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RESEARCH ARTICLE

Developed spectrophotometric method for thorium determination in different Rosetta monazite concentrates using thorin dye

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Abstract

A developed, sensitive and direct spectrophotometric determination of leached thorium from different Rosetta monazite concentrates using thorin dye was studied for optimum thorium determination using thorin dye. Leached thorium was determined without prior separation using either solvent extraction or ion exchange techniques. Optimization of pH of different mineral acids, buffer pH, dye concentration and thorium concentration were studied for optimum thorium determination. After three leaching steps of thorium from monazite using 10M HNO_3, solid to liquid (acid) ratio 1:60, two hours stirring at 60^oC, the percentage leaching of thorium was 98.9%. Interference due to traces of rare earths was overcome using 3% H_2O_2. Beer's law was obeyed from $0.1 \mu g\ ml^{-1}$ to $100\ \mu g\ ml^{-1}$ with molar absorptivity (ϵ) value $0.173x10^4\ mol^{-1}cm^{-1}$ and standard deviation 0.133. The % RSD for 10 replicate measurements of 4ppm thorium was 1.48%.

INTRODUCTION

The Rosetta monazite concentrate, one of Egypt's main sources of thorium, uranium and rare earth elements was obtained as a by-product of a mining operation designed to recover the more abundant minerals such as ilmenite, magnetite, zircon and rutile from the black sand deposits of Rosetta, north coast of Nile Delta, Egypt. Monazite from this source was generally obtained in the form of concentrate containing about 40% of the pure mineral and was further upgraded to different purity concentrates by subjecting to magnetic and electrostatic separators. Monazite is one of the main sources of thorium. Its recovery requires accurate method for analysis in different monazite concentrates and throughout the the hydrometallurgical processing for mass balance calculations. For its leaching long and severe acid conditions for thorium separation was used for accurate analysis. Various analytical techniques as thin layer chromatography **(Soran et al., 2005)**, gravimetric **(Arora, and Rao, 1981)** volumetric **(Banjeree, 1955)**, reversed phase liquid chromatography **(Hao et al., 1996)**, fluorimetry **(Pavon et al., 1989)**, potentiometry **(Tewari and Srivastava, 1972)**, energy dispersive X-ray fluorescence **(Mirashi et al., 2010)** and inductively coupled plasma mass spectrometry **(Shinotsuka et al., 1996)** were reported for Th (IV) determination. Some reported methods such as liquid chromatography, X-ray fluorescence, and inductively coupled plasma mass spectrometry were sensitive but expensive due to high running cost and specific procedures required prior to the analysis of thorium (IV) **(Hao et al., 1996)**.

Spectrophotometry was an alternative method which provided some advantages such as simplicity, and moderately low cost. The determination of thorium required high accuracy coloring reagent and low detection limits due to strong association with other elements **(Sahoo et al., 2004)**. Recently a number of reagents were used for spectrophotometric determination of thorium such as PAR **(Abbasi, 1988)**, TAR **(Saki and Tonosaki, 1969)**, EBT **(Lott et al., 1960)**, chromtrope 2B **(Sangal, 1965)** and thoron **(Cheng, 1963)**. It was determined spectropho-

-tometrically based on the reaction with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol in the presence of sodium acetate-acetic acid buffer solution of pH 4.86 at 580nm **(Aydin and Soylak, 2007)** sodium 4,8-diamino-1,5-dihydroxyanthra-quinone- 2,6-disulphonate in acidic pH at 685 nm **(Abu zuhri, 1984)**, sodium 5-(4-diethylamino-2-hydroxyl phenyl azo) 1,2,4-triazole-3-carboxylate in acidic pH at 535 nm **(Navas and Garcia-Sanchez, 1979)** and bromocresol orange at 560 nm **(Thimmaiah et al., 1984)**. Two extractive spectro-photometric methods were utilized for thorium estimation based on isoamyl alcohol extractable ion pair complex of thorium(IV) with 2-hydroxy-1-napthaldehyde iso-nicotinoylhydrazone at a pH 3 at λ_{max} 420 nm **(Khalifa and Hafez, 1998)** and chloroform extractable ion pair complex with 8-quinolinol in the presence of acidic buffer at 390 nm **(Kalventis, 1988)**.

