

Spectrophotometric Determination of Cerium in Some Ore in Kurdistan Region – Iraq

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Abstract

A simple and Sensitive Spectrophotometric method was observed for trace measurement of Cerium (IV) in different serpentinite rocks in two different positions in Kurdistan region of Iraq.

The method is depended on absorbance measurement at (490 nm.) for the red complex (Ce - Sulphanilic acid) at pH = 4.75 reproducible results were obtained (Recovery 98 – 103) % for both ores and synthetic Samples of cerium in trace levels.

Keywords: red complex, serpentinite rocks, spectrophotometric, cerium

Introduction

Cerium is a rare earth metal used as a getter in the metal industry in nuclear reactor, in alloy with nickel and chromium, and in microwave devices, laser, masers and in television sets, besides agriculture, forestry, animal husbandry and in environment optimum concentration of some light rare earth element including Cerium, and also useful for studies of biochemical processes. (Le van 2011 and Sadallah T 2013).

Cerium is the most abundant of the rare earth elements making up about 0.0046% of the earth's crust by weight (Visual elements 2009).

Cerium in its tetravalent state Ce(IV) differs significantly from all other lanthanides due to its immense oxidizing ability in acidic solution especially in sulphuric acid solution (B. Qunzhou 1999).

This property of Cerium (IV) stands in the way of its determination using organic reagents.

For this purpose a convenient and reliable analytical methods for the determination of Cerium has been established different analytical techniques has been used such as ICP – AES (Y. K. Agrawal 2004, N. Daskalova 1992 and T. Prasada Rao 2000) or electrothermal vaporization ICP-AES after HPLC separation (Joseph A 2000, Q. Shuai 2000), Stripping Voltammetry (C. Giridhar 2013 Giridhar, C 2013), ion selective electrode (Gholamhossein Rounaghi 2011, Abbas Afkhamia 2012), Spectrofluorometry (R. Yener 1998, N. Jie, I. Yang 1994).

These methods are of high cost and may be not being available at most laboratories.

Reversed DIE technique has also been used for determination of Ce (IV) depended on the exothermic reaction of Sufanilic acid with Ce(IV) (Fadhil M. Najib 2007).

enerally the Spectrophotometric methods are economic and Sensitive for this purpose, various complexing agents have been proposed for the determination of Ce(IV) Such as:

desferrioxamine B, (Hafes M B. 1998), phenothiazine derivative (Masti S P 2002), decolonization reaction with arsenazo(III) (Zhu X. 2008), O-Iodobenzoyl -O-tolyl hydroxyl amine (B. K. Pal 1988), malachite green-iodide (Etesh K. Janghel 2009), 3-thianaphthenoyltrifluoroacetone (Mathew B. 2005), 2-4-dihydroxy benzo-phenonebenzoic hydrazone (C. Kesava Rao 1994), O- phenylene diamine (A. Agarwal 1995), 2-thenolyl trifluoro acetone (R. C. Saxana 1995), N-P-Chlorophenyl -2-furyl acrylo-hydroxamic acid (S.A. Abbasi 1998), pyrogallol red (J. Mendina- Escriche 1985), triphenylformazan derivatives (I.S. Ahmed 2006) and Azocalixarene Derivative (Le Van Tan 2011).

Nowaday the determination of Ce(IV) is of great importance specially after the advent of atomic energy programs using thorium extracted from Ores like monazite (a common Ore of Cerium) as a result of this the presence of Ce(IV) in the environmental increased to high level, therefore it is of quite importance to Gdevelop a simple, low cost method for determination of cerium depending on Spectrophotometric method.

In our study we use a simple method which is the spectrophotometric study of the exothermic reaction of Ce(IV). The factors that affecting on the Sensitivity and Stability of the coloured complex were carefully studied.

Results and Discussion:

Optimization

Reagents: All reagents used were of analytical grade, all glasses were washed with cleaning Solution, then thoroughly with distilled water.

A series of solutions of Ce(IV) ion for preparation of the calibration curve were prepared by serial dilution for stock solution of (0.5 M Cerium sulphate in (1:1) sulphuric acid solution).

The 0.01 M sulphanilic acid solution was prepared in acetate buffer solution (pH= 4.75) which was prepared by dissolving 4.3297 g of solid reagent in a 250 ml buffer solution of (1M HAc + 1M NaAc)

Apparatus:-

1 cm matched quartz cell was used for absorbance measurement, with UV-Visible spectrophotometric type (Heliasa, UV-Visible spectrophotometer, V4.6).

Glass apparatus for preparation of solution, beakers, volumetric flask, pipettes and reagent bottles.

