 4 grams solid sodium nitrate. After adding 25 ml 1 M nitric acid and 5 ml TOPO solution the solution was shaken for 10 minutes on an automatic shaker. The two phases were allowed to separate, after which the organic phase was transferred into a second separating funnel for subsequent extraction of thorium and the aqueous phase was preserved for the determination of rare earth elements if desired. The organic phase was equilibrated for 10 minutes with 15 ml 0.3 M sulphuric acid and the phases were allowed to separate. From the aqueous phase, which contains thorium, 2 ml solution was pipetted and evaporated to dryness. The residue was dissolved in 0.25 ml 60% perchloric acid and the solution was brought to 25 ml with distilled water in a volumetric flask. The solution, which is called solution B, was used for the subsequent spectrophotometric measurement.

3 ml of solution B was pipetted into a 25 ml volumetric flask containing 2.5 ml thorin solution and 2.5 ml 60% perchloric

acid. (The remaining 13 ml was kept for the studies of titrimetric method which will be described in the subsequent section.) The solution was made into 25ml by addition of distilled water. An orange-red colour developed immediately when solution B was added into the thorin solution. From trial experiments it was discovered that the colour came to and remained constant by 45 minutes after mixing. So the absorbance of the solution was measured after allowing the solution to stay for 45 minutes. The absorbance was measured at 545 nm. vs. a reference solution which was prepared by diluting 2.5 ml 60% perchloric acid and 2.5 ml of thorin solution to 25 ml with water. The thorium content of the solution could be read from the calibration curve which is presented in Figure 2.3.

2.3.4 <u>Calibration curve for the spectrophotometric determination of thorium</u> Standard solutions of thorium in various concentrations were prepared by pipetting the thorium nitrate stock solution which contained 1000 μg thorium per ml into mixtures of 2.5 ml 60% perchloric acid and 2.5 ml thorin solution. The volume of the stock solution varied between 0.25 to 4.5 ml. Water was added into the solutions to bring the volumes to 25 ml. Consequently, the thorium concentration in the solutions varied from 1 to 14 μg/ml. The absorbances of the solutions were measured vs. a reference blank solution which was prepared in similar manner, except that no thorium was added. The results of the measurements are shown in Table 2.4. When the absorbance is plotted as a function of the thorium concentration, the calibration curve, Figure 2.3, is obtained. From

Figure 2.3, it is obvious that Beer's law is valid only when the concentration of thorium is lower than about 10 ppm.

Table 2.4

Absorbance measurements of thorium-thorin complexes for the determination of the calibration curve.

Concentration of Th (IV) in ppm.	Absorbance at 545 nm
1	0.056
2	0.121
4	0.255
6	0.381
8	0.492
10	0.627
14	0.827
18	0.992

FIGURE 2.3

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CALIBRATION CURVE FOR THE DETERMINATION OF
THE THORIUM CONTENTS BY SPECTROPHOTOMETRY
(ABSORBANCE V.S. CONCENTRATION OF THORIUM)