An improved analogue reagent, arsenazo-III was reported to be suitable for the photometric determination of thorium and some other elements **(Goto et al., 1966), (Kuroda, et al., 1990) and (Ramkrishna, 1979).** The determination of thorium using arsenazo-III was reported to exhibit a relatively narrow concentration range and low value of molar absorptivity **(Petrow and Strehlow, 1967).**

Direct, derivative, and simultaneous spectrophotometric methods were developed for determination of uranium and thorium individually and simultaneously through the reaction of 2-hydroxy-1-naphthaldehydihydroxybenzoic-hydrazone (HNAHBH) with thorium (IV) and uranium (VI) **(Savvin, 1961)**. The applicability of the developed methods was tested by analyzing water, ore and fertilizers.

Thorium (IV) reacts to give a yellow colored soluble complex with 5-Bromo-2-hydroxy-3-methoxybenzaldehyde-hyde-4-hydroxy benzoichydrazone [Th(IV)-5-BHMBHBH] in acidic buffers. In the pH range 1.5-2.5, maximum absorbance was at λ_{max} 400 nm. The system obeyed Beer's law in the range 1.16- 18.5 µg/ml. The present method was applied for thorium determination in monazite sand. **(Reddy, et al., 2014)**

A rapid and sensitive spectrophotometric method was developed for thorium determination in ore samples using 0.04% arsenazo-III in 2M perchloric acid solution. Beer's law was obeyed in the range 1–60 $\mu g.g^{-1}$ with molar absorptivity value $3.07x10^5$ $M^{-1}.cm^{-1}$ at 654 nm. The method was applied on certified reference material for thorium determination after extractive separation and the result was found in good agreement with the certified values with a precision of ±0.04%. The method was also applied successfully to determine thorium at $\mu g.g^{-1}$ level. **(Fukuma, et al., 2001).**

Cationic surfactant, cetyldimethylethylammonium bromide (CDMEAB), sensitizes the color reaction of Th (IV) and U(VI) with chrome azurol S (CAS). Beer's law was obeyed in concentration range 0.12-0.185 ppm for Th (IV) and 0.13-0.162 ppm for U (VI) in presence of CDMEAB. **(Haleem, et al., 2001)**.

A method for thorium determination in monazite sand involved its fusion with potassium hydrogen fluoride, separation of the insoluble rare earths and thorium fluorides by centrifugal action, followed by extraction of thorium into mesityl oxide where it was spectrophotometrically determined in the extract with thorin. **(Upase, et al., 2011)**

Thorium, a highly reactive metal, at standard temperature and pressure, was slowly attacked by water, but does not readily dissolve in most common acids. It was dissolved in concentrated nitric acid containing small amounts of catalytic fluoride or fluorosilicate ions. **(Blair, and Callis, 1952)**

A sensitive spectrophotometric method was developed for the determination of microamounts of thorium using 0.05% thorin in a 3M perchloric acid solution at 544 nm. Beer's law was obeyed from 0 to 25µg g^{-1} thorium in solution with molar absorptivity $\epsilon_{544\ nm} = 1.69x10^4\ M^{-1}\ cm^{-1}$ at 26^oC. **(Hyde, 1960)**

In the present work, several parameters for maximum thorium leaching from monazite were studied. A developed, direct, sensitive and accurate spectrophotometric method for determination of leached thorium from different monazite concentrates using thorin dye was adopted without prior separation of thorium from its leach liquor using either solvent extraction or ion exchange resin techniques.

Material and Methods

Analysis of thorium in different monazite grades

Thorium concentrations were analyzed **(Fukuma et al., 2001)** in the monazite mineral concentrates of different purities (50%, 90%, 97% and standard monazite; 99.8%) and their thorium analyses were shown in Table 1.

