Trop J Nat Prod Res, September 2020; 4(9):545-549 ISSN 2616-0684 (Print)
ISSN 2616-0692 (Electronic)

Tropical Journal of Natural Product Research

Available online at https://www.tjnpr.org

Original Research Article

Quantitative Analysis of Thorium in Standard Samples and Monazite Sands using Nornicotine Alkaloid

Nashat M. M. Abd-Alaty[1]* and Mohamed E. El-Awady[2]

[1]Department of Medical and Radiological Research, Nuclear Materials Authority, Cairo, Egypt
[2]Department of Reactor Materials, Nuclear Materials Authority, Cairo, Egypt

ARTICLE INFO

Article history:
Received 06 August 2020
Revised 28 August 2020
Accepted 23 September 2020
Published online 03 October 2020

ABSTRACT

A rapid, sensitive, and selective method was developed for the quantitative determination of thorium concentration which is an important natural-mineral based on the complex formed with natural phytochemical nornicotine alkaloid at pH 4 – 6, the coloured complex was extracted in chloroform with a linear relationship in a concentration range from 6-50 µgmL^{-1} with molar absorptivity 1.8 x 10^4 (1 mol^{-1} cm^{-1}), Sandell's sensitivity (µgcm^{-2}) 2.3 × 10^{-2}, correlation coefficient 0.9998, limit of detection 0.57 µg ml^{-1} and limit of quantification 1.88 µg ml^{-1}at 430 nm. The effects of pH, nornicotine concentration, temperature and time were also studied. The method shows high selectivity for thorium and holds its accuracy and precision well. Therefore, the method is useful when applied to the determination of thorium in synthetic solution and in the monazite sample.

Keywords: Thorium, Nornicotine, Spectrophotometry, Monazite.

Introduction

Thorium has extensively been used in a variety of applications such as industrial energy and environmental issues.[1-3] The main source of thorium is monazite sands mainly associated with a small amount of uranium and other rare earth metals.[4,5] Many procedures have been developed for the determination of thorium, including liquid–liquid extraction,[6,7] floatation using complex formation of complex with Eritochrome cyanine R,[8] ion-exchange resins, [9] liquid membrane[10] and solid phase extraction (SPE).[11-14] Solvent extraction processes were the most interesting technique for separation and recovery of thorium.[15] Various extractants such as amines,[16-18] isoxazolones, crown ethers,[19] organophosphorus reagents[20] and ionic liquids[21,22] have been employed for the extraction of thorium and rare earth metals. Extracting a trace amount of thorium spectrophotometry has been introduced as a powerful technique due to its acceptable precision and accuracy, in addition to its lower cost compared to the other techniques.[23,24]

Nornicotine is an alkaloid found in various plants, it is chemically similar to nicotine, but does not contain a methyl group,[25] nornicotine is a hygroscopic, colourless to yellow-brown oily liquid,[26] the synthetic pathway of nornicotine involves a demethylation of nicotine[27] or partial reduction of 3-myosmine with palladium[28] or sodium borohydride[29] as a catalyst.

Various analytical methods have been reported for the assay of nornicotine including spectrophotometry,[30-32] hromatography[33,34] and capillary electrophoresis with electrochemical detection.[35] Extraction of nornicotine had been done by several compounds as nicotine demethylase CYP82E4,[36] enantioselective demethylation of nicotine in Tobacco leaf[37] and sodium hydroxide with ethyl ether. [38]

*Corresponding author. E mail: Nashat.alanwar@yahoo.com
Tel: +201006782093

Citation: Abd-Alaty NM and El-Awady ME. Quantitative Analysis of Thorium in Standard Samples and Monazite Sands using Nornicotine Alkaloid. Trop J Nat Prod Res. 2020; 4(9):545-549. doi.org/10.26538/tjnpr/v4i9.9

Official Journal of Natural Product Research Group, Faculty of Pharmacy, University of Benin, Benin City, Nigeria.

Materials and Methods

Apparatus

SP-8001 UV–VIS spectrophotometer Instruments Metertech Inc. with 1 cm quartz cells connected to an I.B.M. computer loaded with a software application, (Taiwan, R.O.C.).

Chemicals and reagents

Chemicals used were of the highest purity available from their sources and pure analytical grade.

Thorium: 1 mgmL^{-1} solution obtained from Sigma Chemical Co. (St. Louis, MO, USA) in diluted nitric acid.

Nornicotine: Purchased from Sigma with purity greater than 98%: prepared as 0.2% w/v by dissolving 0.2 g of nornicotine in 100 mL chloroform.

