CHAPTER III

RESULTS AND DISCUSSION

General

This chapter discusses the results that reached through the treatment of thorium standard solution by suitable factors controlling the extraction and stripping processes. In the present work, batch studies were carried out to know the optimum conditions for the extraction of thorium from aqueous medium by trioctyl phosphine oxide (TOPO) and to investigate the parameters affecting the extraction process. Stripping investigations in the recovery of thorium from the loaded organic phases were also carried out. The main parameters affecting the extraction processes are diluents, temperature, pH, shacking time, aqueous to organic phase ratio, extractant concentration, the effect of interfering ions and finally the effect of different stripping agents were investigated (Table 5). The different factors studied were optimized and applied to extract and determine Th^{4+} in a synthetic solution, certified reference samples and geologic samples collected from South Eastern Desert, Egypt (Abu-Rusheid area).

Also thorium was separated in a laboratory scale from a representative sample of the geologic samples comprised six samples (1M to 6M) in a pure state as thorium oxide. Statistics were performed to evaluated the importance of the data collected of both certified reference samples and geologic samples and therefore to set limitations on each step of the analysis.

Table (5): Factor affecting extraction and stripping of thorium:

Factor	Range
Organic solvent	Trioctylphosphine oxide (TOPO), tributyl Phosphate (TBP) and tri-n-octylamine (TOA)
pH values	pH 1 to 10
Shaking time	1 to 10 minutes
Aqueous to organic phase ratio (A/O)	1:1, 1:2, 1:3, 1:4 and 1:5
Temperature	22 to 100 ºC
Extractant concentration (TOPO)	0.02, 0.04, 0.06, 0.08, 0.1 and 0.2M
Different diluents	Benzene, carbon tetrachloride, chloroform, cyclohexane, kerosene, toluene, and *o*-xylene.
Stripping agents	H_2SO_4, HCl, HNO_3, H_2O, NaOH, $Ca(OH)_2$
Interfering ions	P^{5+}, Fe^{3+}, Al^{3+}, Mg^{2+}, Si^{4+}, Ca^{2+}, Ti^{4+}, K^{+}, Na^{+}, Sr^{2+}, U^{6+}, Co^{2+} and Ni^{2+}

3. Factors affecting the extraction of thorium.

3.1. Effect of different organic solvents as extractant.

Many experiments have been performed to elucidate the effect of different organic solvents as an extractant for thorium in order to choose the best extractant for use. Three extractants were used: trioctyl phosphine oxide (TOPO), tributyl phosphate (TBP) and tri-n-octylamine (TOA). The data obtained showed that TOPO has the high efficiency (99.99%) to extract thorium from its mineral acid solutions if compared to TBP and TOA. Accordingly TOPO was chosen as a solvent for thorium extraction from its solutions (Fig. 7).

It's clear that TOPO > TBP > TOA for the extraction of thorium. This can be interpreted through the following:

Because TOPO or TBP extracted the metal ions by the solvation mechanism where the organic solvent replace the water in the

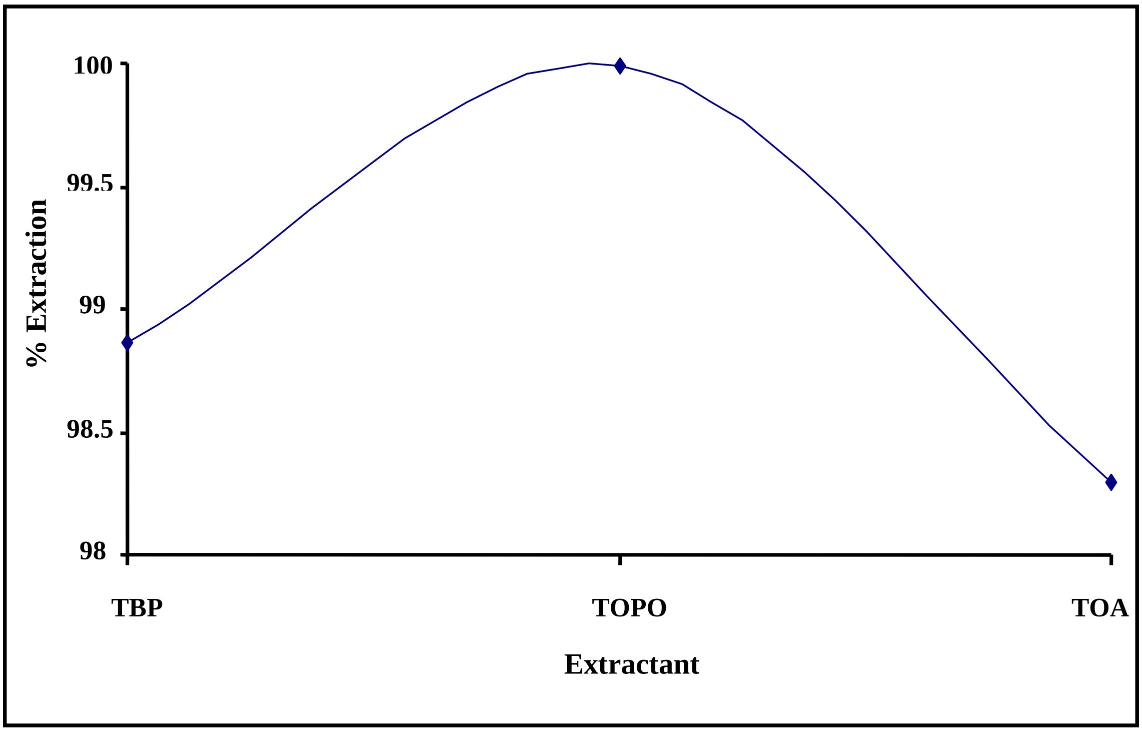


Fig. (7): Effect of organic solvents on thorium extraction.

Outer coordination sphere around the metal ion of interest. So that the metal ion extracted by TOPO or TBP must be in a neutral form. But TOA extract the metal ion by ion exchange mechanism therefore it extracts the charged species only while thorium was in the neutral form, so that the extraction efficiency of TOPO and TBP is higher than TOA.

Th^{4+} $(H_2O)_n$ + TOPO or TBP $\longrightarrow$ Replacement of water molecules (solvation)

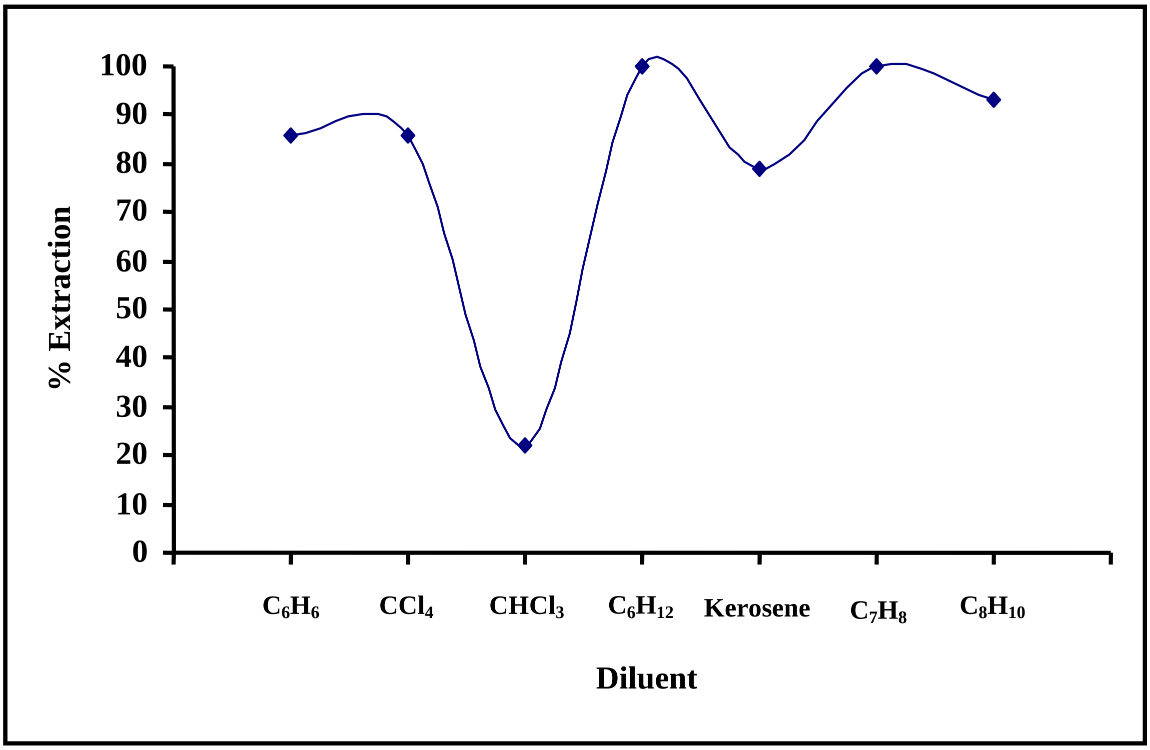
The factor controlling this replacement is the bascity, as it increases the replacement of this solvent for water molecules increases and vise versa.

The TOPO have three repellent group (C_8H_{17}) which facilate the exit of the lone pair on the oxygen atom of (P = O) group which increase the bascity. While in the TBP having three alkoxy groups and it also repellent groups but the minus inductive effect of their oxygen atoms decrease their donation so that its bascity decreases than TOPO that is can interpret the higher extraction efficiency of TOPO than TBP (**Watanabe, 1964**).

3.2. Effect of different diluents.

To choose which diluent is the best for thorium extraction, the organic extractant (TOPO) was dissolved in the diluents: benzene (C_6H_6), cyclohexane (C_6H_{12}), carbon tetrachloride (CCl_4), chloroform ($CHCl_3$), toluene (C_7H_8), *o*-xylene (C_8H_{10}) and kerosene, It was found that cyclohexane and toluene give high extraction (99.9%), for thorium from its acid mineral solutions when compared to the other diluents used (Fig. 8).

The priority at which the extraction increases is:
chloroform > toluene and *o*-xylene > benzene > carbon tetra chloride > cylohexane $\longrightarrow$ order of the decrease of dielectric constant.



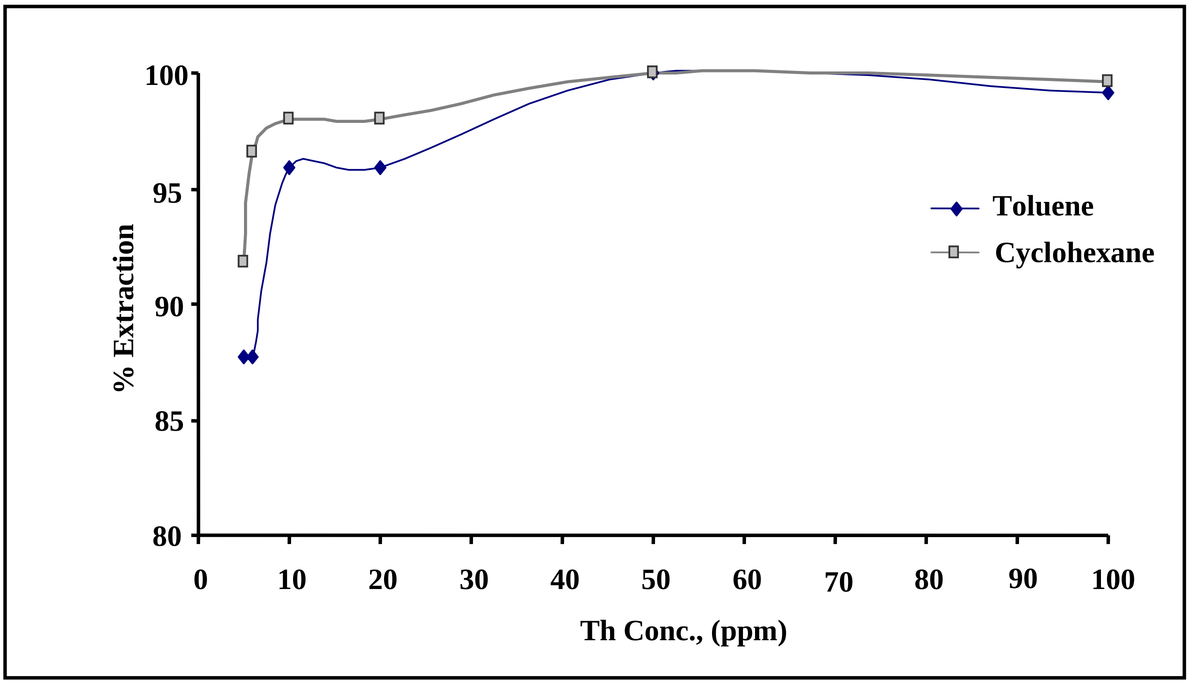
Extraction conditions:
- *TOPO used as extractant dissolved in suitable solvent, pH =1, shaking time 4min.,*
- *A/O ratio 1/2, Temp. 22±1°C.*
- *Extractant concentration is 0.08M, diluent is variable.*

Fig. (8): Effect of diluents on thorium extraction.

3.2.1. Differentiation between cyclohexane and toluene as diluents.

For studying the effect of cyclohexane and toluene on %E. the extraction of thorium was carried out using different concentrations of standard pure thorium nitrate; ($Th(NO_3)_4.4H_2O$, ranges from 5 to 100 ppm using TOPO dissolved in cyclohexane and toluene then the extraction experiments were run.

It is clear that, the extracted thorium reaches its maximum efficiency (99.96%) at the concentration 50ppm for both diluents meanwhile cyclohexane gives a good extraction efficiency in all concentrations of thorium when compared to toluene. Accordingly cyclohexane was chosen as a diluent due to its dielectric constant where it is lower than toluene and also for its availability (Fig. 9).



Extraction conditions:

- TOPO used as extractant dissolved in both solvents, pH =1, shaking time 4min., A/O ratio (1/2), Temp. 22 ±1°C, Extractant concentration 0.08M.

Fig (9): Differentiation between cyclohexane and toluene in extraction of thorium using TOPO.