Instrumentation

A double beam UV – Visible spectrophotometer model Labomed (UVD 2950), USA, was used for measuring the absorbance of thorium–thorin dye complex. All measurements were carried out at room temperature (25° C, ± 5°C) using 1 cm matched glass cuvettes. A pH meter, model Jenway 3150, was used for recording the pH values of different solutions. A daily calibration of the pH meter was performed using two successive buffer solutions (4 and 7 or 7 and 10).

Preparation of stock solutions

In the present work various stock solutions were prepared including stock solutions of thorium, thorin dye, different acidic media, buffers and the studied interfering elements.

Thorium stock solutions

A weight of 0.0595 g thorium nitrate dissolved in 100ml distilled water gave a stock solution of 1000 ppm thorium. By proper dilution different concentrations were prepared for studying different factors.

Dye stock solutions

A weight of 0.0576 g of thorin dye dissolved in 100 ml distilled water gave a concentration of 10^{-3} M.

Acid stock solutions

Different concentrations of perchloric acid ($HClO_4$) and nitric acid (HNO_3) were prepared by proper dilutions from concentrated acids for further studies.

Buffer stock solutions

A buffer stock solution was prepared by mixing a constant volume of 0.1M sodium hydroxide with constant volumes of 0.5M perchloric acid, where different pH values (0.65, 0.7 and 0.75) were prepared.

Leaching of thorium from monazite

Thorium phosphate reacted with nitric acid, and produced soluble thorium nitrate. Several authors discussed the availability of thorium leaching from monazite sand. The concentration of nitric acid may vary widely, but about 20% was preferable for leaching. A quantity of 3.5 parts of 20% nitric acid per one part of monazite sand was found suitable. However, nitric acid concentration of the solution to be extracted preferably was not above 4 N because higher acidities do not change the degree of extraction sufficiently to warrant the higher expense **(Bridger, et al., 1952)**. Authors reported that leaching of thorium from monazite took place on three leaching steps using 1:1 HNO_3 for two hours **(Khan, et al., 1994)** where nitric acid dissolved ThO_2 poorly. In the present work different monazite concentrates (50%, 90% and 97%) beside a local standard monazite (99.8%) were applied for the efficacy of the developed method.

Results and Discussion

This section discussed two categories namely; the optimization of different parameters for thorium determination using thorin dye and the optimum conditions for maximum leaching of thorium from different monazite concentrates for its determination using the developed thorin method. Parameters studied for thorium determination included effect of acid media, buffer pH, dye concentration, molar ratio and duration time of the complex.

Effect of different pH acid media on complex formation

Different acid media concentrations were studied for optimum formation of thorium-thorin complex. The effect of different pH values of hydrochloric acid, sulphuric acid, perchloric acid and nitric acid were studied for the optimum complex formation. From Figure 1 it was observed that high absorbance values were recorded for $HClO_4$ rather than HCl and HNO_3 hence $HClO_4$ (pH 0.7, 0.2M) was selected as acid medium for optimum complex formation.

Selection of suitable buffer pH solution

The optimum pH selected was 0.7 (0.2M $HClO_4$) for optimum thorium-thorin complex formation, hence three pH values were studied; 0.65, 0.70 and 0.75. Different volumes from the studied buffer solution (0.5M perchloric acid and 0.5M sodium hydroxide) were added. From Table 2 it was recognized that the highest absorbance value was observed with addition of 1ml from buffer pH 0.65.

Effect of thorin dye concentration on optimum complex formation

The study of thorin dye concentration was important for optimum complex formation and its stability. A dye concentration, less or higher than necessary, would cause deviation from Beer's law and overlapping of dye spectra with other ion-dye complex. The optimization of the dye consumption and addition beside pH value would prevent, to a certain extent, the dye from the formation of complexes with other ions that may be present in the aqueous solution. From the obtained data, it was found that maximum absorbance for Th-thorin complex was observed when adding 3 ml dye (10-3M) at λ_{max} 542 nm as shown in Figure 2.