Analysis of thorium in pure form

Accurately measured aliquots of pure standard thorium nitrate solutions (0.15-1.25 mg) in 10 mL chloroform in heating tubes at pH 4.6 adjusted by using sodium acetate and acetic acid buffer solution to give a maximum and constant absorbance, 1 mL of 0.2% nornicotine was added successively. The contents were mixed well and placed in a water bath at 60°C for 20 minutes to develop the coloured complex formation. 1 g of anhydrous Na_2SO_4 was added to remove contaminated water then filtered and transferred to 25 volumetric flasks. The volume was made up to the mark with chloroform and the content of Th(IV) (6, 17, 28, 39 and 50 µg) was determined spectrophotometrically at λmax 430 nm against a reagent blank prepared simultaneously. The results obtained were compared with the official method.[39]

Analysis of thorium in natural sample

A 0.5 g finely powdered monazite sand containing 6% ThO_2 was weighed and mixed well. A quantity equivalent to 15 µg thorium was accurately weighed. Digestion was done by leaching the monazite with hot concentrated sulfuric acid (98%) at 230°C for 4 h at pH 0.8 using 13.4 M NH_4OH.[40] The mixture was evaporated to near dryness on a hot plate then extracted with 4×10 mL portions chloroform, the mixture was homogenized by shaking then filtered. An amount equivalent to 0.05 mg was taken from the leached liquor and added to

the standard solution (0.1, 0.375, 0.65, 0.925 and 1.2 mg) applying the standard addition technique, 1 mL of 0.2% nornicotine was added at pH 4.6 adjusted by HNO_3 and NaOH, then transfer the organic layer to heating tubes and the procedure was completed as investigated under standard thorium procedures. The results were compared with the official method.[39]

Effect of interfering cation

The determination of Th(IV) (28 µg) in the synthetic mixture of cations (60 µg) as Al^{3+}, Ni^{2+}, Hf^{4+}, Zr^{4+}, Ce^{4+}, Fe^{3+} and Pb^{2+} was done following the same procedure.

Results and Discussion

The main idea of this study is to find a fast and selective spectrophotometric method for the quantitative determination of thorium. A deep yellow coloured complex was obtained due to the selective chelation of the high electropositive thorium ion with a specific adjusted concentration of nornicotine alkaloid. The absorption spectra of nornicotine alkaloid, thorium and the complex formed between thorium ion and nornicotine were observed. This formation of nornicotine-thorium chelate may be by the mechanism shown in Figure 1.

Effect of solvents on the complex formation

The effects of chloroform, ethanol, methanol, methylene chloride, toluene and benzene on the nornicotine-thorium complex were studied. Chloroform gave a deep yellow colour with the maximum colour intensity. The absorption spectra for nornicotine alkaloid and thorium were at λmax 263 nm and 295 nm, respectively, while the yellow coloured complex shows λmax at 430 nm. This indicates the selective chelation of the high electropositive thorium ion with nornicotine alkaloid (Figure 2).

The conditions affecting the formation of the coloured complex between thorium and nornicotine were carefully studied and mentioned as follows:

Effect of pH

The pH plays an important role in the chelation process, so it was carefully examined from 3 to 7 using HNO_3 and NaOH, in case of monazite sample and using sodium acetate and acetic acid buffer solution in standards thorium test which shows that pH 4.6 at 60°C for 20 minutes gives the maximum absorbance.

Effect of temperature

The experiments were carried out at different temperatures starting from room temperature and gradually increasing to 90°C. The intensity of colour increased gradually with temperature till 60°C and became constant, then slightly decreased. The suitable temperature for the determination of thorium by nornicotine was 60°C for 20 minutes at pH 4.6.

Effect of heating time

The maximum absorption of the complex was observed from 20 to 60 min at 60°C with pH 4.6, so we consider that 20 minutes were sufficient to obtain the maximum absorbance.

Effect of reagent volumes

The experiments were carried out on several volumes (0.5-4.0 mL) of 0.2% nornicotine at pH 4.6 by heating at 60°C for 20 minutes, the optimal volume was one milliliter of 0.2% nornicotine to maximize the colour intensity to the highest absorbance.

Stoichiometry

To study the stoichiometry of the reaction, the molar ratio between thorium and nornicotine in equimolar solutions and in the presence of an excess amount of nornicotine was determined using Job's method.[41] It was found that the ratio was 1:3, as shown in Figure 3.

Linearity and quantification

A linear relationship was obtained for the absorbance in the concentration range of 6-50 µgmL^{-1} (Figure 4).