μg Th/ml
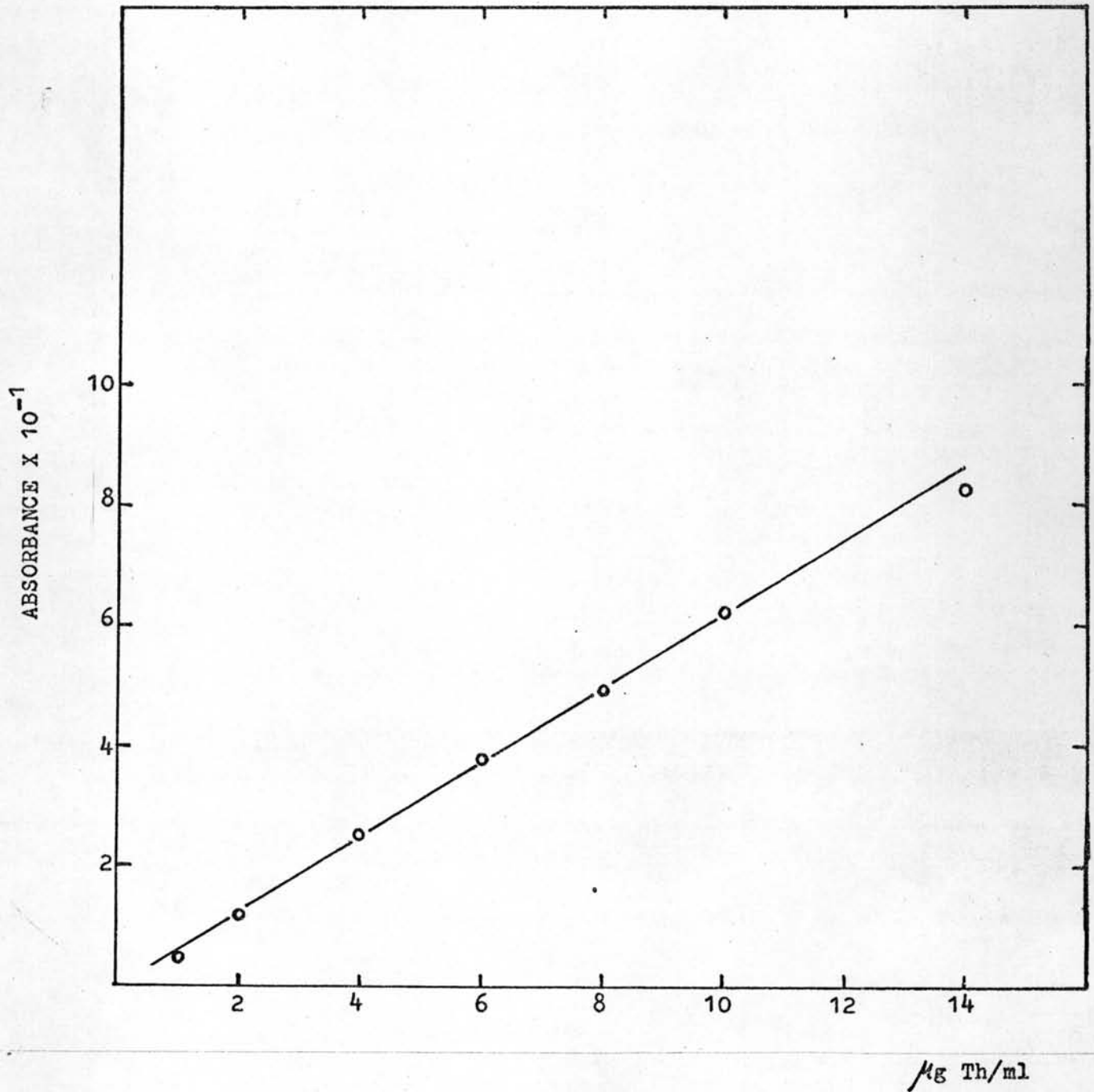
2.3.5 <u>Evaluation</u> An example for the calculation of the thorium content is given in the present section.

Solution A was obtained by digesting 0.5 gram standard monazite NBL-7A with concentrated sulphuric acid and subsequent dilution to 100 ml with water. 25 ml of solution A was extracted with TOPO. After back extraction with 15 ml 0.3 M sulphuric acid, 2 ml of the aqueous phase was evaporated to dryness and the volume was brought to 25 ml with water. The resulting solution was called solution B. 3 ml of solution B was mixed with perchloric acid and thorin to give a final solution of 25 ml which is ready for the spectrophotometric measurement. ·

The absorbance of the solution was found to be 0.384 which corresponds to a thorium concentration of 6.1 ppm. Hence the total amount of thorium in solution B.

$$= 6.1 \times \frac{25}{3} \times 25 \qquad \mu g.$$

The total amount of thorium in solution A

$$= 6.1 \times \frac{25}{3} \times 25 \times \frac{15}{2} \times \frac{100}{25} \times \frac{1}{1000} \quad mg.$$

The thorium content in monazite

$$= 6.1 \times \frac{25}{3} \times 25 \times \frac{15}{2} \times \frac{100}{25} \times \frac{1}{1000} \times \frac{100}{500}$$

$$= 7.63 \ \%$$

2.4 Titrimetric method

Since no special equipment is needed for the determination of thorium via titrimetric method, this method was examined. The general procedure described by J. Korbl et al. (19) using EDTA as complexing agent and xylenol orange as indicator was followed.