Preliminary experiments:

Preliminary experiments show formation of an intense red colour upon mixing the sulphanic acid solution with Ce(IV) solution as indicated from study (Fadhil M. Najib 2007). Maximum absorbance for this complex was found at wave length equal to 490 nm. While for the absorbance sulphanic acid reagent and Ce(IV) solution there are no such absorbed show in the fig (1) & fig (2).

Following parameters have been investigated.

1- Absorption Spectra:

As described in the experimental part we used an acidic solution of sulphanic acid buffered to (pH= 4.75) to make a complex with Ce(IV) solution using Cerium sulphate solution for this purpose.

The absorption such absorbed show in the fig (1) & fig (2)

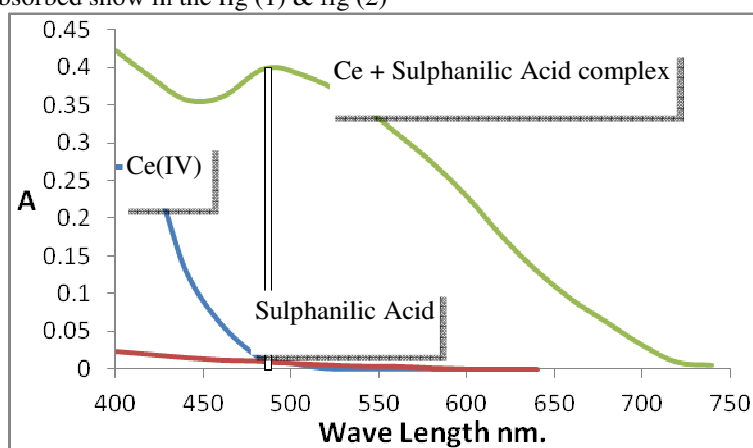


Figure1. The Spectra for the complex against distilled water as a blank

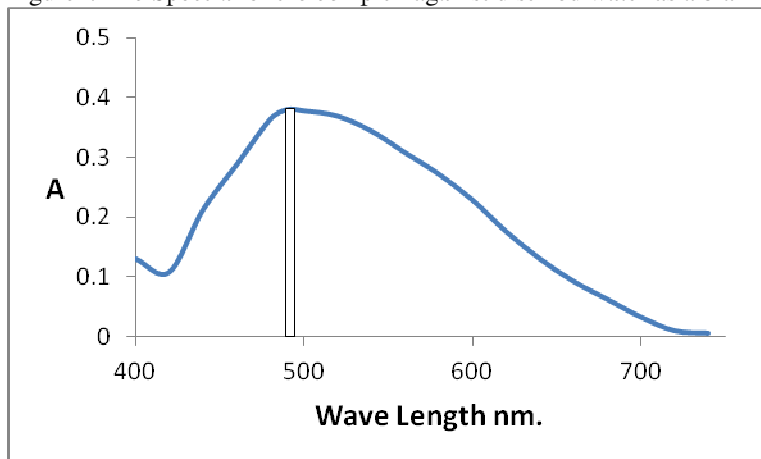


Figure2. The Spectra for the complex against Cerium (IV) as a blank

2- The volume of sulphanic acid solution.

Different volume of sulphanic acid were added to constant volume (3 ml) of Cerium (IV) solution, the optimum volume was found to be equal to (3 ml) of the sulphanic acid as shown in Fig (3)

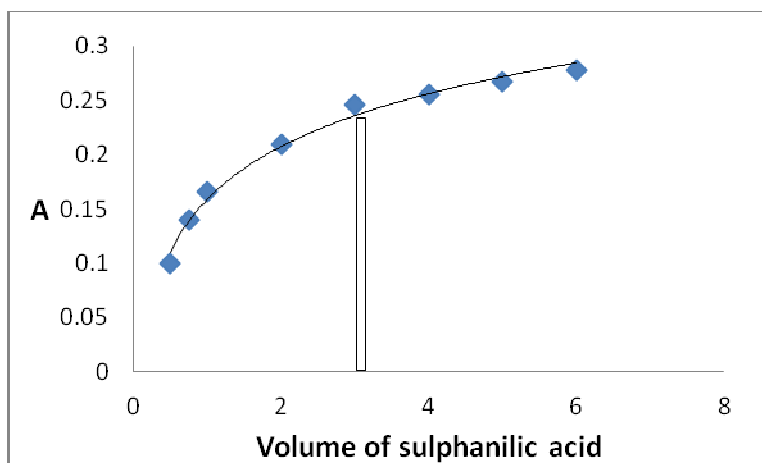


Figure3. Optimum volume of sulphanic acid with 3 ml of Ce(IV)

3- Effect of pH:

Several Solutions of sulphanic acid was prepared in different pH of acetate buffer solution ranged between pH (1 – 6), the best result was obtained at pH (4.75) as shown from fig (4) , so the (pH = 4.75) was selected.