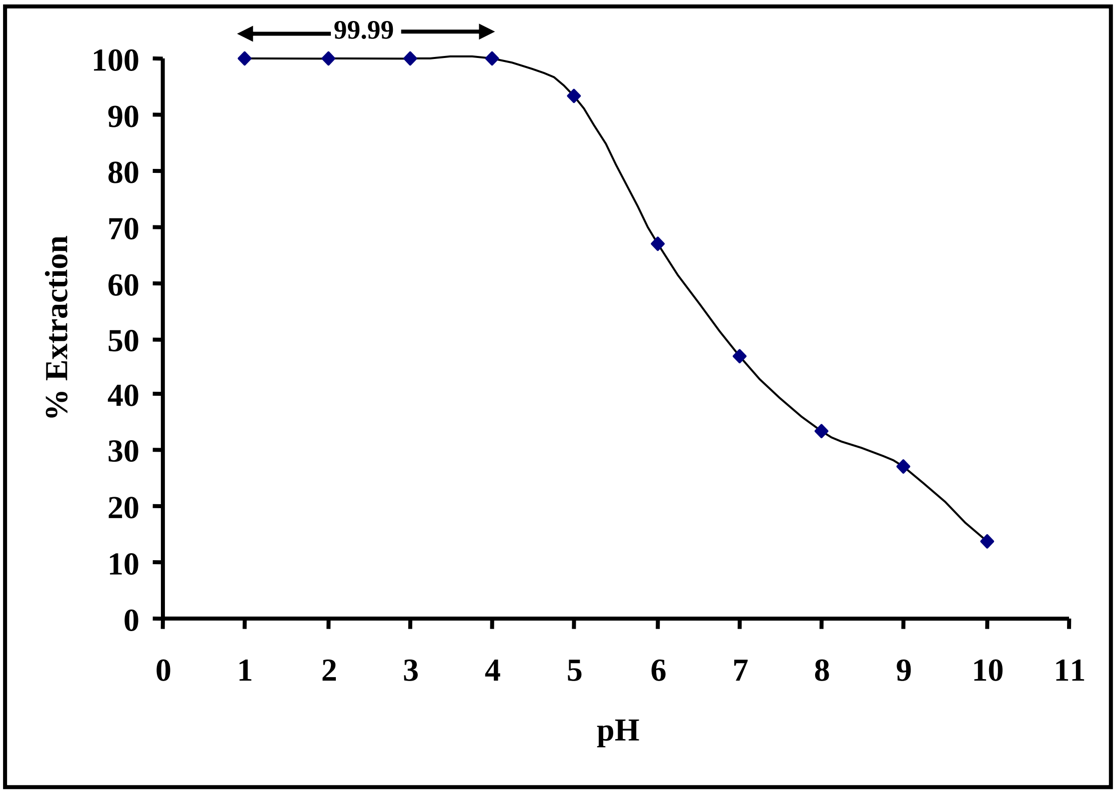
The role of diluent in the extraction of thorium using TOPO is generally important because it affects its distribution between the aqueous and organic phases. The diluents themselves are unable to extract metal ions from the aqueous phase, but they greatly affect the extraction behavior of the extractant used. The dielectric constant of the medium is a major factor controlling the preference of the diluents.

The dielectric constant of the diluent is a measure of the electrostatic polarization, which reduces the forces between charges. The diluents having the least dielectric constant leads to a best extraction which may explain the higher extraction efficiency of cyclohexane and toluene than the other diluents.

3.3. Effect of pH value.

The pH is indicating of the concentration of hydrogen ions in solution which affects the equilibrium and kinetics of a wide variety of chemical and biochemical reactions. Also this factor controls the condition of the reaction progress in which the reaction occur in acidic or basic medium and controlling the interfering process which prevent the other ions of elements to react with thorium.

The effect of pH on thorium extraction was studied in the range between 1 and 10 where the other factors were kept fixed (Fig. 10). The results indicated that, from pH 1 to 4 the extraction reaches its maximum value (99.99%), followed by decreases in the extraction from pH 5 to 10. This means that TOPO is not active in neutral or alkaline medium, but it is activated at acidic medium. Accordingly, it was possible to conclude that pH 1 is the best to reach the thorium maximum extraction (99.99%) from its mineral solutions. The increase in pH makes the hydrolysis of the formed Th-TOPO complex results in precipitation of thorium. This is quite clear in the state of pH 5 and higher which makes an emulsion solution.



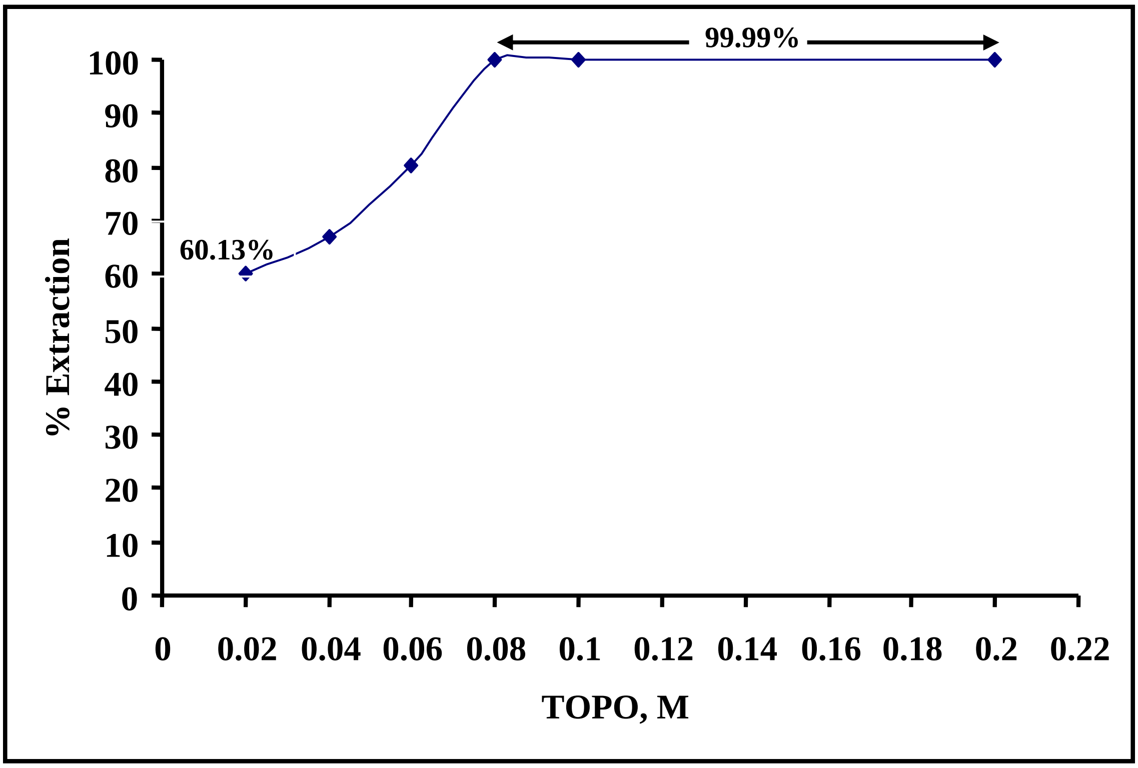
***Extraction conditions*.**

- TOPO used as extractant dissolved in cyclohexane, pH is variable.

Fig. (10): Effect of pH on thorium extraction (%E).

3.4. Effect of extractant concentration (TOPO) on thorium extraction (%E).

The effect of trioctyl phosphine oxide (TOPO) concentration on thorium extraction (%E) was studied with concentrations ranges from 0.02 to 0.2M. The obtained results indicated that the extraction efficiency increases from 60.12 to 99.99% with increasing the TOPO concentration from 0.02 to 0.08M, and kept constant from 0.08 to 0.2M. (Fig. 11). This means that, the best concentration of TOPO is 0.08M for achieving the higher extraction (99.99%).



Extraction conditions:

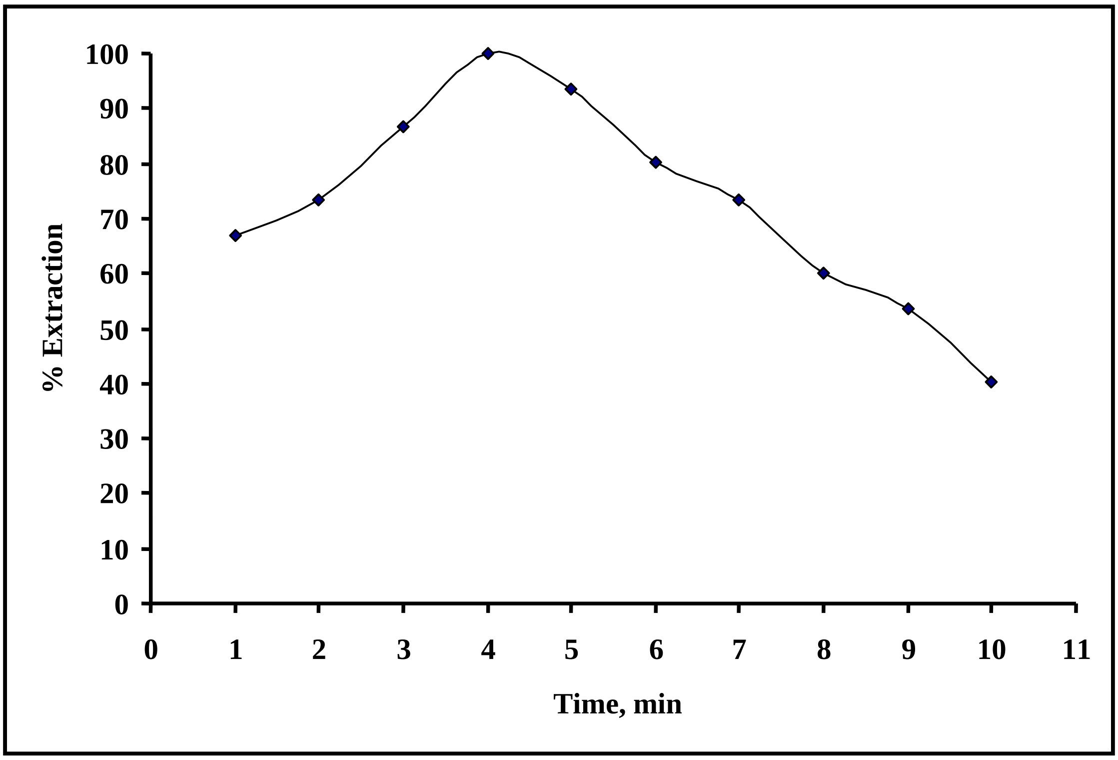
- *TOPO used as extractant dissolved in cyclohexane, pH =1, shaking time 4min.,*
- *A/O ratio is 1/2, Temp. is room temp. 22 ±1°C.*
- *Extractant concentration is variable,*

Fig. (11): Effect of extractant concentration (TOPO) on thorium extraction (%E).

3.5. Effect of shaking time on the thorium extraction (%E).

The shaking time is determined by physical properties such as viscosity, interfacial tension and density differences between the two phases. The low shaking causes the formation of large droplets and decreases interfacial area, which reduces the mass transfer and decreases the extraction efficiency, while the high shaking time minimizes the mass transfer resistance during reactions and extraction.

The effect of shaking time on the extraction of thorium (%E) was studied by varying the shaking time from 1 to 10 minutes using TOPO as an extractant. The extraction increased with increasing the shaking time till 4 minutes then it tends to decrease from 5 to 10 minutes. Accordingly it can be concluded that, the best shaking time for thorium maximum extraction (99.99%) is 4 minutes (Fig. 12), which was chosen for the following investigations.



Extraction conditions

- TOPO used as an extractant dissolved in cyclohexane, pH =1, shaking time is variable.

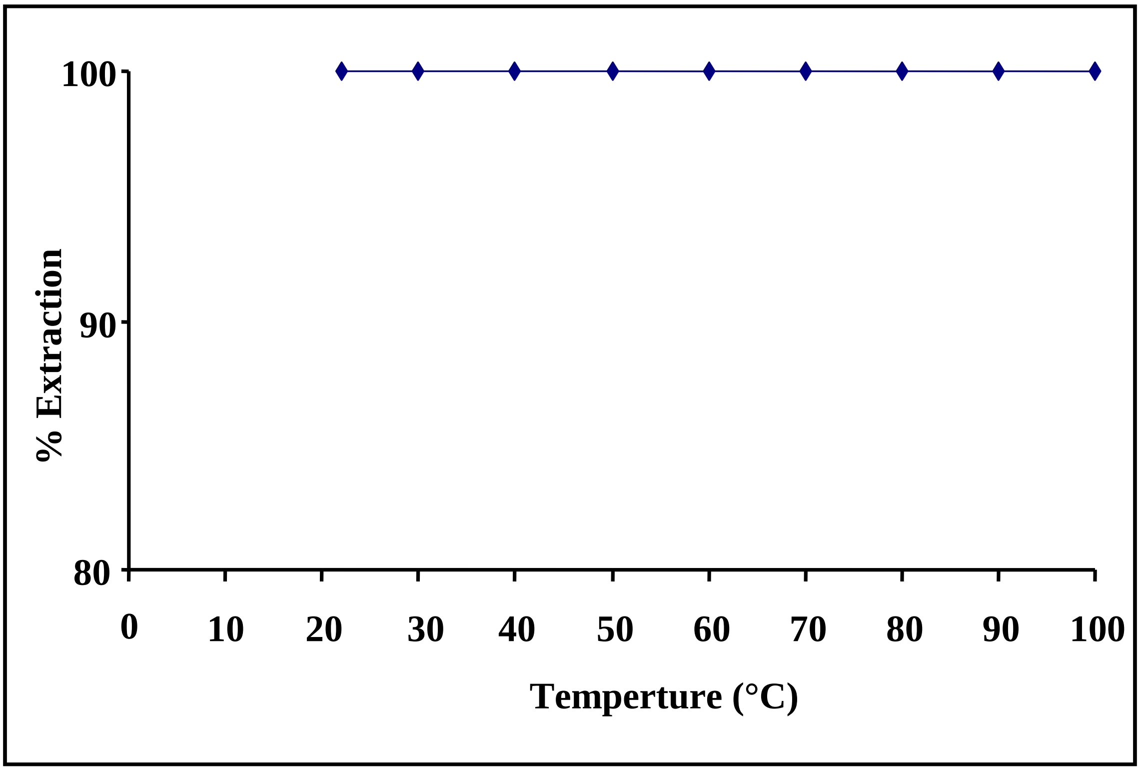
Fig. (12): Effect of shaking time on the extraction of thorium using TOPO as an extractant.

3.6. Effect of temperature on the extraction of thorium (%E) using TOPO as extractant.

The temperature plays a vital role in the extraction reaction which determines the reaction way, if it is exo-thermic or endo-themic and also may accelerate or slow-down the reaction.

The effect of temperature on thorium extraction was carried out using an electric thermostat, with the range from 22 to 100°C.

It is clear from the obtained data that the ambient lab. temp. (22 ±1°C) is the best to reach maximum extraction (99.99%), and the temperature not affect the extraction efficiency. This mean that the reaction is neutral not exo-thermic or endo-thermic (Fig. 13). And this also may be due to the stability of the complex formed between thorium and TOPO.



Extractionconditions:
TOPO used as extractant dissolved in cyclohexane, pH =1, shaking time 4min.,
A/O ratio is 1/2, Temp. is variable.