Molar ratio method

The molar ratio determination between metal and dye was determined by preparing three different concentrations of both thorium and thorin dye (1.5x10^{-4} M, 2x10^{-4} M, 2.5x10^{-4} M), in such a way that the total volume of both components was kept constant. From Figure 3 it was found that the optimum molar ratio was 1:1.

Effect of duration time on the stability of thorium – thorin dye complex

After optimizing the complex formation of thorium - thorin complex, the duration of the stability of complex was studied. All optimized additions were added; 1ml Th (10^{-3}M), 2ml from 1N $HClO_4$ (0.2M), 1ml buffer (pH 0.65) and 3ml thorin dye (10^{-3}M), up to volume in 10ml volumetric flask and measure the absorbance at 542nm. From the recorded data in Table 3, it was observed that the complex was formed instantly and was stable for 15 minutes, after which it began to dissociate.

Construction of calibration curve

A calibration curve was constructed where different concentrations of thorium and the previously studied optimized reagents were added. Beer's law was obeyed from a minimum concentration of 0.1ppm till a maximum concentration of 100 ppm after which a plateau was formed.

Analysis of Thorium in Monazite

After optimizing several parameters for determination of thorium using thorin dye, analysis of thorium in monazite concentrate (97%) was used for the applicability of the present studied method.

Leaching of different grades of monazite concentrates

Thorium, a highly reactive metal, was slowly attacked by water but it was dissolved in concentrated nitric acid containing small amounts of catalytic fluoride or catalytic fluoride or fluorosilicate ions **(Hyde, 1960)**. Authors mentioned that nitric acid (1:1) was used for leaching thorium from monazite sand using several conditions for maximum leaching **(Khan, et al., 1994)**. In the present work, several leaching factors were optimized for maximum leaching of thorium from monazite 97% (ThO_2 was 5.80%) namely; nitric acid concentration, solid to liquid ratio, temperature, agitation time and number of leaching steps.

Effect of nitric acid concentration on thorium leaching

To 1g ground monazite (-200 mesh), 100ml of different concentrations of nitric acid were added (2M, 4M, 6M, 8M, and 10M) at 100°C for two hours agitation time. From Figure 4 it was found that 10M nitric acid was the nearest molarity for thorium leaching giving the closest thorium concentration value (3.48% ThO_2) to the analyzed one (5.80 % ThO_2).

Effect of solid to liquid ratio on thorium leaching

To several individual weights (1g) of ground monazite, 10M nitric acid were added where the solid to liquid ratio was varied from 1:20 to 1:100 with two hours agitation time at 100°C. Figure 5 showed that the most compromised thorium concentration was attained at 1:60 solid to liquid ratio, above which higher concentration values of thorium was observed and this may be due to the presence of some interfering ions which enhanced thorium concentration values.

Effect of temperature on thorium leaching

In glass beakers add several weights (1g) of ground monazite (97%), 60ml of 10M nitric acid were added to each beaker and heated at different temperatures; 40°C, 60°C, 80°C and 100°C with 2 hours stirring. Filter and keep the filtrate for thorium analysis. The precipitate was treated with the same previous additions for another two times. Total thorium concentration was analyzed in the three filtrates at different temperatures. It was observed from Figure 6 that the best thorium leaching was at 60°C, above which enhanced thorium concentration values than normal were recorded due to partial dissolution of some associated ions which may interfere during thorium determination.

Effect of agitation time on thorium leaching

The effect of agitation (stirring) time on thorium leaching from monazite was studied. Different weights of monazite (1g) were weighed in glass beakers using the previously studied optimized additions; 10M nitric acid, S/L ratio 1:60, at 60°C using different time intervals of stirring; 1h, 2h and 4h. This was repeated twice again for complete leaching of thorium where its total concentration was the sum of the three leached steps. From the data obtained in Table 4, it was evident that 2 hours agitation time was sufficient for maximum leaching of thorium from monazite with slight interference effect (true concentration was 5.80% ThO_2). This may be due to the previous conditions used which may leach traces of rare earths that interfered during thorium determination.