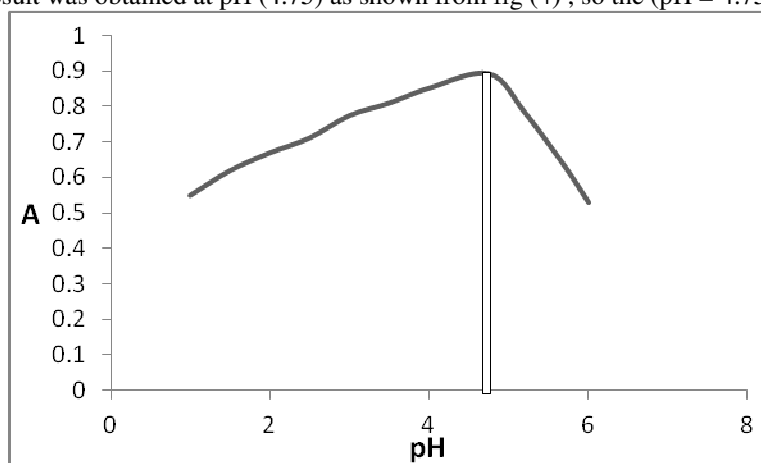


Figure4. study pH for complex Cerium and sulphanic acid

4- Effect of Time:

Different absorbance measurement was performed at different times after preparation of the red complex, as shown from fig (5) the complex has stable absorbance after 20 min. of mixing the Cerium solution with the sulphanic acid reagent.

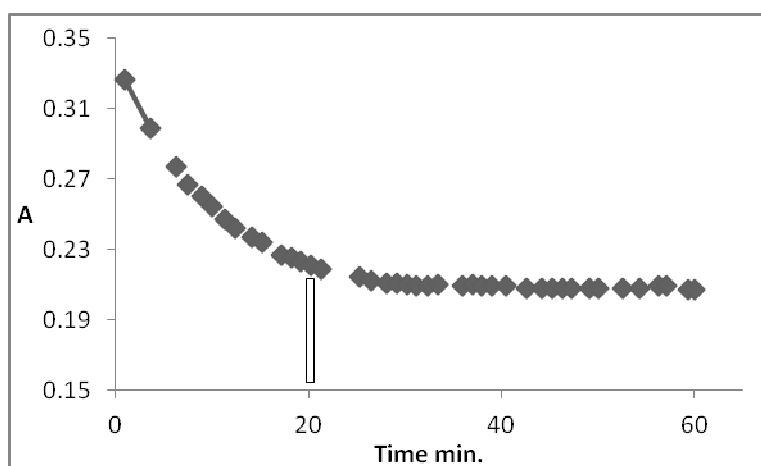


Figure5. Stability of the complex (Cerium - sulphanic acid)

5- Stoichiometric ratio of the complex formation (Ce-sulphanilic acid):

Job method was applied to study and predict the stoichiometric ratio, as shown from Fig (6) the stoichiometric ratio was found to be equal to (1:1)

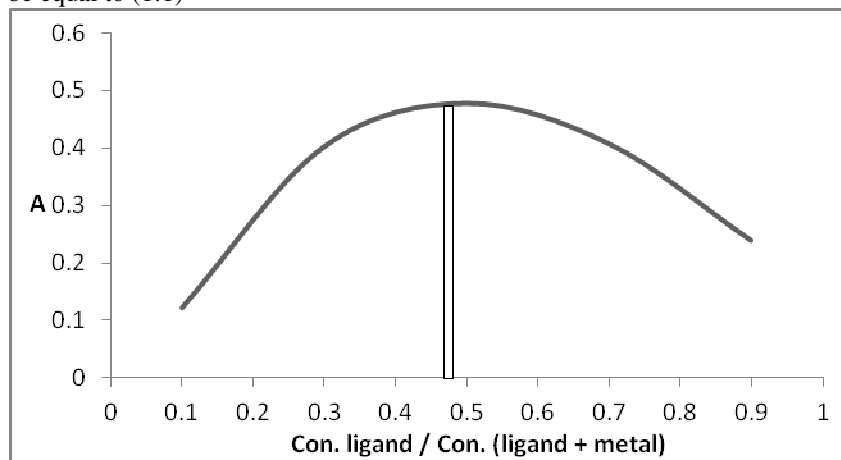


Figure6. Job method for complex of (Cerium - sulphanilic acid)

Calibration Curve:

The calibration Curve was prepared after optimization of different factor by taking the Absorbance measurements as the follows:

Different volumes (0.5 - 3.5) ml of Ce(IV) solution were added to (3 ml) of sulphanilic acid solution , after 20 min. of mixing the Absorbance of red complex was measured , the calibration curve shown in Fig (7) .