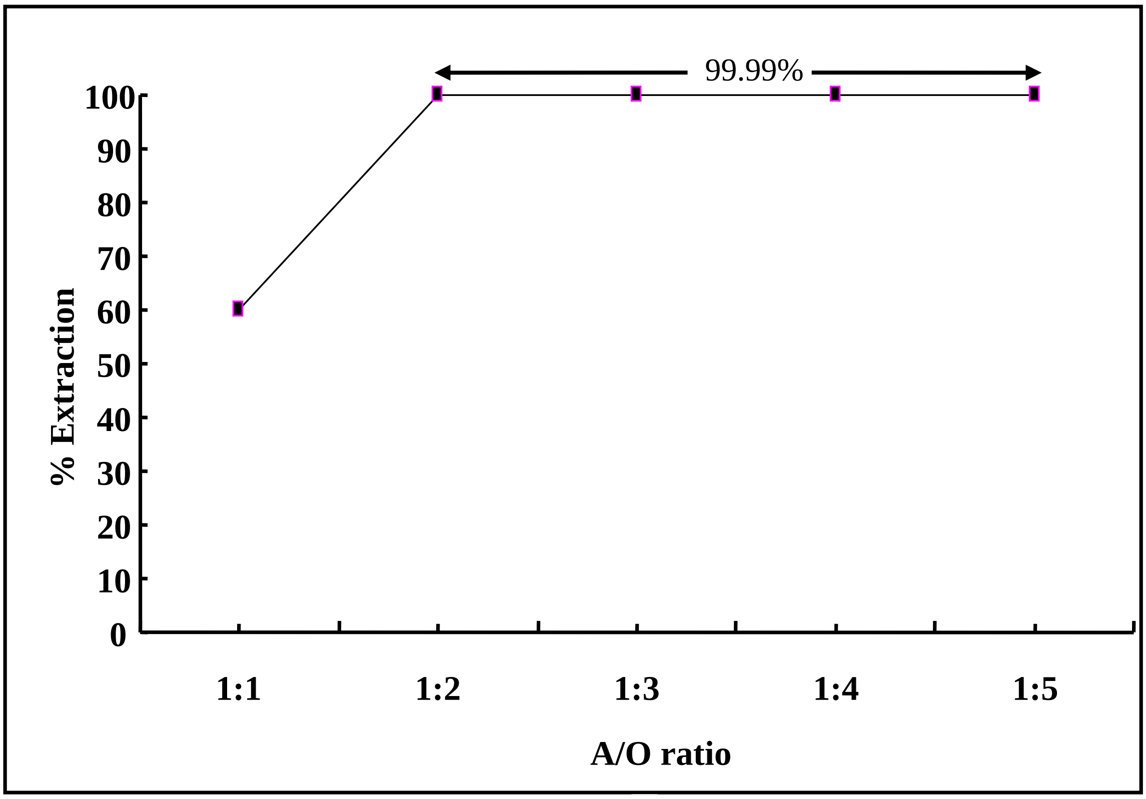
Fig. (13): Effect of temperature on thorium extraction (%E).

3.7. Effect of aqueous to organic phase ratio (A/O) on thorium extraction (%E).

The effect of aqueous to organic phase ratio (A/O) on thorium extraction was studied, covering the range between 1:1 and 1:5 while the other factors were kept constant.

The obtained results indicated that the extraction of thorium increases gradually from the ratio 1:1 to 1:2 after that it is constant till the ratio 1:5. Therefore, the best A/O ratio is 1:2 to extract 99.99% of thorium from its acid mineral solutions (Fig. 14). And this was chosen the best one, where the capacity of TOPO reaches its maximum (99.99%) at this ratio 1:2.

With the increase in A/O ratio the capacity remained at its maximum. A/O phase ratio was chosen in the following investigations.



Extraction conditions:
TOPO used as extractant dissolved cyclohexane, pH =1, shaking time 4min.,
A/O ratio is variable.

Fig. (14): Effect of aqueous to organic phase ratio (A/O) on thorium extraction (%E).

3.8. Effect of interfering ions on the extraction of Th (IV):

The presence of interfering ions in an analytical procedure is one that causes a systematic error in the analytical results, and consequently affect the efficiency of extraction and determination of the element **(Landen, 1989),** it was classified according to certain principles:

a) Interfering ions properties.
b) Interfering ions effects.
c) Interfering ions mechanism.

Certain interfering ions generally affect the extraction of thorium by enhancement or depression of extraction efficiency. Some elements of interfering ions were selected, because these elements are usually composing the matrix of the most geologic samples which used for application in this work.

The effect of interfering ions on extraction and determination of 5ppm Th(IV) from $Th(NO_3)_4.4H_2O$ solution was studied. In this respect, the extraction of Th(IV) was performed at first in absence of any interfering ions to notice any changes which might be caused in presence of these ions.

The effect of certain interfering ions concentration on thorium extraction was investigated by preparing a series of standard solutions from the salts of these ions (Table 6).

The experiments were carried out by adding certain concentrations of these ions (P^{5+}, Fe^{3+}, Al^{3+}, Mg^{2+}, Si^{4+}, Ca^{2+}, Ti^{4+}, K^{+}, Na^{+}, Sr^{2+}, U^{6+}, Co^{2+} and Ni^{2+}), while the other factors were kept constant (5ppm of standard Th(IV) solution, 0.08M TOPO in cyclohexane, pH 1, A/O phase ratio 1:2 and 4 min. shaking time at 22±1°C).

It is clear that most metal ions slightly interfere, while the increase in the concentration of Fe^{3+}, Al^{3+}, Ca^{2+}, Si^{4+} and Ti^{4+} decreased the extraction efficiency. But a reverse effect of sodium appears with the efficiency increase, while U^{6+}, Ni^{2+}, Co^{2+} and Sr^{2+} affect the extraction efficiency of Th(IV) by depression (Table 6).

Table (6): Effect of interfering ions on 5ppm thorium extraction (E%)from HCl acid medium by TOPO.

Thorium extraction % per one cycle								
Interfering ions / Conc. ppm	**Salt used**	**Source**	**Without**	**10**	**20**	**40**	**80**	**100**
P^{5+}	KH_2PO_4	ADWIC	99.9	98.14	98.14	97.52	97.52	97.52
Fe^{3+}	$FeCl_3$	FLUKA	99.9	97.99	97.52	97.06	96.91	96.95
Al^{3+}	$AlCl_3$. $6H_2O$	WIN.LAB.	99.9	97.62	97.23	96.91	96.29	96.29
Mg^{2+}	$MgCl_2$. $6H_2O$	PANREAC	99.9	97.52	96.99	96.91	96.91	96.91
Si^{4+}	SiO_2. Na_2O. $5H_2O$	ADWIC	99.9	97.82	97.52	97.52	97.61	96.91
Ca^{2+}	$CaCl_2$	ADWIC	99.9	97.52	97.16	97.06	97.16	97.26
Ti^{4+}	$TiCl_4$	MERCK	99.9	96.91	96.95	96.75	95.76	95.05
K^{+}	KCl	MERCK	99.9	97.52	97.52	97.4	97.52	97.84
Na^{+}	NaCl	ADWIC	99.9	98.14	98.76	98.76	98.76	98.88
Trace elements								
Sr^{2+}	$SrCl_2$. $6H_2O$	MERCK	99.9	99.62	96.21	88.63	80.82	77.27
U^{6+}	$UO_2(NO_3)_2.6H_2O$	BDH	99.9	99.6	96.01	88.02	88.02	76.04
Co^{2+}	$CoCl_2$. $6H_2O$	MERCK	99.9	91.88	90.7	90.22	89.28	86.88
Ni^{2+}	$NiCl_2$. $6H_2O$	ADWIC	99.9	97.82	87. 82	87.51	81.88	79.59

Extraction conditions:

- *Organic phase: 0.08M TOPO in cyclohexane.*
- *Thorium concentration: 5 ppm.*
- *Aqueous to organic ratio: 1:2, pH =1, shaking time =4min.,*
- *(A/O) ratio =(1/2), Temp. =22 ±1°C.*

Khosla, (1970), found that using 0.1M EDTA prevents the interfering of vanadium(V), iron(III), chromium(VI), osmium(VIII), ruthenium(VIII), titanium(IV) and cerium(IV) in the extraction of thorium. While **Fletcher et al. (1957),** stated that meso-tartaric acid plays a major role in reducing the effect of interfering ions during thorium determination using thoron.

X-ray fluorescence method depends on the interaction between the inner electrons in the atom with the incident photons.

When an electron from an inner shell from the nucleus is knocked away from the atom, by X-ray, it leaves a gap that is immediately filled by an another electron from an outer shell creating a new gap which in turn is filled from a higher shell with the subsequent emission of a fluorescent radiation characteristic of the element and the involved electronic shell.

Many elements can be interfered with the measure of thorium element, so X-ray fluorescence (XRF) analysis is used, which is characterized by its sensitivity to the composition content element of the analyzed matrix which may interfere with thorium, and which of them can make a great interfere with thorium extraction and determination (Table 7). To overcome this problem, certain masking agents were added in order to reach the best extraction efficiency.

Table (7): XRF analysis for certain trace elements of geologic samples collected from South Eastern Desert, Egypt.

Sample No.	Trace elements (ppm)												
	Cr	**Ni**	**Cu**	**Zn**	**Zr**	**Rb**	**Y**	**Ba**	**Pb**	**Sr**	**Ga**	**V**	**Nb**
1M	12	7.5	69.5	360	211	404	63.5	148	82.5	59	56	16	324
2M	11	6	128	189	1413	435	47	82.5	27.5	42.5	79.5	1.5	1835
3M	10.5	10	71	194	1869	746	92.5	81.5	71	75.5	87.5	1	3681
4M	15.5	5.5	34	692	2030	353	32	37.5	213	19	84.5	3	3810
5M	10.5	7	55	51.5	1018	593.5	44.5	51	120	20.5	78	2.5	2916
6M	10	5.5	130	181	1269	404	44	107	21	40	79.5	3.5	1771

3.8.1. Masking agents study

It is clear from Table (6) that the interfering ions have certain effects on the extraction and determination of thorium. In order to reduce these effects certain compounds were used as masking agents: oxalic, citric acids, sodium potassium tartarate, potassium cyanide and meso tartaric acid. The preparation of masking agents was done by taking a weight ranged from 5% (5g in 100ml) to 10% (10g in 100ml) of the material that acts as a masking agent where 3 ml were added in each sample (Table 8). The obtained results showed that meso tartaric acid is the best one for extraction when compared to the other masking agents used (Table 9).

Table (8): Preparation of masking agents for the extraction and determination of thorium.

Masking agent (3ml in original solution)	Preparation
Sodium potassium tartarate	10%
Meso-tartaric acid	5%
Oxalic acid	10%
Citric acid	5%
Potassium cyanide	5%

Several steps were performed to choose the suitable materials with the best concentration. these materials were selected based on their previous fame in prevention of interference, such as tartaric acid which has ability to mask the ions of Al^{3+}, Ba^{2+}, Be^{2+}, Bi^{3+}, Ca^{2+}, Cd^{2+}, Ce^{4+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Ga^{3+}, Mg^{2+}, Mn^{2+}, Mo^{6+}, Nb^{5+}, Pb^{2+}, Rh^{3+}, Sb^{5+}, Sc^{2+}, Sn^{4+}, Sr^{2+}, Ta^{5+}, Th^{4+}, Ti^{4+}, Tl^{3+}, U^{6+}, W^{6+}, and Zr^{4+}. Also citric acid can be used as masking agent for the ions of Al^{3+}, Ba^{2+}, Be^{2+}, Bi^{3+}, Ca^{2+}, Cd^{2+}, Ce^{4+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Ga^{3+}, In^{3+}, Mg^{2+}, Mn^{2+}, Mo^{6+}, Nb^{5+}, Pb^{2+}, Rh^{3+}, Sb^{5+}, Sc^{3+}, Sn^{4+}, Sr^{4+}, Ta^{5+}, Th^{4+}, Ti^{4+}, Tl^{3+}, U^{6+}, W^{6+}, and Zr^{4+}.

As well as oxalic acid is known to be used as a masking agents for the ions of Al^{3+}, Cr^{3+}, Fe^{3+}, Ga^{3+}, Ge^{4+}, In^{3+}, Mg^{2+}, Mn^{2+}, Mo^{6+}, Nb^{5+}, Pt^{4+},

Sn^{4+}, Ta^{5+}, Tl^{3+}, U^{6+}, V^{5+}, W^{6+}, and Zr^{4+}. Finally Pot. cyanide was used for masking the ions of Ag^{+}, Au^{3+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, Ni^{2+}, Os^{4+}, Pd^{4+}, Pt^{4+}, Ru^{4+}, and Zn^{2+} **(Marczenko, 1986).**

Table (9): Effect of masking agent on the extraction efficiency (%E).

100ppm of interfering ions	**Th (%E) without interfering ions**	**Th (%E) with interfering ions**	**Masking agent**				
			Sod. Pot. tartarate	**Oxalic acid**	**Citric acid**	**Meso-tartaric acid**	**Pot-cyanide**
Fe^{3+}	99.9	96.95	97.53	97.05	97.25	98.1	96.95
Al^{3+}	99.9	96.29	96.87	96.43	96.97	98.08	96.29
Mg^{2+}	99.9	96.91	97.49	97.1	97.33	98.1	96.91
Si^{4+}	99.9	96.91	96.85	97.2	97.6	98.05	96.91
Ca^{2+}	99.9	97.26	97.84	97.35	97.8	98.09	97.26
P^{5+}	99.9	97.52	98.1	98.42	98.16	98.35	97.61
K^{+}	99.9	97.84	98.41	98.75	98.49	98.66	97.89
Na^{+}	99.9	98.88	99.47	99.81	99.55	99.71	98.96
Ti^{4+}	99.9	95.05	97.15	95	97.1	98.1	95.05
Trace elements							
Sr^{2+}	99.9	77.27	97.1	78.42	83.62	98.96	77.27
U^{6+}	99.9	76.04	96.61	89.5	84.57	98.81	76.04
Co^{2+}	99.9	91.88	91.82	91.1	91.6	97.88	91.88
Ni^{2+}	99.9	79.59	96.7	91.5	87.4	98.2	92.3

The extraction process was performed first without adding any masking agent with the application of the optimum reached extraction conditions, and then the masking agent were added. The obtained results are listed in Table (9) were meso tartaric acid is shown as the best one.

3.9. Re-extraction process (stripping)

The stripping process is the recovery of the metal value from the organic phase. A general procedure for this technique is as follows, the loaded solvent is contacted with a suitable strip solution, acid or base, at an appropriate phase ratio until equilibration is attained. The aqueous phase is then removed and analyzed for thorium.

Stripping process depends on a number of factors in order to obtain the best stripping. These factors are the effect of different reagents and their concentrations effect for aqueous to organic phase ratio, temperature, shaking time, and pH.

The type of the stripper depends upon the mechanism of the extraction. The extraction mechanism can be classified in to three types:

1- Solvation mechanism.
2- Cation exchange mechanism.
3- Anion exchange mechanism.

The solvation is the replacement of the water molecules which depends upon the bascity so that it must be present for the stripper more than the extractant. The cation exchange is the replacement of the proton (H^+) with a positive charged ion. The anion exchange is the replacement of the hydroxyl group (OH^-) with a negativity charged ion.

The stripping of Th(IV) from loaded organic phase (TOPO) was tested using certain stripping agents including sodium hydroxide, water, sulfuric, hydrochloric and nitric acids in concentrations range between 0.25 and 2M. The two phases were contacted for 4 minutes with varying the aqueous to organic phase ratio from 1:1 to 4:1 at 22 ± 1°C.

3.9.1. Alkaline stripping

Different bases were used as stripping agents, the hydroxyl group acts to liberate the metal ions from the extractant. The alkaline is not common as a stripper but it is possible to be done, the alkaline acts as the following reaction:

$$M^{2+} + X(OH)_2 \longleftrightarrow M_2X + 2\ OH^-$$

where M^{2+} is the metal ion and $X(OH)_2$ is the base.

3.9.1.1. Stripping of Th(IV) using sodium hydroxide as a stripper.

Batch experiments on the stripping of extracted Th(IV) from TOPO in cyclohexane were carried out using different concentrations of sodium hydroxide solution ranges from 0.5 to 1 M, keeping the other variables constant. Meanwhile the effect of aqueous to organic phase ratio ranges between 1:1, 2:1 and 3:1. The obtained data revealed that 1 M NaOH can strip 9.5%, (Table 10).

Table (10): Effect of sodium hydroxide on the stripping of thorium (%S).