Effect of Interfering Ions

Some accompanying elements were leached with thorium from monazite (97%) which may interfere during its determination, such as phosphoric acid, uranium and traces of rare earth elements, Table 5. As shown the maximum concentration of phosphoric acid after leaching was 1.78% and this concentration has no interference effect on thorium determination **(Fukuma et al., 2001)**. On the other hand, uranium has no adverse effect on thorium determination since interference begins when U : Th ratio was above 6:1 which is not the case in monazite **(Kuroda et al., 1990)**. Only traces of leached rare earths (1.37%) caused interference during thorium determination.

From Table (5) it was observed that one of the advantages of selective thorium leaching from monazite using the previous optimized conditions was the highest leaching percentage of thorium and the least concentrations of accompanying interfering elements where it was overcome using masking agents without the need for a separation process such as solvent extraction or ion exchange. The use of 3% hydrogen peroxide was recommended for masking rare earths, where different volumes were added, and it was found that 0.1ml from 3% H_2O_2 was efficient to overcome the rare earth elements interference during determination of thorium using thorin dye, Table 6.

By applying the optimized developed method for thorium determination in different concentrates of monazite (50%, 90% and standard local monazite sample) it was found that thorium concentrations were very close to that using the severe conditions procedure using sulphuric acid leaching, Table 7.

Statistical evaluation of the developed method

Some statistical parameters were calculated for the evaluation of the developed method, where 10ppm of synthetic thorium was determined ten times for calculating some statistical parameters. From results obtained in Table 8 it was found that acceptable statistical results were obtained where a standard deviation of 0.133and %RSD value of 1.48% which is spectrophotometrically an acceptable result.

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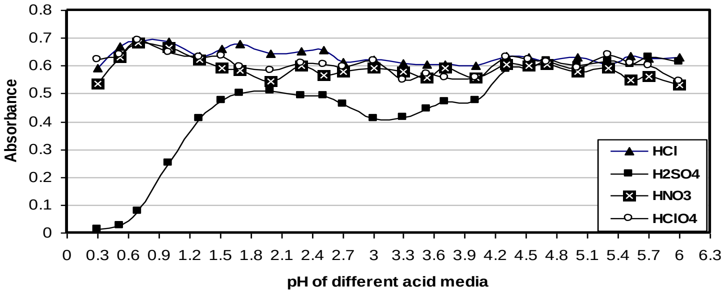