The calibration graphs are described by the following equations at λ max 430 nm

$$A = 0.01828\ C$$

Where A is the absorbance and C is the concentration of thorium in solution in µg mL^{-1}.

The previous conditions were applied to different concentrations (6-50 µgmL^{-1}) of standard solutions of thorium, the results obtained are shown in Table 1. Monazite sands, applying the standard addition technique by adding an amount equivalent to 2 µg to the concentrations of standard solution (4, 15, 26, 37, and 48 µg). The results compared with the official method[39] as shown in Table 2.

Effect of interfering cations

The proposed method has been successfully applied to the determination of Th(IV) in the presence of different cations. Results indicated a clear determination of Th(IV) ions in the presence of Al^{3+}, Ni^{2+}, Hf^{4+}, Zr^{4+}, Ce^{4+}, Fe^{3+} and Pb^{2+} cations with recovery 98.4, 100.2, 98.8, 99.5, 99.9, 100.05 and 98.9 respectively indicating a negligible effect on the determination method.

Accuracy and precision

The results obtained from standard and real sample methods were compared with the reference method[39] and are shown in Tables 3 and 4. The precision and accuracy studies of the proposed methods were done by carrying out 5 independent determinations at three concentration levels, the relative standard deviations (RSD) were calculated and the results indicated an excellent accuracy and precision than the official reference method (Table 5). The confidence limits at 95% were calculated and the results showed that there is no significant difference between the three sets of results.

Table 1: Determination of pure thorium using nornicotine alkaloid at λmax 430 nm

Taken (µg mL^{-1})	Found (µg mL^{-1})	Recovery** (%)
6	5.94	99
17	16.97	99.8
28	27.72	99
39	38.29	98.2
50	50	100

(**) Average of three experiments

Table 2: Determination of thorium in monazite solution through complexation with nornicotine alkaloid using standard addition technique

Taken (µg mL^{-1})	Added (µg mL^{-1})	Recovery** (%)
2	-	-
2	4	99.1
2	15	99
2	26	99.3
2	37	99.5
2	48	99.8

(**) Average of three experiments

ISSN 2616-0684 (Print)
ISSN 2616-0692 (Electronic)

Table 3: Statistical data for determination of thorium with nornicotine alkaloid at λmax 430 nm compared with the reference method

Statistic	Reference method	Standard thorium
Mean recovery* ± S.D	99.8 ± 0.903	99.2 ± 0.721
N	5	5
Varince	0.815	.052
S.E	0.4037	0.322
t-test		1.162 (2.77)
F-test		1.567 (6.39)

(*) Mean ± S.D

Table 4: Statistical data for determination of thorium in monazite sands with nornicotine alkaloid at λmax 430 nm compared with the reference method

Statistic	Reference method	Monazite sands (6% Tho_2)
Mean recovery* ± S.D.	99.8 ± 0.903	99.34 ± 0.321
N	5	5
Variance	0.815	0.103
S.E	0.4037	0.144
t-test		1.073 (2.77)
F-test		5.777 (6.39)

(*) Mean ± S.D

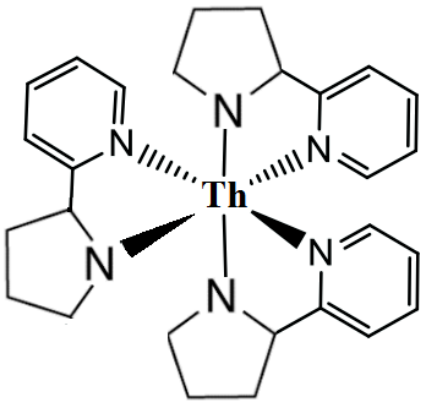

Figure 1: A suggested structural mechanism of the formed colored complex between thorium ion and nornicotine measured at λ max 430 nm

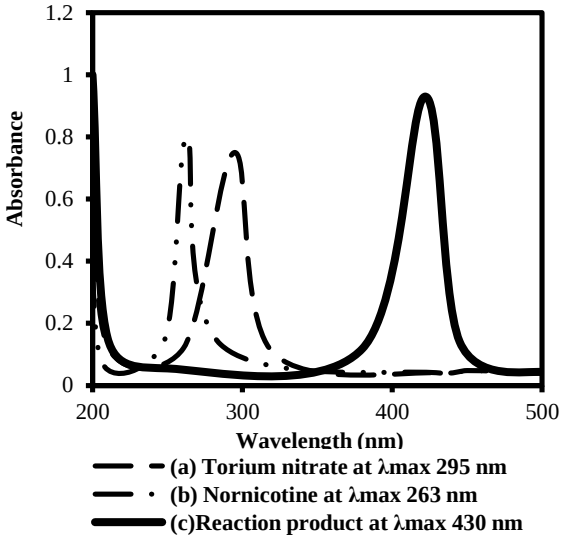

Figure 2: Absorption spectra of (a) 50 ppm of thorium nitrate in chloroform at λmax 295 nm, (b) 0.2% nornicotine in chloroform at λmax 263 nm and (c) Reaction product of 50 µg ml^{-1} thorium and 0.2% nornicotine at λmax 430 nm