S%			
Ratio of A/O **Conc., of NaOH, M**	**1:1**	**2:1**	**3:1**
0.5	3.4	5.32	6.47
1	8.15	**9.5**	4.62

3.9.1.2. Stripping of Th(IV) using calcium hydroxide.

A series of stripping experiments were carried out using $Ca(OH)_2$ solution with concentrations ranging from 0.5 to 1 M. The obtained data showed that 0.5 M $Ca(OH)_2$ can strip 7.1% at the A/O phase ratio 3: 1 (Table 11).

It is clear that the stripping of thorium using hydroxide ions (NaOH and $Ca(OH)_2$) showed a weak effect in the stripping of Th(IV), so other types of agents are to be experimented.

Table (11): Effect of calcium hydroxide on the stripping of thorium (%S).

S%			
Ratio of A/O Conc., of $Ca(OH)_2$, M	**1:1**	**2:1**	**3:1**
0.5	4.4	2.8	**7.1**
1	6.15	5.9	4.62

3.9.2. Acidic stripping

Acids are the common materials used as stripping agents due to the variability in strength which is the basis to break the complex formed between organic phase and the metal ion. The acid acts as the following reaction:

$$M^{2+} + H_2X \longleftrightarrow MX + 2H^+$$

where M^{2+} is the metal ion and H_2X is the mineral acid.

3.9.2.1. Effect of nitric acid concentration on the stripping of Th(IV).

By changing the nitric acid concentrations from 0.25 to 2M with an aqueous to organic phase ratio (A/O) ranges from 1:1 to 4:1. The obtained results showed that at 1M HNO_3 with A/O ratio 2/1 gave stripping of (28.42%), while at 0.25M HNO_3 with A/O ratio 4/1 gave the maximum stripping 94.91% (Table 12 and Fig. 15).

Table (12): Effect of HNO_3 concentration on the stripping of Th(IV), (%S).

Conc., of HNO_3 acid, M \ (A/O) ratio	S% 1:1	2:1	3:1	4:1
0.25	65.71	42.63	49.73	**94.91**
0.5	43.81	35.52	56.84	73.01
0.75	36.51	49.73	42.63	65.71
1	58.41	**28.42**	78.15	43.81
2	87.61	71.05	63.94	65.71

Stripping conditions:

- pH =1, shaking time =4min.,
- thorium conc. = 3ppm
- A/O ratio variable, Temp. is 22±1°C,
- extractant concentrations 0.08M, dissolved in cyclohexane
- stripping agent conc. variable.

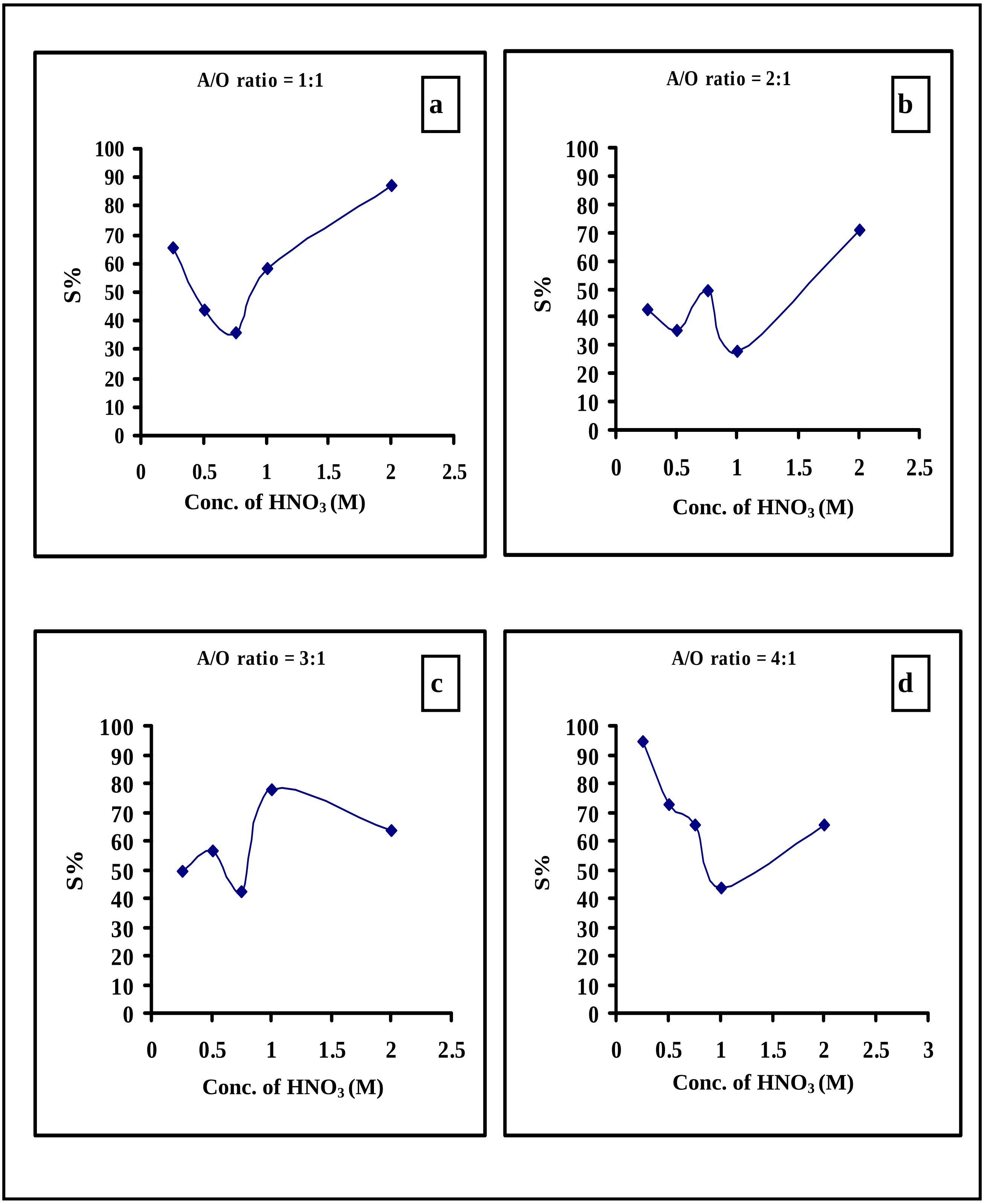


Fig. (15): Effect of HNO_3 on the stripping process of thorium (S%).

3.9.2.2. Effect of hydrochloric acid concentration on the stripping of Th(IV) (%S).

The experimental investigations on the stripping of extracted Th(IV) from TOPO in cyclohexane were carried out using different concentrations of HCl acid ranges from 0.25 to 2M with an aqueous to organic phase ratio ranges from 1:1 to 4:1.

The obtained data revealed that at 0.25M HCl with A/O ratio 4/1 gave the minimum stripping 27.27%, while with 0.75M HCl at A/O ratio 2/1 gave the maximum stripping; 95.16% (Table 13 and Fig. 16).

Table (13): Effect of HCl concentration on the stripping of Th(IV) (%S).

	S%			
A/O ratio / Conc. of HCl	**1:1**	**2:1**	**3:1**	**4:1**
0.25	35.05	47.58	40.78	**27.27**
0.5	42.06	40.78	67.97	34.09
0.75	77.11	**95.16**	81.56	47.72
1	56.08	67.97	74.77	40.9
2	70.1	61.17	88.36	61.35

Stripping conditions:

- *pH =1, shaking time =4min.,*
- *thorium conc. = 3ppm*
- *A/O ratio variable, Temp. is 22±1°C,*
- *extractant concentrations 0.08M, dissolved in cyclohexane*
- *stripping agent conc. variable.*

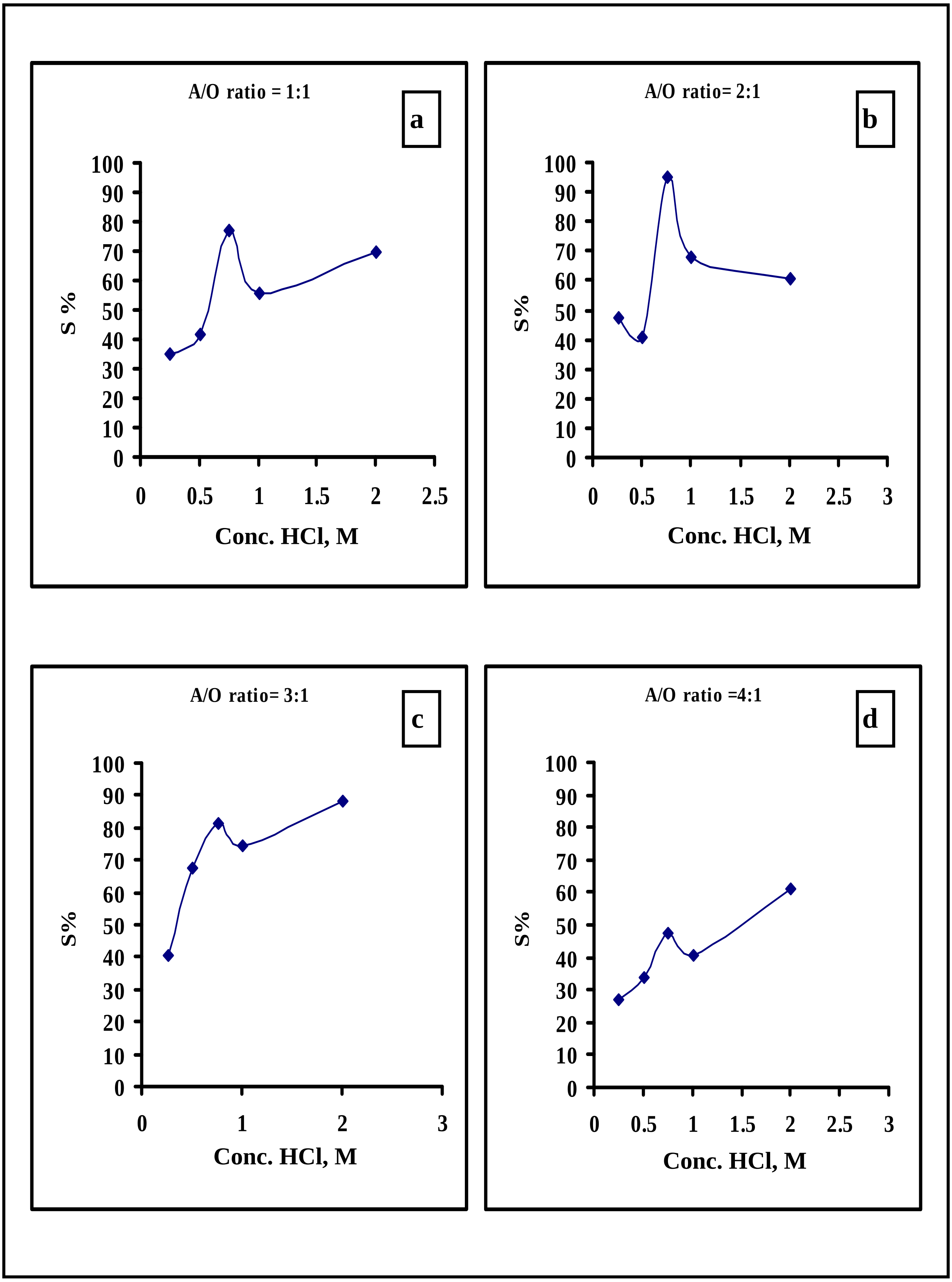


Fig. (16): Effect of HCl on the stripping process of thorium (S %).

3.9.2.3. Effect of sulfuric acid concentration as a stripping agent.

Different concentrations of sulfuric acid solution ranges from 0.25 to 2M with aqueous to organic phase ratio A/O from 1:1 to 4:1 were used to strip thorium from its solution.

The obtained results showed that at 0.25M H_2SO_4 with A/O ratio 3/1 gave the minimum stripping 16.61%, while 2M H_2SO_4 with A/O ratio 4/1 gave the maximum stripping 99.82% (Table 14 and Fig. 17).

Table (14): Effect of H_2SO_4 concentration on the stripping of Th(IV) (%S).

S%				
A/O ratio **Conc. of H_2SO_4**	**1:1**	**2:1**	**3:1**	**4:1**
0.25	37.67	40.55	**16.61**	57.04
0.5	60.27	24.33	45.02	51.03
0.75	30.14	48.66	22.51	71.3
1	15.07	56.77	37.52	78.43
2	7.53	73	56.77	**99.82**

Extraction conditions:

- pH =1, shaking time =4min.,
- thorium conc. = 3ppm
- A/O ratio variable, Temp. is 22±1°C,
- extractant conc. 0.08M, dissolved in cyclohexane
- stripping agent conc. variable.

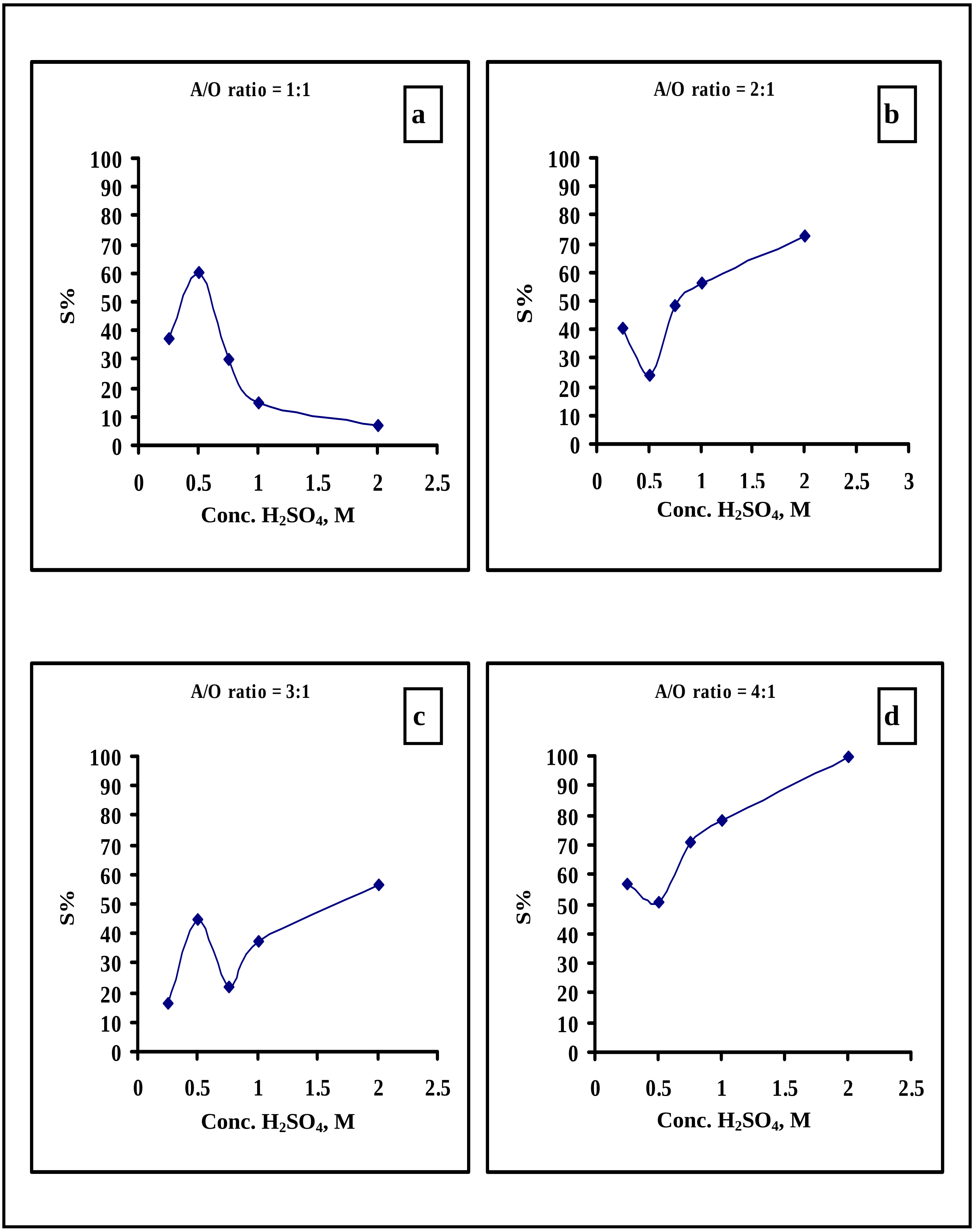


Fig. (17): Effect of H_2SO_4 on the stripping process of thorium (S%).