2.4.1 Reagents Thorium nitrate stock solution described in 2.3.2 was used.

EDTA, 0.05 M solution, was prepared by dissolving 1.8615 grams of reagent grade disodium ethylenediamine tetraacetate dihydrate from BDH in 100 ml water. Solution of 10^{-3}M was prepared by diluting 20 ml of the stock solution to 1000 ml with distilled water.

Xylenol orange, 0.5% solution, was prepared by dissolving 0.5 gram xylenol orange in 100 ml water.

Buffer solution, pH 2.8, was prepared by mixing 100 ml 0.1 M potassium hydrogen phthalate with 57.8 ml 0.1 M hydrochloric acid.

2.4.2 Determination of the accuracy of the method The accuracy of the method was determined by titrating five standard thorium nitrate solutions containing various amount of thorium ranging from 60 ppm to 300 ppm. The pH value of the standard solutions, 10 ml each, was adjusted to 2.8 by addition of the buffer solution in small volumes. The solutions were then titrated with

10^{-3} M EDTA using xylenol orange as indicator. At end point the colour of the solution changed from orange red to lemon yellow. The results obtained from titration agree within 5% with the real values, as it can be seen from Table 2.5.

Table 2.5

Data of titration of thorium nitrate solution with 10^{-3} M EDTA

| ppm of Th(IV)	ml of buffer solution	ml of 10^{-3} M EDTA used			Experimental value ppm of Th
		1st	2nd	average	
60	5	2.55	2.50	2.53	58.71
120	5	5.00	4.95	4.98	115.57
180	5	7.60	7.50	7.55	175.21
240	6	10.10	10.05	10.08	233.92
300	6	12.65	12.60	12.63	293.09

When the concentration of thorium is plotted against the ml EDTA, a straight line is obtained, as is shown in Figure 2.4.

FIGURE 2.4

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TRITRATION OF THORIUM NITRATE $\left\{Th(NO_3)_4\right\}$ WITH EDTA
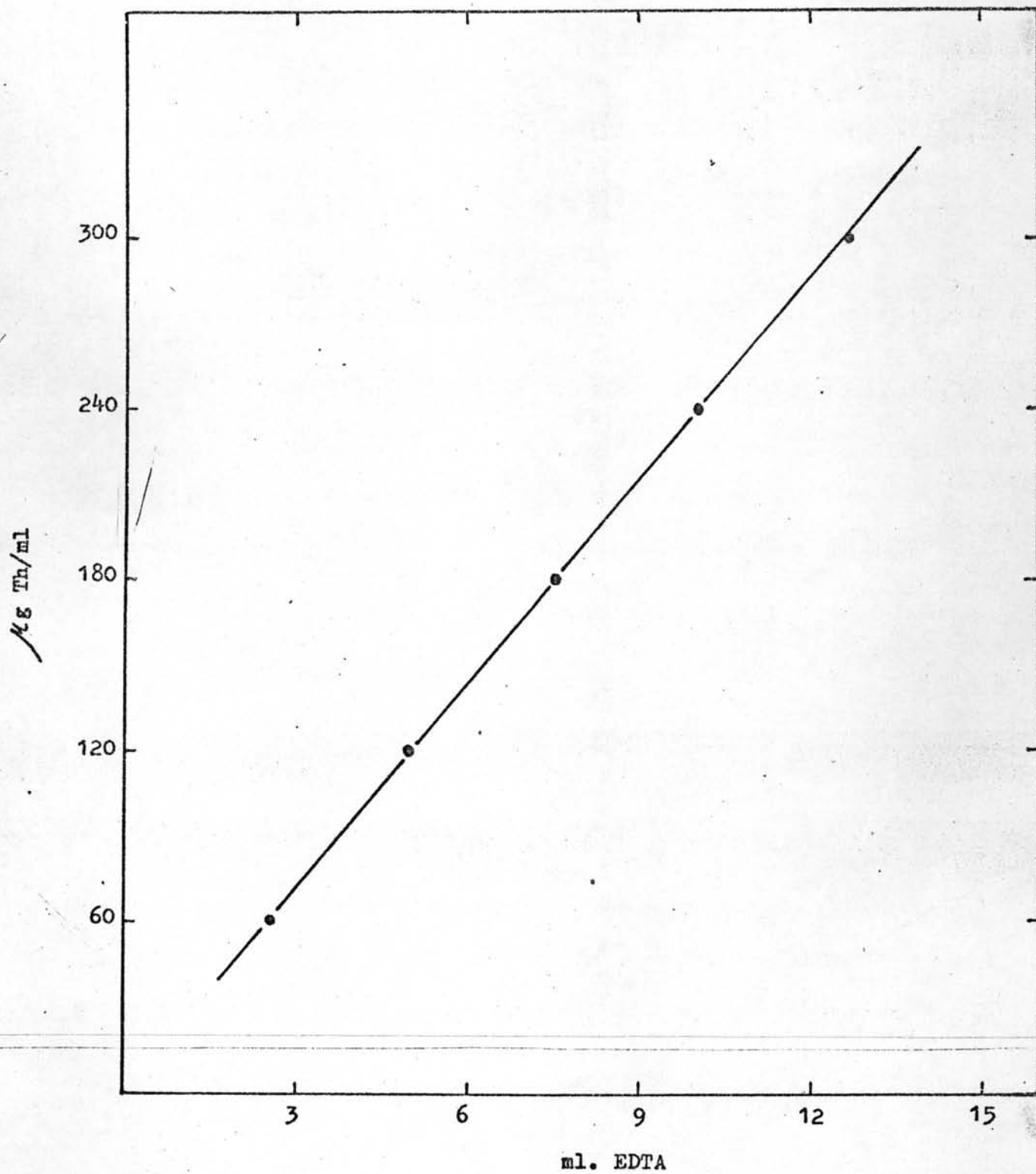
The pH value of the solution plays an important role in the titration. According to J. Korbl et.al. (19), when the pH value is lower than 2.5, the colour will change sooner than it should be and causes a lower value of thorium content. When the pH value is higher than 3.5, the end point will be indistinct.