Fig 1 Effect of different pH values on complex formation

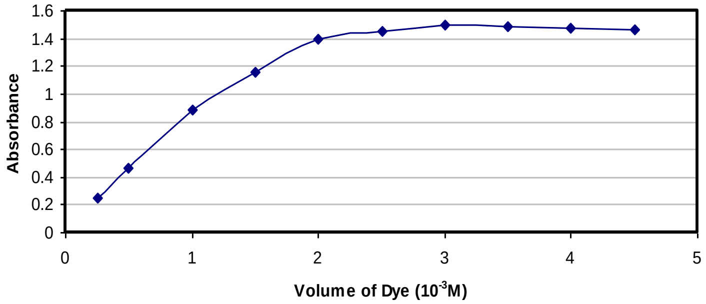

Fig 2 Effect of thorin dye concentration on the absorbance of Th-thorin complex

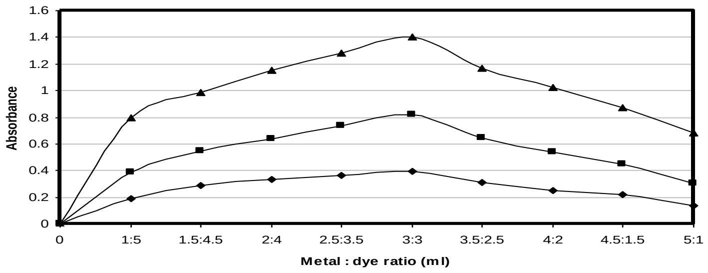

Fig 3 Molar ratio method for thorium thorin complex

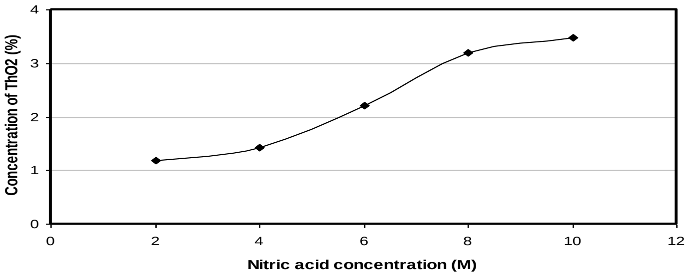

Fig 4 Effect of nitric acid concentration on thorium leaching

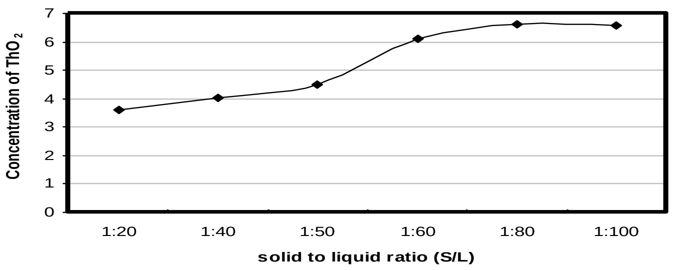

Fig 5 Effect of solid/liquid ratio on thorium leaching

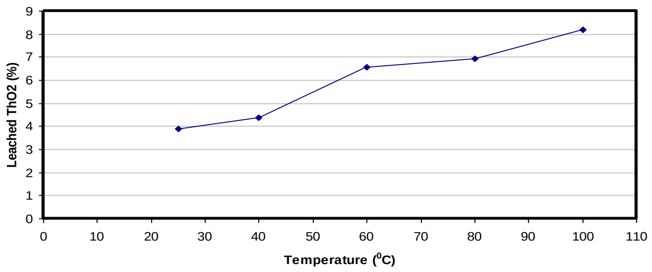

Fig 6 Effect of temperature on thorium leaching

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Table 1. Chemical analysis of thorium in different studied monazite concentrates

Monazite Concentrates	Thorium Concentration (%)
50%	3.15
90%	5.40
97%	5.80
Standard Monazite (99.8%)	6.20

Table 2. Effect of buffer solution of different pH values

Volume Of Buffer (ml)	pH 0.65		pH 0.7		pH 0.75	
	Wave-length (λ,nm)	Abs.	Wave-length (λ,nm)	Abs.	Wave-length (λ,nm)	Abs.
0.1	542	1.017	542	0.946	542	0.930
0.2	542	1.021	542	0.958	542	0.988
0.3	542	1.024	542	0.959	542	1.014
0.5	542	1.037	542	0.966	542	0.928
1.0	542	1.054	542	0.969	542	0.998
1.5	542	1.050	542	0.971	542	1.006
2	542	1.048	542	0.964	542	0.957
2.5	542	1.028	542	0.955	542	0.994
3	542	1.016	542	0.950	542	0.973

Table 3. Effect of duration time on the stability of thorium

Time (minutes)	Absorbance
zero	1.433
5	1.435
10	1.433
15	1.434
20	1.420
25	1.410
30	1.404
35	1.398
45	1.388
50	1.376

Table 4. Effect of agitation time on thorium leaching

Time (hours)	Th Conc. (ppm)	Th Conc. (%)	ThO_2 Conc. (%)
Step1(1 hour)	20.58	5.14	8.74
Step2(1 hour)	4.70	1.17	
Step 3 (1 hour)	5.47	1.37	
Step1 (2 hours)	10.90	2.18	6.14
Step 2 (2 hours)	6.80	1.36	
Step 3 (2 hours)	9.30	1.86	
Step 1 (4 hours)	16.70	4.17	10.58
Step 2 (4 hours)	12.13	3.03	
Step 3 (4 hours)	8.45	2.11	