3.9.2.4. Effect of water with different pH values as a stripping agent.

The stripping of Th(IV) from the loaded organic phase was also tested using H_2O with different pH values ranging from pH 1 to 5. The obtained data, showed that pH 4 of H_2O gives the best Th(IV) stripping 96.39% at A/O ratio 2: 1 (Table 15 and Fig. 18).

Meanwhile that after pH 5 the mixture of aqueous and organic phases form an emulsion solution, which can not be separated and prevent the occurrence of the re-extraction process so that the best condition for thorium re-extraction was restricted in the ranges from pH 1 to 5.

Table (15): Effect of using water as stripper on thorium stripping (%S).

S%				
A/O ratio **pH of water**	**1:1**	**2:1**	**3:1**	**4:1**
1	55.17	6.89	65.49	65.48
2	37.37	**13.77**	21.83	80.03
3	62.06	20.66	43.66	65.48
4	55.17	**96.39**	87.31	87.31
5	27.58	27.54	80.03	94.59

Stripping conditions:

- *pH =1, shaking time =4min.,*
- *thorium conc. = 3ppm*
- *A/O ratio variable, Temp. is 22±1°C,*
- *extractant conc. 0.08M, dissolved in cyclohexane*
- *stripping agent conc. variable.*

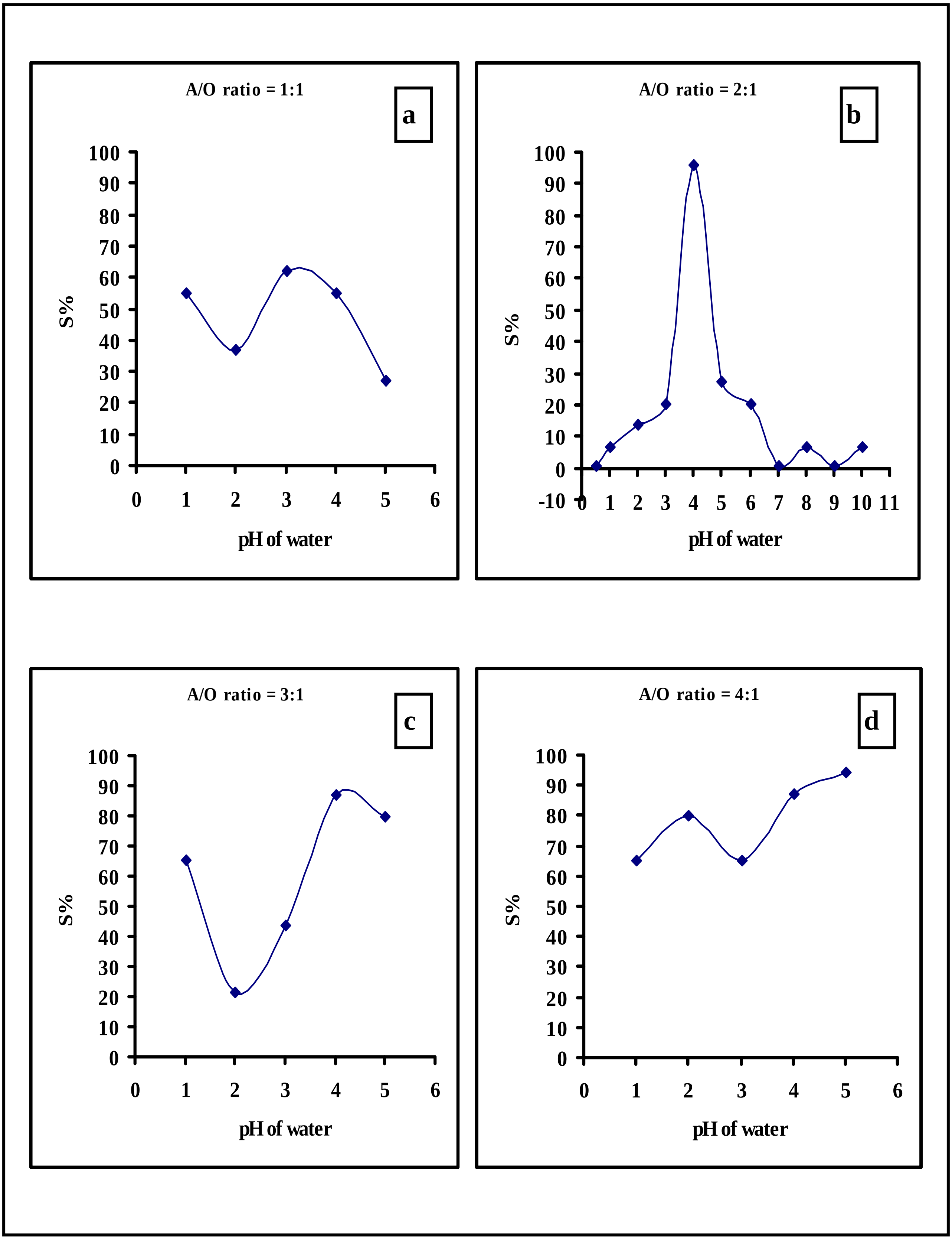


Fig. (18): Effect of H_2O on stripping process of thorium (S%).

From the pervious discussion, it is quite clear that the alkaline medium not affect on the stripping of thorium from organic phase and so water with variable pH value may give a good stripping in comparison. Meanwhile different stripping agents including nitric, hydrochloric and sulfuric acids in concentrations range between 0.25 and 2M were used. It was found that the best stripping agent is 2M H_2SO_4 which strips 99.82% (Table 16).

Increasing the acid concentration changes the nature of the complex species of thorium in the aqueous phase from neutral to charged. While TOPO molecules extract only the neutral metal (not charged) so that it is leaves thorium ions free in the solution.

So increasing H^+ ions facilitate the liberation of thorium from TOPO resulting in increasing the stripping efficiency. The degree of change depend upon the type of acid $H_2SO_4 > HCl \geq HNO_3$ and that can interpret the high stripping efficiency of H_2SO_4.

Table (16): Effect of different stripping agents on the stripping process of thorium.

Stripping agent	**HNO_3**	**HCl**	**H_2SO_4**	**H_2O**	**NaOH**	**$Ca(OH)_2$**
Conc. of the agent (M)	0.25	0.75	2	pH 4	0.5	0.5
A/O ratio	4:1	2:1	4:1	2:1	2:1	3:1
Stripping percent (%S)	94.91	95.16	**99.82**	96.39	9.5	7.1

Stripping conditions:

- pH =1, shaking time =4min.,
- thorium conc. = 3ppm
- A/O ratio variable, Temp. is 22±1°C,
- extractant conc. 0.08M, dissolved in cyclohexane
- stripping agent conc. variable.

3.10. Application of the proposed procedure on the extraction and determination of thorium.

Several methods for digestion of the geologic samples (1M-6M) that collected from South Eastern Desert, Egypt (Abu-Rusheid area) were tested to facilitate the analysis and choose the best one which reduce the interfering ions that affects thorium extraction and determination.

The obtained controlling factors affecting the extraction and determination of thorium element were applied for both certified reference samples and geologic samples. The extraction and stripping results obtained represent the best conditions for thorium element (Table 17).

Table (17): Controlling factors for extraction and stripping of thorium

Factors	Range
Organic solvent	Trioctylphosphine oxide (TOPO)
pH	pH 1
Shaking time	4 minute
Aqueous to organic phase ratio (A/O)	1:2
Temperature	22 ± 1˚C
Extractant concentration (TOPO)	0.08M
Diluent	cyclohexane,
Stripping process	2M H_2SO_4 with A/O ratio (4:1)
Different interfering ions	Removal using suitable sample digestion (proposed method) and using 3ml of 5% meso-tartaric acid as a masking agent.

The sample decomposition is the first step in each analysis, which consists of destruction of some or all the original material. The decomposition process varies considerably, from digestion with water, organic solvents or mineral acids to the more elaborate techniques of sintering or fusion.

These methods are: complete attack (C.A.), nitric acid 6M, mixture of nitric and hydrofluoric acids (Mix) and the proposed procedure.

(A) -Complete attack (C.A.):

0.2g of sample was mixed with a mixture of conc. 10ml HNO_3, 10ml HF and 5ml $HClO_4$ in a teflon beaker, was heated till dryness after that 20 ml of 1:1 HCl was added then completed to the required volume. The thorium concentration was determined by thoron method.

(B) -Nitric acid:

0.2g of sample mixed with 25 ml 6M HNO_3, then heated for 20 minutes, removed from the hot plate then settled for one day, filtrated and completed to the required volume using 6M HNO_3.

(C) -Mixture of nitric and hydrofluoric acid (Mix):

0.2g of sample was mixed with 20 ml conc. HNO_3 and 10 ml conc. $HClO_4$, were heated tell dryness, then 20 ml 1:1 HCl added, filtrated and completed to the required volume using distilled water.

(D) -The proposed procedure:

0.2g of sample was mixed with 20 ml HF, evaporated till dryness, diluted with 15 ml HF (1:1) then filtrated and treated the precipitate with 10 ml conc. $HClO_4$ and 5 ml conc. HNO_3 and heated till dryness. 15 ml 1:1 HCl was added to the residue and completed to the required volume.

The final solutions from all methods of digestion were analyzed spectrophotometrically to measure the major oxides concentrations (Table 18). The data showed that the proposed procedure is the best one used for digestion not only for remove most of interfering ions but also it gives the maximum extraction efficiency of thorium (99%).

Table (18): Chemical analysis of major oxides (wt %), with different methods of digestion for the samples collected from South Eastern Desert, Egypt.

Sample No.	Oxides% / Opening	SiO_2	Al_2O_3	TiO_2	P_2O_5	Fe_2O_3	CaO	MgO	Na_2O	K_2O
1M	C.A.	62.49	13.88	0.088	0.066	3.6	5.6	5	5.175	3.27
	6M HNO_3	3.85	0.755	N.D	0.061	0.4	0.42	0.2	0.207	0.196
	Mix	1.64	1.34	0.047	0.053	N.D	0.28	0.1	0.932	0.589
	Proposed	0.924	1.08	0.0198	0.039	0.2	0.14	0.2	0.376	0.491
2M	C.A.	66.67	13.98	0.0405	0.088	1.6	4.2	4	4.88	3.6
	6M HNO_3	3.64	0.504	N.D	0.065	0.399	0.42	0.3	0.195	0.18
	Mix	1.07	N.D	0.04	0.077	N.D	0.14	0.1	0.878	0.65
	Proposed	2.8	0.199	0.031	0.019	0.109	0.36	0.3	0.171	0.168
3M	C.A.	63.58	14.06	0.036	0.11	2.4	4.2	4	7.43	2.83
	6M HNO_3	1.99	0.504	N.D	0.108	0.799	0.42	0.3	0.297	0.169
	Mix	0.499	2.27	0.0179	0.074	N.D	0.14	0.2	1.34	0.509
	Proposed	1.2	0.197	0.0183	0.081	0.399	0.28	0.1	0.260	0.156
4M	C.A.	68.2	12.17	0.072	0.009	2.797	5.6	3	5.27	1.29
	6M HNO_3	2.21	0.94	N.D	0.007	0.4	0.14	0.1	0.211	0.077
	Mix	1.64	1.76	0.034	0.005	1	0.28	0.2	0.843	0.206
	Proposed	2.7	0.383	0.006	0.005	0.2	0.28	0.1	0.184	0.071
5M	C.A.	66.6	11.41	0.045	0.044	3.196	4.2	4	6.415	2.74
	6M HNO_3	2.35	1.131	N.D	0.022	0.3995	0.56	0.2	0.257	0.164
	Mix	1.927	1.09	0.01	0.038	N.D	0.14	0.2	0.898	0.384
	Proposed	0.726	1.042	N.D	0.026	0.2	0.28	0.1	0.225	0.151
6M	C.A.	65.01	13.24	0.036	0.022	2.797	5.6	4	5.025	2.75
	6M HNO_3	2.2	1.799	N.D	0.01	0.799	0.56	0.1	0.201	0.191
	Mix	2.067	1.168	0.0214	0.01	N.D	0.28	0.1	0.955	0.495
	Proposed	0.927	1.052	0.004	0.014	0.4	0.14	0.1	0.176	0.151

C.A. = Complete attack *Mix= mixture of nitric and hydrofluoric acids*

N.D. = under detection

The obtained results are given in the Table (18) and plotted in Figs. (19-24). It is found that, normal values of the major oxides were given by the complete attack while these values were tended to be reduced to very low levels using the different methods of digestion (6M nitric acid and mix), but it is nearly disappear using the proposed procedure for opening the samples.