2.4.3 <u>Procedure</u> The remaining 13 ml of solution B from section 2.3.3 was evaporated to dryness after which the residue was taken into 50 ml distilled water. 10 ml of the solution was transfered into a conical flask and the pH of the solution was adjusted to 2.8 by addition of the buffer solution in small aliquots. Then 3 drops of xylenol orange were added and the solution was titrated with 10^{-3}M solution of EDTA until the colour changed from orange red to lemon yellow.

2.4.4 <u>Evaluation</u> Since a 1 : 1 complex is formed between Th^{4+} ions and EDTA, 1 ml 0.001 M EDTA will react with 232.06 μg of thorium. The reaction may be represented by the following equation:

$$M^{4+} \quad + \quad H_2Y^= \quad \rightleftharpoons \quad MY \quad + \quad 2\ H^+$$
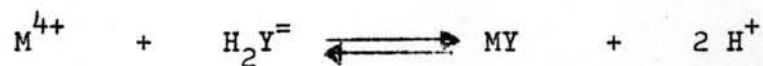
where M^{4+} represents tetravalent ions and $H_2Y^=$ denotes the anion of the disodium salt of EDTA. According to Schwarzenbach (42) the complex between tetravalent ions and EDTA has the structure of
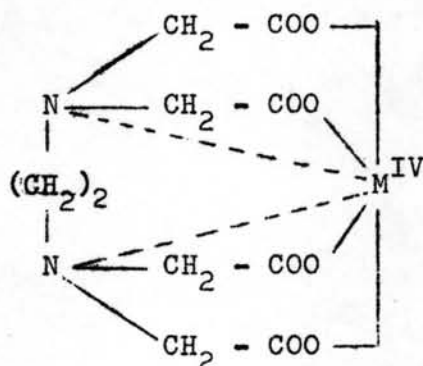
From four replicate runs of mon.NBL-7A it was found that an average of 6.68 ml. of 0.001 M EDTA was needed to form complexes with thorium in the solution which was obtained as described in section 2.4.2

Hence the thorium content in solution B

$$= 232.06 \times 6.68 \times \frac{50}{10} \times \frac{15}{13} \quad \mu g$$

The thorium content in solution A

$$= 232.06 \times 6.68 \times \frac{50}{10} \times \frac{15}{13} \times \frac{100}{25} \times \frac{1}{1000} \quad mg$$

The thorium content in monazite NBL-7A

$$= 232.06 \times 6.68 \times \frac{50}{10} \times \frac{15}{13} \times \frac{100}{25} \times \frac{1}{1000} \times \frac{100}{500}$$

$$= 7.15 \%$$