The final concentration of Cerium (IV) was found to be ranged between (10-100) ppm , a linear relationship were obtained as shown from the fig(7) , with a correlation coefficient equal to 0.9939 and the recovery test was performed also the results was between (98.5 – 102)%

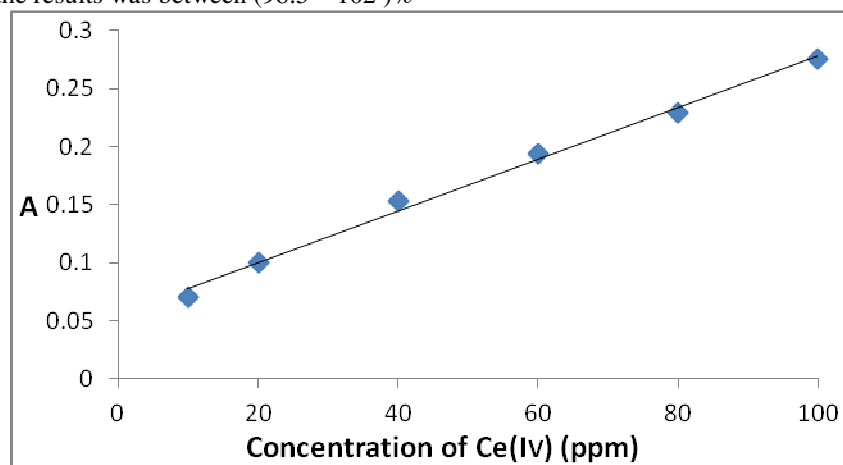


Figure7. Calibration Curve for determination of Ce(IV)

Determination of Ce(IV) in Synthetic sample and Ore:-

Some Ore of serpentinite rock was selected from different positions in Kurdistan region of Iraq, strictly in Mawat and Penjween positions the content of the cerium was found by the observed method in these Ores trace of Ce(IV) were found in the ores , so the procedure of standard addition method was employed for this purpose to obtain a maximum sensitivity as shown in fig(8).

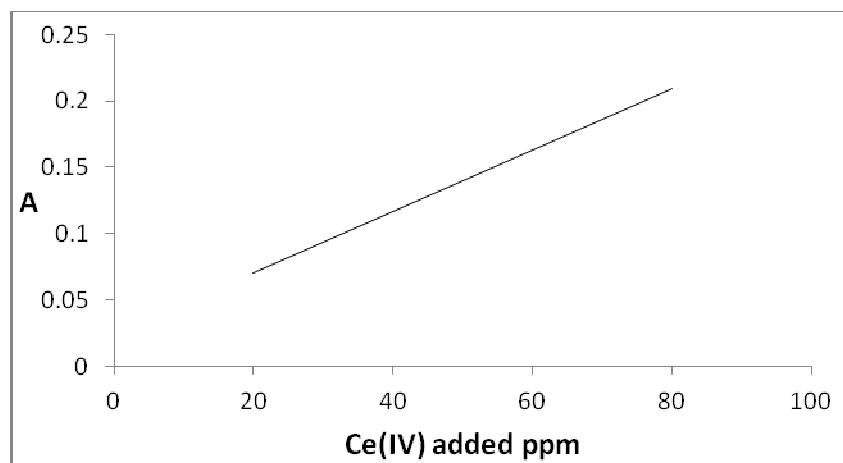


Figure8. Standard Addition

The same procedure was applied for determination of Ce(IV) in synthetic Samples, the recovery tests for both results of ores and synthetic samples was found to be of reproducible results (98 – 103) % as shown in table (1).

Table1. Determination of Ce(IV) in Serpentine rock in Kurdistan region of Iraq and synthetic samples of cerium.

Sample	ppm Ce	Recovery %
Rock from (Mawat)	2.43	101.5 *
Rock from (Penjween)	3.52	102.1 *
Synthetic sample (5 ppm Ce)	5.16	103.2
Synthetic sample (10 ppm Ce)	9.83	98.3

* using Std. addition method.

Conclusion:-

This procedure is simple, accurate, and sensitive method for the determination of Ce(IV) in ore sample after dissolving it in acid medium and reaction with sulphanic acid in pH= 4.75 from direct or standard addition methods.

The good analytical values were obtained from the determination of Ce(IV) and the high value of merits with simplicity in instruments and chemicals suggest the utility of the proposed method in routine analysis.

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