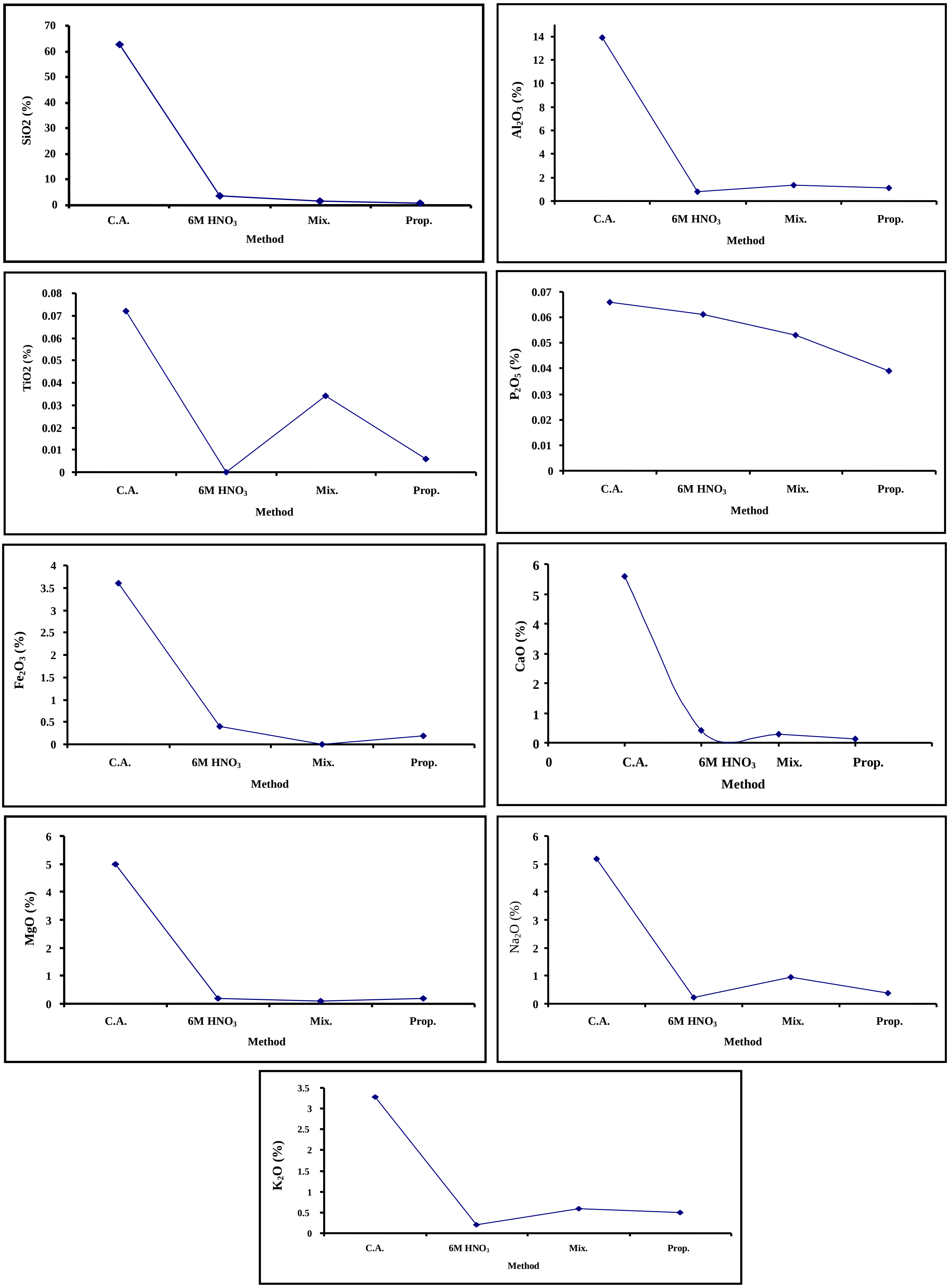


Fig. (19): Values of SiO_2, Al_2O_3, TiO_2, P_2O_5, $Fe_2O_3^T$, CaO, MgO, Na_2O, and K_2O of sample 1M after digestion with different methods.

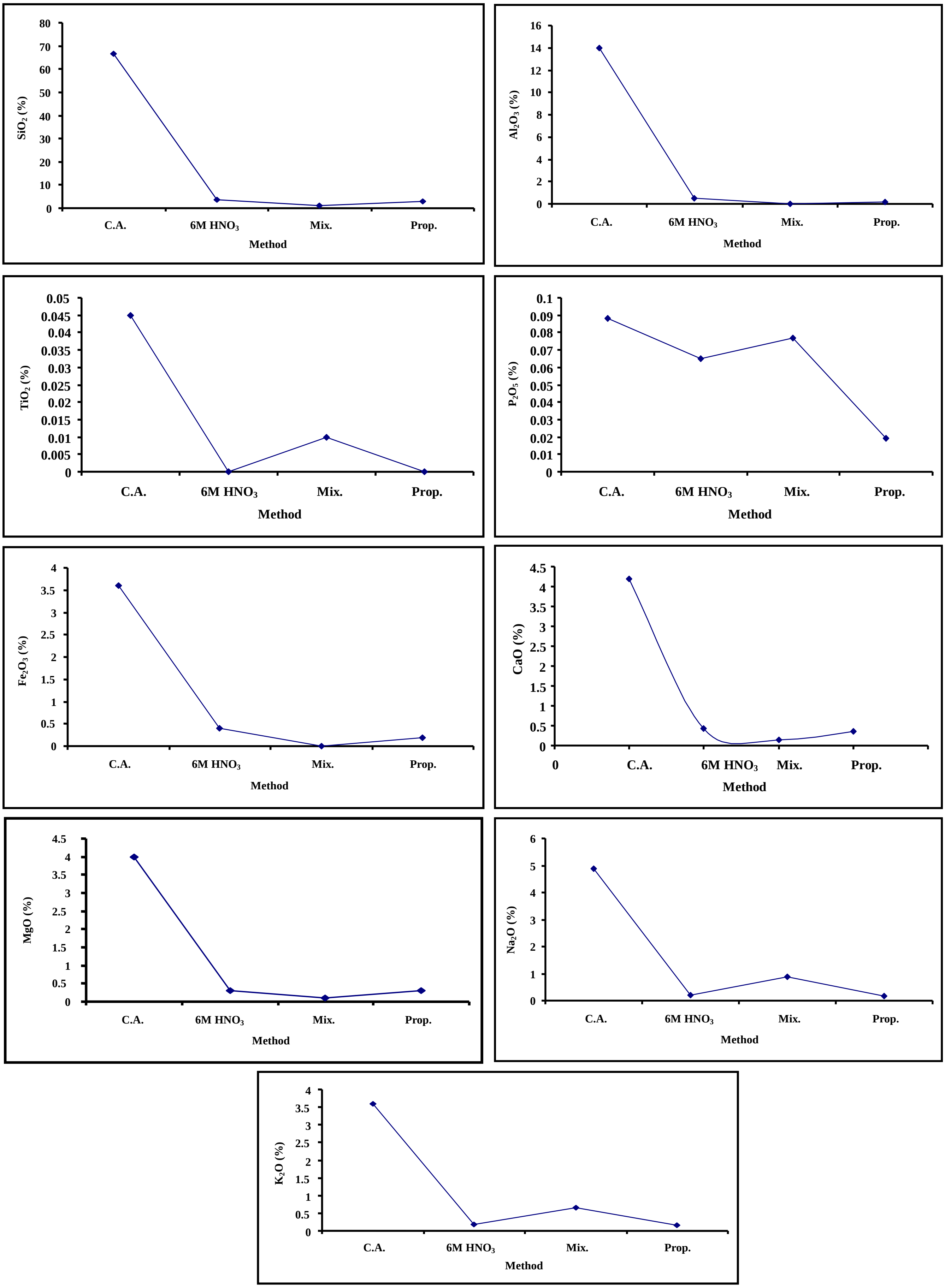


Fig. (20): Values of SiO$_2$, Al$_2$O$_3$, TiO$_2$, P$_2$O$_5$, Fe$_2$O$_3$^{T}, CaO, MgO, Na$_2$O, and K$_2$O of sample 2M after digestion with different methods.

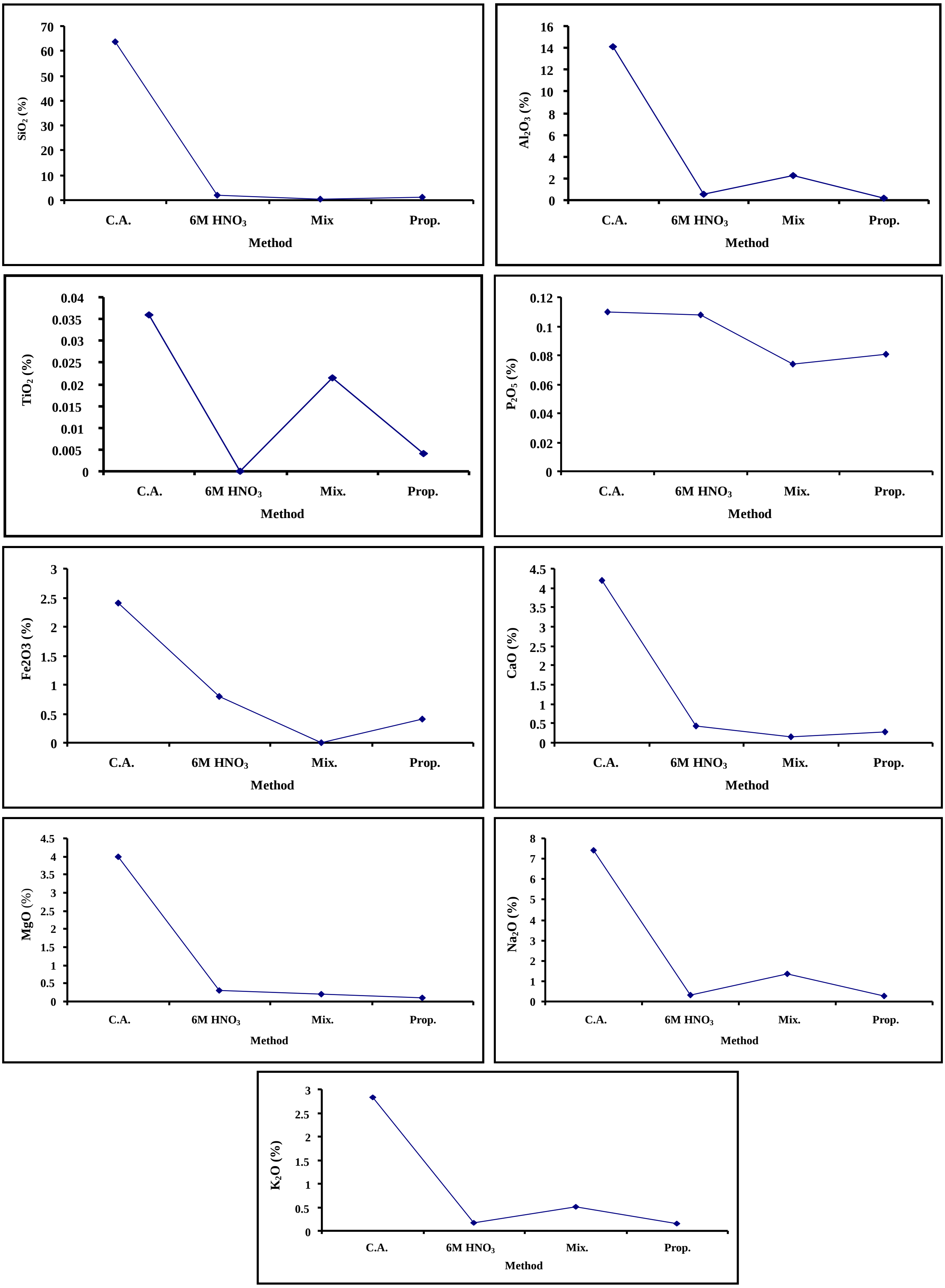


Fig. (21): Values of SiO_2, Al_2O_3, TiO_2, P_2O_5, $Fe_2O_3^T$, CaO, MgO, Na_2O, and K_2O of sample 3M after digestion with different methods.

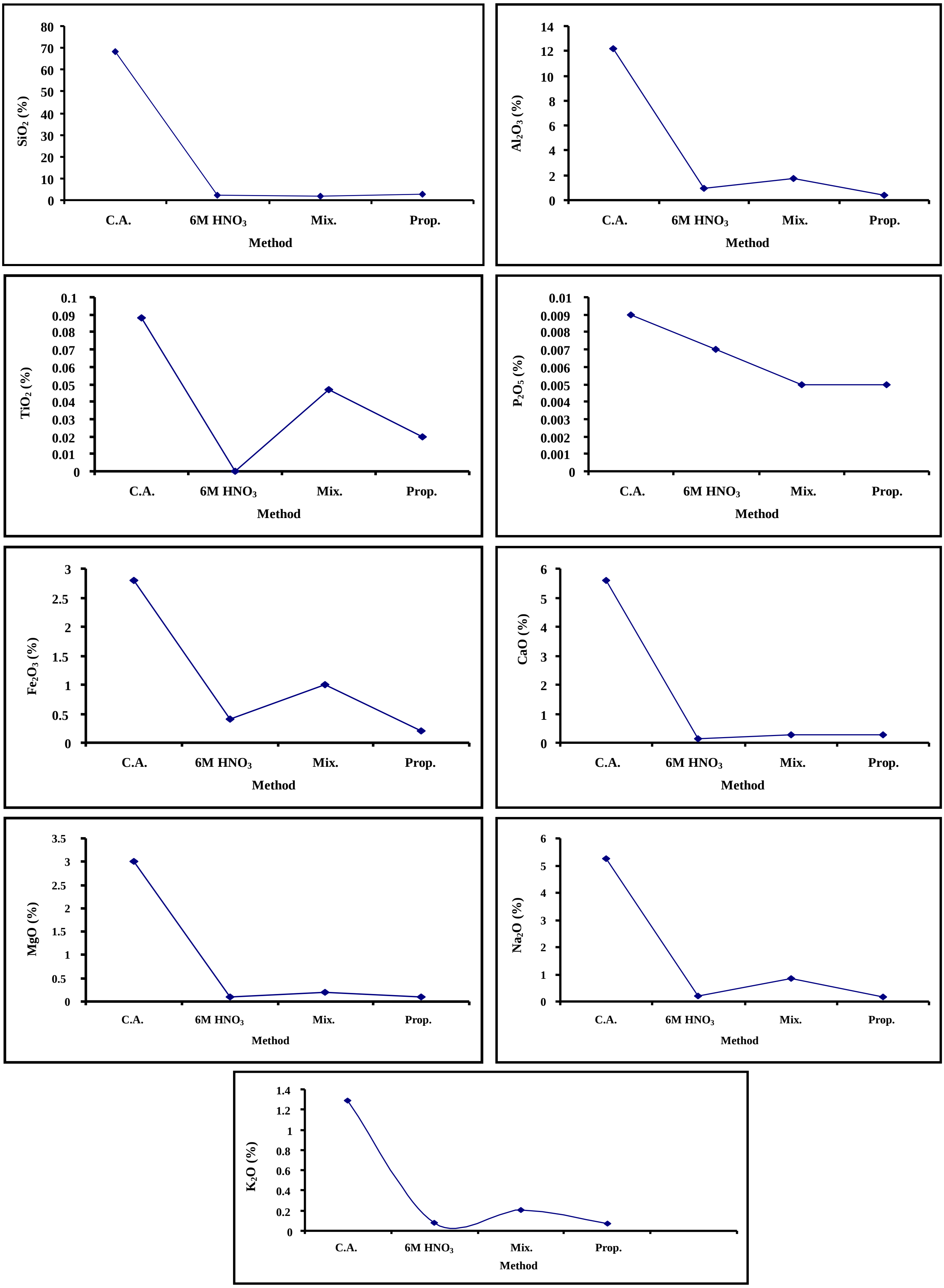


Fig. (22): Values of SiO_2, Al_2O_3, TiO_2, P_2O_5, $Fe_2O_3^T$, CaO, MgO, Na_2O, and K_2O of sample 4M after digestion with different methods.