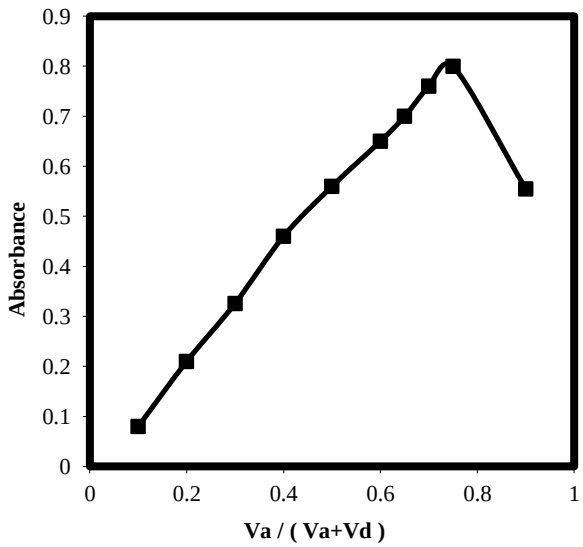

Figure 3: Continous variation plot for (1.5×10^{-3} M) thorium and (1.5×10^{-3} M) nornicotine Va=thorium and Vd=nornicotine

Table 5: Evaluation of the accuracy and precision of the proposed methods

Statistical Parameter				
Taken[a] µg mL^{-1}	Found ± SD[b]	RSD (%)	SAE [c]	Confidence limit [d]
10	9.91±0.015	0.15	0.006	0.013
30	29.7±0.036	0.12	0.016	0.032
50	49.6±0.027	0.05	0.012	0.024

[a]Standard thorium; [b]Mean ± standard deviation for five determinations; [c]Standard analytical error; [d] Confidence limits at P = 0.95 and 4 degree of freedom .

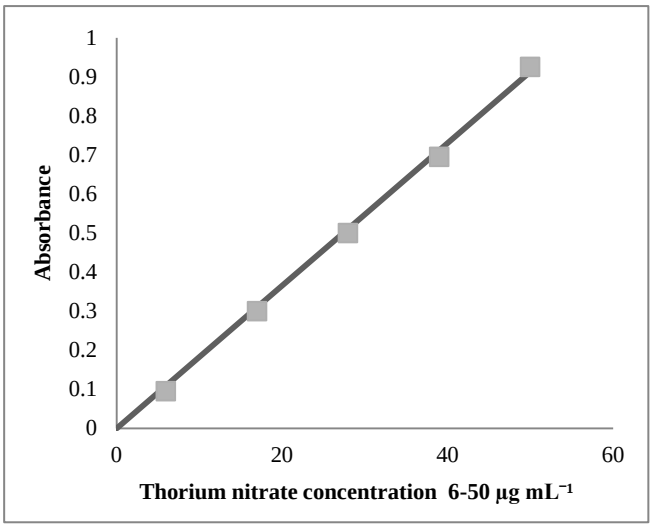

Figure 4: Calibration curve of the reaction product between thorium and nornicotine at λmax 430 nm

Conclusion

The developed method is economical ,simple, sensitive and accurate and can be used for the determination of thorium in their pure and sand form. The results showed that the proposed procedure is more sensitive, simple, precise and accurate than the official reference method. This work describes a quantitative method for spectrophotometric determination of high electropositive thorium through the complexation with nornicotine in chloroform. The factors affecting the formation of the complex such as the type of solvent, pH, temperature, time, and volume of nornicotine were studied and represented graphically. Chloroform was shown to be the most suitable medium for complexation with thorium which gives yellow colour by adding 1 mL of 0.2% nornicotine at pH 4.6 and heating the complex at 60°C for 20 min to develop the colour. There were no interferences that occurred in its pure form and monazite sample. The results obtained were compared with the reference method and indicated excellent accuracy and precision.

Conflict of interest

The authors declare no conflict of interest.

Authors' Declaration

The authors hereby declare that the work presented in this article is original and that any liability for claims relating to the content of this article will be borne by them.

Acknowledgements

The corresponding author acknowledges Nuclear Materials Authority for facilitating the research work.

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