Table 5. Concentration of leached elements with thorium

Element (%)	Monazite (50%)	Monazite (90%)	Monazite (97%)	Standard Monazite
$H_3PO_4(\%P_2O_5)$	0.80	0.49	0.60	1.78
Uranium (%)	$0.2x10^{-5}$	$0.02x10^{-4}$	$0.38x10^{-3}$	0.005%
ΣREE (%)	1.26	1.31	1.27	1.37

Table 6. Effect of hydrogen peroxide as a masking agent for rare earths during Thorium determination in monazite (97%)

Leaching Steps	Volume of H_2O_2 (ml)	Th conc (%)	Total [ThO_2] (%)
Leach 1 (97%)	0.1ml	1.66	5.54
Leach 2 (97%)		1.42	
Leach 3 (97%)		1.79	
Leach 1 (97%)	0.2ml	2.14	6.3
Leach 2 (97%)		1.37	
Leach 3 (97%)		2.03	
Leach 1 (97%)	0.3ml	2.11	6.14
Leach 2 (97%)		1.42	
Leach 3 (97%)		1.87	
Leach 1 (97%)	0.5ml	2.27	6.18
Leach 2 (97%)		1.29	
Leach 3 (97%)		1.87	
Leach 1 (97%)	0.7ml	2.29	6.46
Leach 2 (97%)		1.49	
Leach 3 (97%)		1.90	

Table 7. Concentrations of thorium in different monazite concentrate using the present developed method for determination

Sample	Leaching Steps	Th conc. (ppm)	Th conc. (%)	ΣThO_2 (%)
Monazite 50%	1st leaching	3.39	1.13	3.17
	2nd leaching	2.52	0.84	
	3rd leaching	3.06	1.02	
Monazite 90%	1st leaching	3.47	1.30	5.46
	2nd leaching	6.66	2.5	
	3rd leaching	2.40	0.90	
Monazite 97%	1st leaching	6.23	1.66	5.54
	2nd leaching	5.31	1.42	
	3rd leaching	6.74	1.79	
Standard Monazite	1st leaching	7.71	2.57	6.19
	2nd leaching	3.54	1.18	
	3rd leaching	5.19	1.73	

Table 8. Replicate measurements for 10ppm thorium

Sample No.	Concentration (ppm)	Mean	SD*	%RSD#
1	10.23	10.29	0.133	1.48%
2	10.25			
3	10.28			
4	10.30			
5	10.32			
6	10.32			
7	10.33			
8	10.33			
9	10.34			
10	10.34			

*SD refers to Standard Deviation
#%RSD refers to percentage Relative Standard Deviation

Conclusions

A developed, direct spectrophotometric method with good precision for thorium determination in different monazite concentrates was studied using thorin dye. Maximum leaching (98.9%) for thorium was reached after three steps leaching using 10M HNO_3, solid to liquid ratio 1:60, at 60^oC for two hours stirring. Direct determination of thorium in the leach liquor was performed using the present optimized developed thorin dye method without its prior separation using either solvent extraction or ion exchange techniques. Optimized parameters for determination of thorium using thorin dye were; 0.2M HNO_3 (pH 0.7), 1ml from buffer (pH 0.65), 3ml from 10^{-3}M dye concentration and thorium concentration (calibration curve). The interference effect was only due to traces of leached rare earths which were overcome using 3% H_2O_2. Beer's law was obeyed from 0.1µg ml^{-1} to 100 µg ml^{-1} with molar absorptivity (ϵ) and standard deviation values of $0.173x10^4$ $mol^{-1}cm^{-1}$ and 0.133 respectively. The optimized developed thorin dye method together with the studied leached parameters lead to direct determination of thorium in different monazite concentrates with good precision value of 1.48%.

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