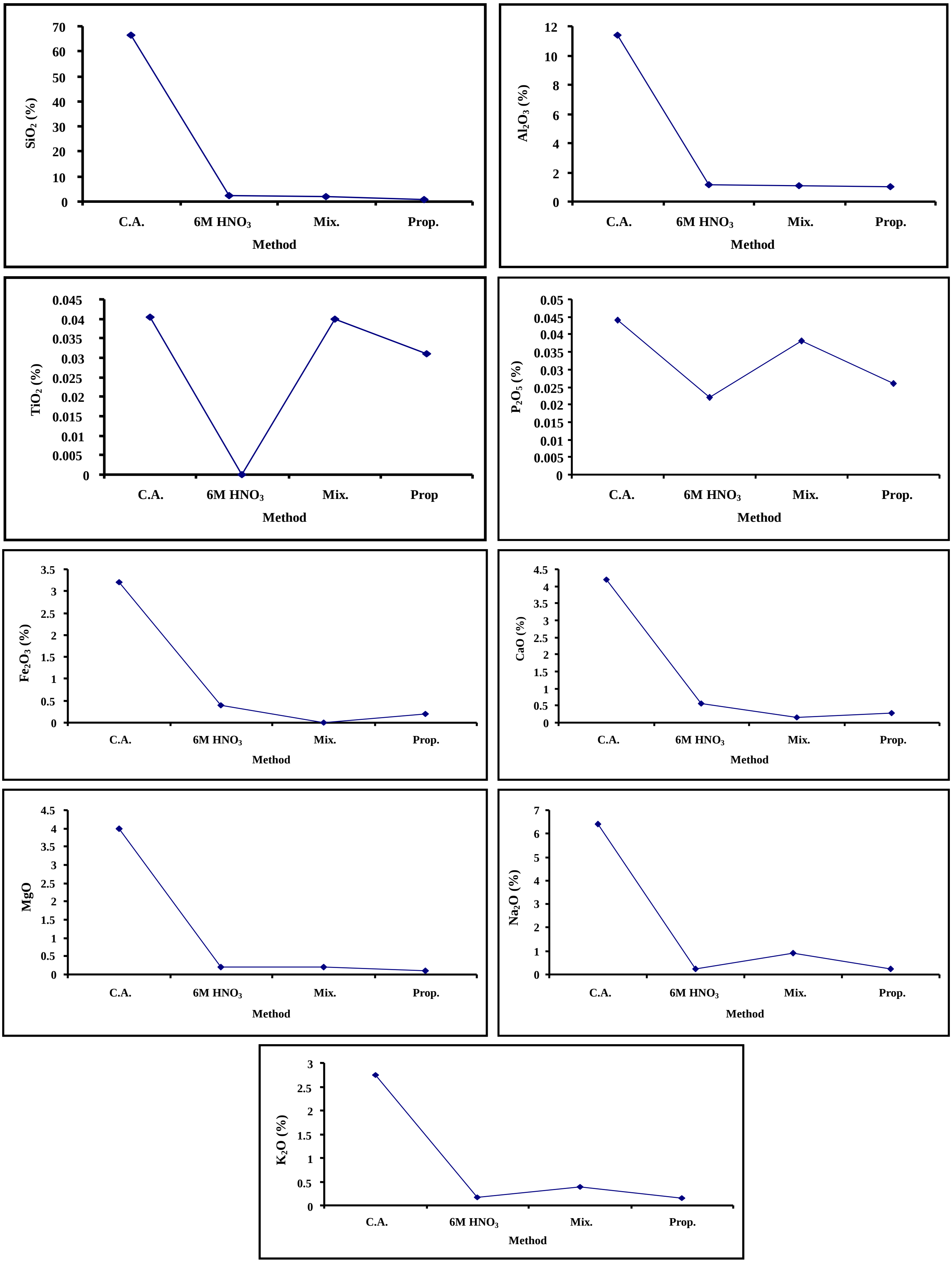


Fig. (23): Values of SiO_2, Al_2O_3, TiO_2, P_2O_5, $Fe_2O_3^T$, CaO, MgO, Na_2O, and K_2O of sample 5M after digestion with different methods.

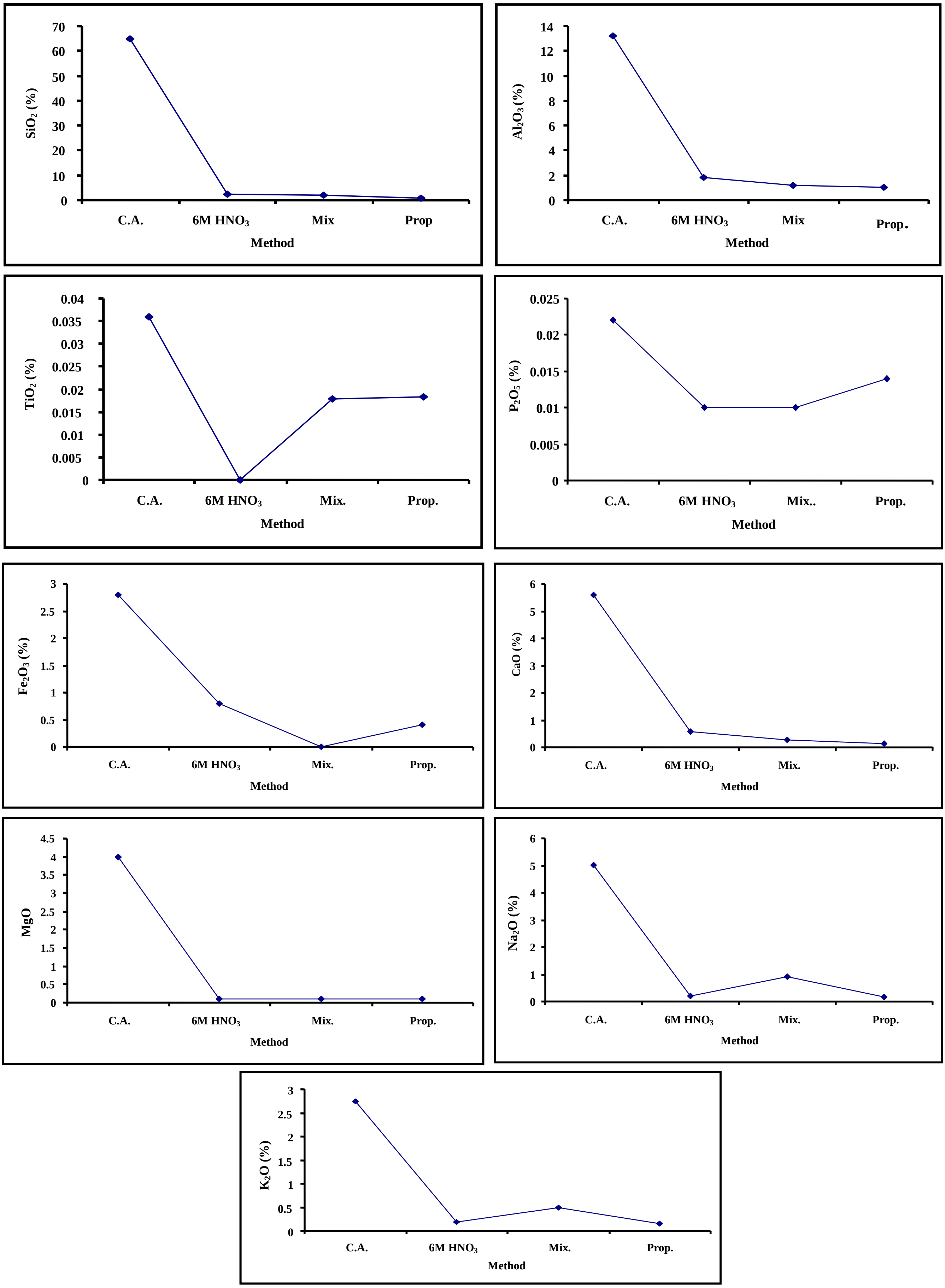


Fig. (24): Values of SiO_2, Al_2O_3, TiO_2, P_2O_5, $Fe_2O_3^T$, CaO, MgO, Na_2O, and K_2O of sample 6M after digestion with different methods.

Through the application of these methods of digestion on the selected certified reference sample GBWO4115 (CNNC), thorium content was spectrophotometrically determined using thoron method on the obtained solution to select the best way that reducing the interfering ions during thorium extraction and determination (Table 19).

Table (19): Methods used for digestion of the certified reference sample (GBWO4115).

Methods	Value of GBWO4115 (CNNC) *	Thorium content on CBWO4115 after determination with thoron	Efficiency (%)
Complete attack	**313.21 ppm**	253.7	80.9
6M nitric acid		241.17	76.9
Mixture of HNO_3 and HF acids		238.04	76
Proposed procedure		**310.1**	99

** Prepared by Bureau of Geology, China National Nuclear Co. operation (CNNC).*

The selected reference sample was digested with the four methods that selected to open the sample to examine which of them is the best one, then the optimum factors of the extraction were applied on the resulted solutions after that the thorium content using thoron method was determined. It is clear from the obtained data (Table 19), that the proposed procedure is the favorite one for opening the sample which gave the maximum extraction efficiency of thorium.

3.10.1. Determination of thorium in the certified reference samples and in the geologic samples:

The proposed method of digestion was applied for both certified reference samples and geologic samples then thorium content was measured before extraction using thoron method. The obtained controlling factors affecting extraction and determination of thorium were applied. These factors were listed in Table (17).

Six geological samples were collected from Eastern Desert of Egypt. There samples were prepared for analysis by crushing about 2Kg of each sample using a laboratory jaw crusher into pea-size and followed by grinding using a blending mill to -60 mesh size.

For each sample, about 50g were separated by quartering before being ground down to -200 mesh size. The pulverized samples were prepared for chemical analysis using the suitable technique.

The investigated samples (certified reference samples and geologic samples) were digested using the proposed procedure, the resulted solutions were undergo extraction process using TOPO dissolved in cyclohexane and the other reached optimum conditions. The thorium content was then measured in the aqueous part using thoron method, while the stripping process was occurred on the loaded organic phase (TOPO) using 2M sulfuric acid then thorium was measured and the results were listed in Tables (20 and 21). All analyses were run in chemical laboratories of Nuclear Materials Authority (NMA), Inshas.

Table (20): Determination of thorium after extraction and stripping process for certified reference samples.

Certified reference samples	Thorium Certified value (ppm)	Extraction process		Stripping process	
		Extracted Th content (ppm) using TOPO	Extraction Efficiency	Stripped Th content by H_2SO_4 acid	Stripping Efficiency %
GBWO4110* (CNNC)	25	24.5	97.6	24.1	98.4
		24.3	97.98	23.8	97.9
		23.6	98.7	22.9	97.03
GBWO4115* (CNNC)	313	312.7	99.8	311.5	99.6
		311.6	99.77	311	99.8
		312	99.7	311.5	99.8
St. GA**	17	19.4	95.56	18.5	93.4
		19.6	97.5	18.8	95.9
		19.3	96.98	18.3	94.8
St. B2*	29.7	28.13	97.9	27.9	99.3
		27.9	97.3	27.4	98.2
		28.1	9.19	27.7	98.5

***Extraction condition**s:*

- Organic phase: 0.08M TOPO in cyclohexane. A/O ratio: 1:2 for extraction, pH =1,shaking time =4min., A/O ratio =(4/1)for stripping, Temp. =22 ±1°C.

** prepared by Bureau of Geology, China National Nuclear Co. operation (CNNC).*

*** Centre of Recherches P'etrographiques et G'eontre of Recherches P'etrographiques et G'eochimiques, France.*

Table (21): Concentrations after extraction and stripping process using the proposed digestion procedure in the samples collected from Eastern Desert, Egypt.

Sample No.	Extraction process			Stripping process	
	Thorium (ppm)	**Extracted Th amount using TOPO**	**Extraction efficiency (%E)**	**Stripped Th amount by H_2SO_4 acid**	**Stripping efficiency (%S)**
1M	387.93	381.1 383.6 382.8	98.6	364.25	95.2
2M	402.297	385.1 384.3 386.1	95.7	368.2	95.8
3M	445.4	423.7 424.2 422.1	95.1	413.2	97.5
4M	129.31	126.5 125.9 126.1	97.5	123.5	97.9
5M	316.09	305.2 305.6 303.8	96.6	300.6	98.5
6M	308.91	304.5 303.3 302.4	98.5	298.3	97.96

Extraction conditions:

- Organic phase: 0.08M TOPO in cyclohexane. A/O ratio: 1:2 for extraction, pH =1,shaking time =4min., A/O ratio =(4/1)for stripping, Temp. =22 ±1°C.

3.11. Separation of thorium from the representative geologic sample

In order to separate thorium from the representative sample comprised from six samples (1M to 6M), three steps were carried out. These steps are leaching, extraction, stripping and precipitation (Fig. 27).

1- Leaching step

1. 250g of the representative sample comprised six geologic samples (1M to 6M), collected from South Eastern Desert, Egypt, were mixed with a mixture of 250ml Conc. HF, 100ml HNO_3 and 100ml $HClO_4$ in a teflon beaker, heated till dryness after that 625ml 1:1 HCl was added to dissolve the sample, then it was filtrated.
2. Concentration of the leach liquor was done by evaporation till reaching 125ml. The thorium content in this leach liquor was determined and found 90.25ppm.

2- Extraction and stripping step

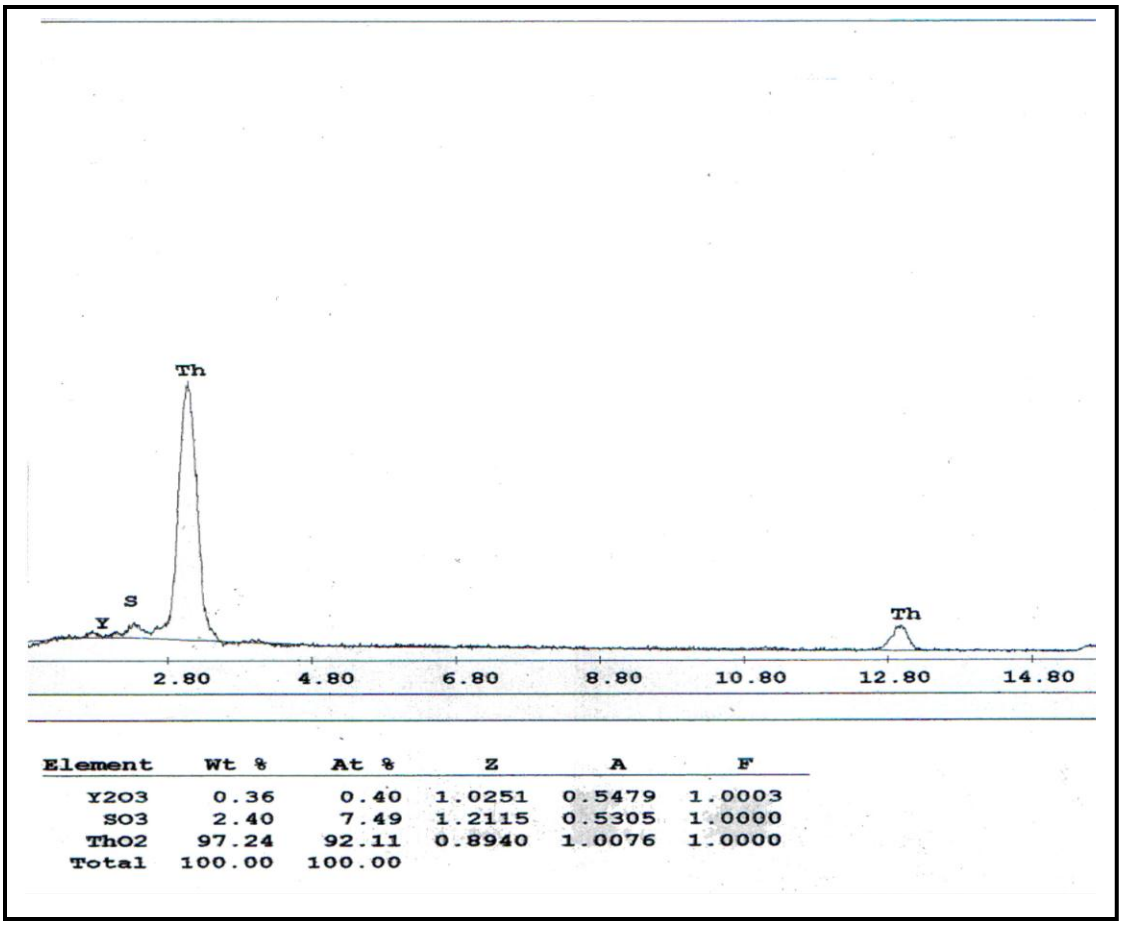
1. The concentrated leach liquor was divided into two portions (62.5ml), the factors controlling the extraction process was applied (pH 1, 125ml TOPO in cyclohexane with A/O ratio 1:2, 4min. shaking time. The stripping process was carried out using 500ml of 2M H_2SO_4 with A/O ratio 4:1 at 22± 1°C.
2. The previous step was repeated twice, accordingly the net solution becomes one liter and was concentrated by evaporation till reaching to 125ml.
3. Thorium content in this leach liquor was determined and found 180ppm.

3- Precipitation step

1- The precipitation step was carried out by adjusting the pH to 2.7 using ammonia solution followed by adding 20% oxalic acid to precipitate thorium as thorium oxalate.

2- Thorium oxalate precipitate was burnt in a furnace oven at 800°C where the final product was ThO_2.

3- XRD and scan electron microscope examination were used to confirm the final product (Figs. 25 and 26).



Element	Wt %	At %	Z	A	F
Y2O3	0.36	0.40	1.0251	0.5479	1.0003
SO3	2.40	7.49	1.2115	0.5305	1.0000
ThO2	97.24	92.11	0.8940	1.0076	1.0000
Total	100.00	100.00			

Fig. (25): EXD analysis of separated ThO_2 from the representative sample, collected from South Eastern Desert, Egypt.

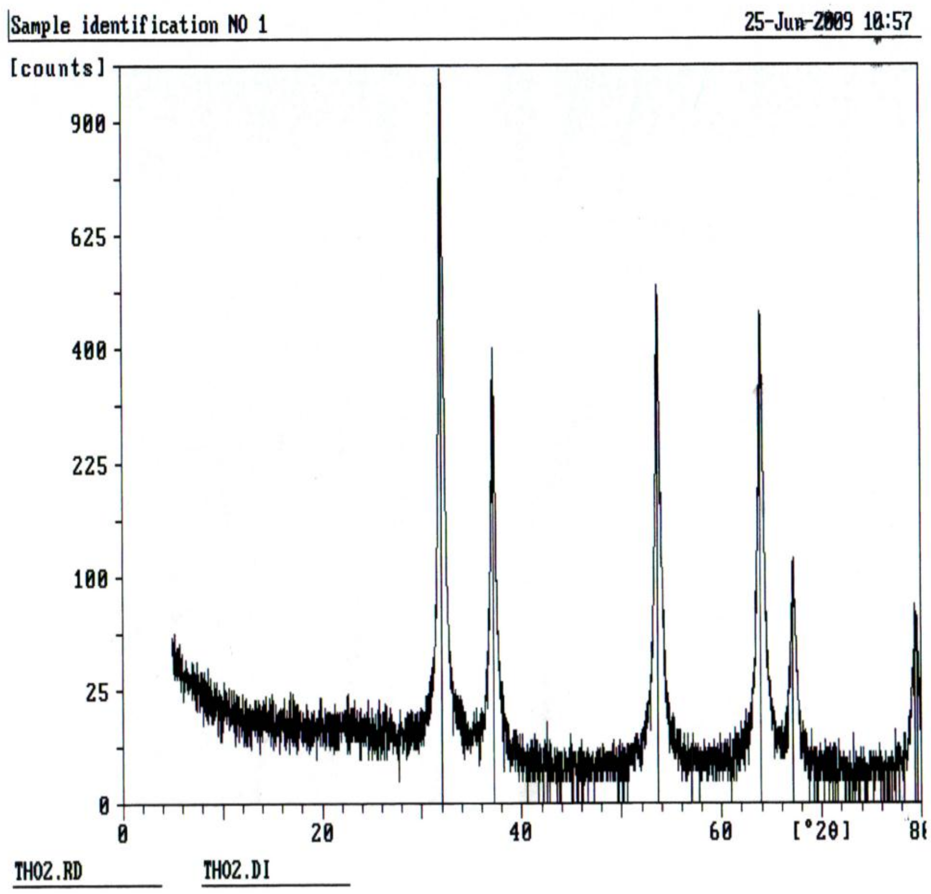


Fig. (26): **XRD analysis of the separated ThO_2 from the representative sample, collected from South Eastern Desert, Egypt.**

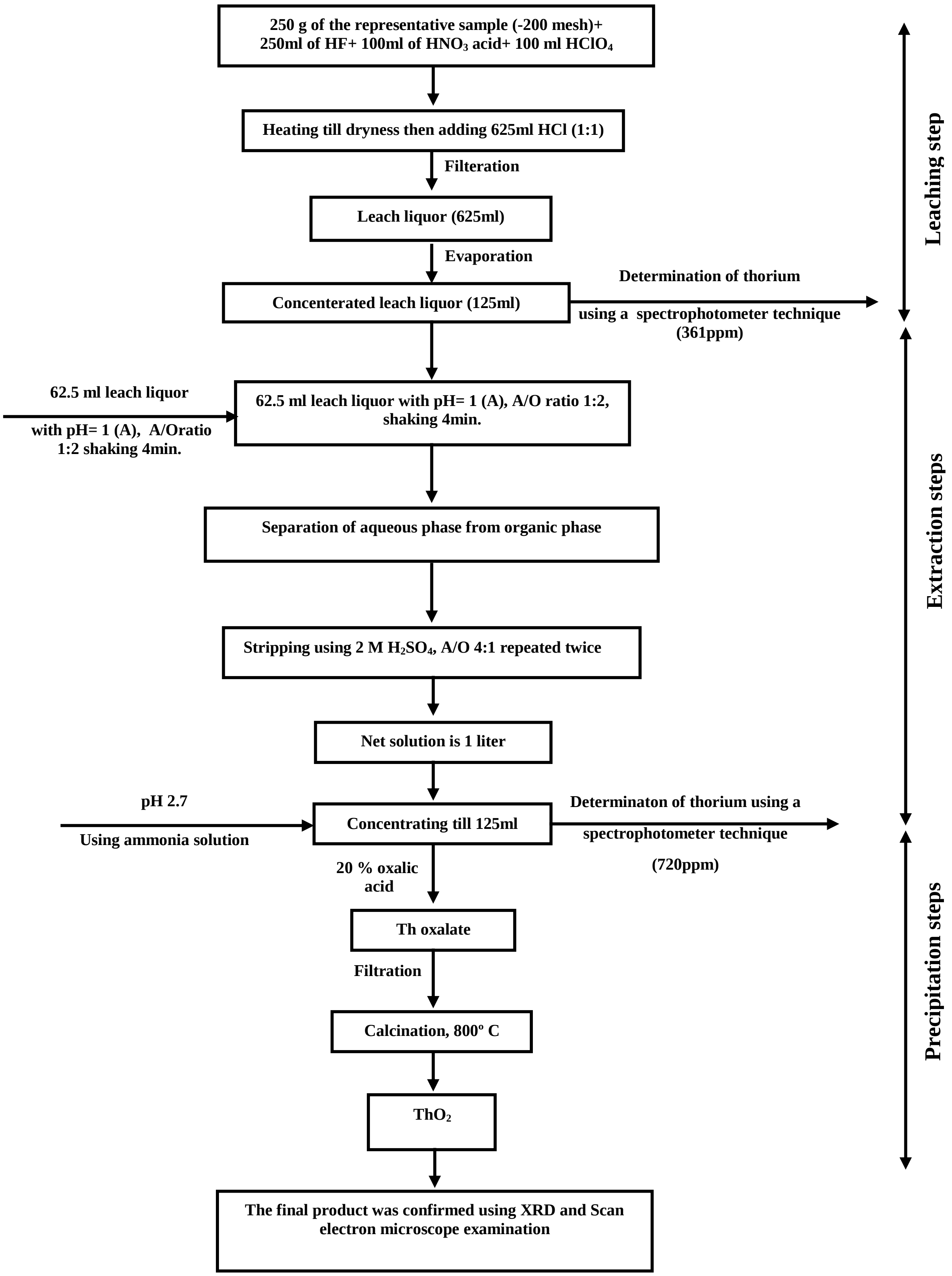


Fig. (27): Flow sheet for recovery of Th(IV) from the representative sample, collected from South Eastern Desert, Egypt.

3.12. Statistical evaluation of the results.

Statistics in chemistry helps to represent the results. It gives a possibility to indicate how precise these measurements are (with a range of errors).

Statistical analyses have been carried out for both the certified reference samples, and the geologic samples collected from South Eastern Desert, Egypt, to find out arithmetic mean ($\bar{X}$), standard deviation (S), σ standard error (S.E) and error in % using the following equtions **(Deim, 1962).**

(a) When using the data of standard reference samples, the following equation is applied:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{i=N} (Xi - \mu)^2}{N}}$$

where

σ = The standard deviation

***X*i** = the measurement values

μ = the mean of the population (value of the reference)

N= number of measurements

(b) When using the data of random samples, the following equation is applied **(Fifield and Kealey, 2000)**.

$$\sigma = \sqrt{\sum_{i=1}^{i=N} \frac{\left(Xi - \bar{X} \right)^2}{N - 1}}$$

where σ = relative standard deviation for the samples

Xi = the individual measurements from i=1 to i= N

$\bar{X}$ = the mean of measurements (average)

(c) The standard deviation of the mean is sometimes referred to the standard error (S.E) and is calculated from the following equation:

$$S.E. = \frac{\sigma}{\sqrt{N}}$$

Where S.E is the means standard error

Little numbers of experiments have been run carried out for each sample to extract thorium. The population of the experiments is very limited which is three times. The arithmetic mean ($\bar{X}$) is greatly depend on the total results of the three experiments divided on the number of the experiments.

The percentage error (error %) is determined using the following equation:

$$\%Error = \frac{S.E.}{\bar{X}} \times 100$$

The percentage error (Error %) in certified reference samples ranges from 0.192 to 1.195%, while in geologic samples ranges from

0.135 to 0.201%; (Tables 22 and 23), this declared high accuracy and precision for the obtained results.

Table (22): Statistical calculations of the certified reference samples by thoron using the proposed procedure for acid leaching method.

Certified sample	Thorium Content (ppm)	Th.(ppm) present study	Arithmatic mean ($\overline{X}$)	Standard deviation (σ)	Standard error (S.E)	Error %
GBWO4110* (CNNC)	**25**	**25.1 24.8 23.9**	**24.6**	**0.509**	**0.294**	**1.195**
GBWO4115* (CNNC)	**313**	**312.7 311.6 312**	**312.1**	**0.455**	**0.263**	**0.084**
St.GA*	**17**	**20.3 20.1 19.9**	**20.1**	**0.163**	**0.094**	**0.468**
St.B2**	**29.7**	**28.73 28.68 28.91**	**28.77**	**0.099**	**0.057**	**0.199**

** prepared by Bureau of Geology, China National Nuclear Co. operation (CNNC).*

*** Centre of Recherches P'etrographiques et G'eochimiques (1994)(CRPG).*

Table (23): Statistical calculations of geologic samples (1M-6M), South Eastern Desert, Egypt, by thoron using the proposed procedure for acid leaching method.

Sample No.	Th (ppm) present study	Arithmatic mean ($\bar{X}$)	Standard deviation (S)	Standard error (S.E)	Error %
1M	381.1 383.6 382.8	382.5	1.277	0.737	0.193
2M	385.1 384.3 386.1	385.17	0.902	0.521	0.135
3M	423.7 424.2 422.1	423.33	1.097	0.633	0.150
4M	126.5 125.9 126.1	126.17	0.306	0.177	0.140
5M	305.6 305.2 303.8	304.87	0.945	0.546	0.179
6M	303.3 304.5 302.4	303.4	1.054	0.609	0.201

3.12.2. Accuracy of thorium determination methods.

Accuracy is the extent of results or readings to the true value.The calculations of the accuracy (Δ) were determined from the following formula **(Davis, 1986)**:

$$\Delta = \pm\sqrt{\frac{d^2}{2N}}$$

where d is the difference between the repeated results

N is the number of differences.

The accuracy (Δ) of the certified reference samples ranges from ±0.121 to ±0.624, but in geologic samples collected from South Eastern Desert of Egypt, the accuracy (Δ) ranges from ±0.306 to ±1.563 (Tables 24 and 25). Accordingly the accuracy (Δ) in both standard reference and geological samples showed values less than ±2, this means high accuracy and precision for the obtained results.

Table (24): Statistical calculations of the certified reference samples by thoron using the proposed procedure for mixed acids leaching method.

Sample No.	Certified value (ppm)	Th (IV) content (ppm)	d	d^2	Accuracy Δ
GBWO4110* **(CNNC)**	25	25.1 24.8 23.9	0.3 1.2 0.9	0.09 1.44 0.81	± 0.624
GBWO4115* **(CNNC)**	313	312.7 311.6 312	1.1 0.7 0.4	1.21 0.49 0.16	± 0.557
St.GA*	17	20.3 20.1 19.9	0.2 0.4 0.2	0.04 0.16 0.04	± 0.2
St.B2**	29.7	28.73 28.68 28.91	0.05 0.18 0.23	0.0025 0.0324 0.0529	± 0.121

** prepared by Bureau of Geology, China National Nuclear Co. operation (CNNC).*

*** Centre of Recherches P’etrographiques et G’eochimiques (1994)(CRPG).*

Table (25): Statistical calculations of geologic samples by thoron using the proposed procedure for acid leaching method.

Sample No.	Th (ppm) present work	d	d^2	Δ Accuracy
1M	381.1	2.5	6.25	± 1.277
	383.6	1.7	2.89	
	382.8	0.8	0.64	
2M	385.1	0.8	0.64	± 0.902
	384.3	1	1	
	386.1	1.8	3.24	
3M	423.7	0.5	0.25	± 1.097
	424.2	1.6	2.56	
	422.1	2.1	4.41	
4M	126.5	0.6	0.36	± 0.306
	125.9	0.4	0.16	
	126.1	0.2	0.04	
5M	305.6	0.4	0.16	± 0.945
	305.2	1.8	3.24	
	303.8	1.4	1.96	
6M	303.3	1.2	1.44	±1.563
	304.5	1.9	3.61	
	301.4	3.1	9.61	

The present study showed that thorium (IV) can be extracted using the reached controlling factors affecting extraction and determination of thorium, which applied for both certified reference samples (CBWO4110, CBWO4115, St.GA, and St.B2) and geologic samples (M1 to M6), collected from South Eastern Desert, Egypt. These factors were, concentration of 0.08M TOPO (solvent extractant) in cyclohexane, pH 1 of aqueous solution, 3 ml of 5% meso-tartaric acid as a masking agent, 2:1 aqueous/organic phase ratio, shaking time 4 min. at 22± 1°C, and stripping using 2M H_2SO_4, 4:1 aqueous/organic phase ratio, shaking time 4min. at 22± 1°C. The final results indicate that it is possible to use TOPO as a selective extractant followed by spectrophotometric determination of thorium using thoron as a specific and sensitive reagent. Statistical calculations indicate that the error percent in certified reference samples and geologic samples ranges from 0.084 to 1.195%. The accuracy (Δ) of certified reference samples and geologic samples ranges between ± 0.121 and ± 1.563, which indicates high accuracy and precision for this method, which the aim of this thesis.