

Spectrophotometric Determination of Praseodymium by 1,4-Dihydroxyanthraquinone after its Selective Separation from Rosetta Monazite Rare Earth Concentrate by Solvent Extraction

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Abstract: A rare earths concentrate of Rosetta monazite assays about 44, 23, 16.94 and 5.91 % for Ce, La, Nd and Pr respectively. Separation of cerium by air oxidation at 200°C. Selective separation of Pr by D2EHPA at pH1 followed by a sensitive spectrophotometric method which described for the determination of praseodymium (Pr) with 1,4-dihydroxyanthraquinone. The calibration curve was linear from 0.1 to 12 μgml^{-1} praseodymium. The influences of various parameters and reaction conditions for maximum colour development were investigated. The relative standard deviation for determination of 1 μgml^{-1} praseodymium has found to be 1.3 after 5 repeated determinations; percent error 5.02%, molar absorptivity (ϵ) was $1.23 \times 10^6 \text{M}^{-1} \text{cm}^{-1}$ and detection limit was $0.1 \mu\text{gml}^{-1}$. The method for determination of praseodymium showed good accuracy and selectivity.

INTRODUCTION

Rare earth elements (REEs), represent one of a set of seventeen chemical elements in the periodic table, specifically the fifteen lanthanides, as well as scandium and yttrium (Connelly, N.G., et al., 2005). It was discovered of the black mineral Gadolinite by Carl Axel Arrhenius in 1787 (Gschneidner, and Cappellen, 1987). Traditionally, the REEs are divided into two groups on the basis of atomic weight; the light REEs are lanthanum through gadolinium (atomic numbers 57 through 64); and the heavy REEs comprise terbium through lutetium (atomic numbers 65 through 71). The most rare earth bearing minerals are Bastnaesite, $(\text{Ce,La})(\text{CO}_3)(\text{OH,F})$; xenotime, YPO_4 ; and monazite, $(\text{Ce,La,Nd,Th})\text{PO}_4 \cdot \text{SiO}_4$ (Christie, T.B., et al. 1998). Bastnaesite and monazite are sources of light REEs and account for 95% of REE currently used (Harben, P.W., & Kuzvart M., 1996). Praseodymium is one of LREEs; which has different application in different fields as used in production of atomic battery (Attallah, M., et al., 2013). Praseodymium is soft silvery metal used as an alloying agent with magnesium for the production of high strength metal alloys used in aircraft engines. It forms the core of carbon arc lights for the motion picture industry and didymium glass to make certain types of welders and glass blowers goggles (with a yellow color). It is added to fiber optic cables as a doping agent where it acts as a signal amplifier (Pourjavid, M., et al., 2012).

There are two ways determination the rare earth elements (REEs) by either selective or separation. The spectrophotometric determination of some lanthanides in the presence of other cations, based on solvent extraction of the ion-associates formed between the Ln^{3+} -hexaaza-18-crown-6 complexes and erythrosine A, is proposed. By use of masking agents, the method can be applied to the determination of 0.02-1 % of Pr(III), Nd(III), Sm(III), Eu(III), Gd(III) and Tb(III) in the presence of a mixture of heavy lanthanides, Y(III), Ga(III), Sc(III), Al(III) and alkaline earth metal cations (Walenty, S., et al., 1992)

The solvent extraction has been widely used for the separation and purification of rare-earth elements (Banda, R., et al., 2012). Solvent extraction separation is based on differences in the solubility of elements in two immiscible liquid phases. Di-(2-ethylhexyl)phosphoric acid (D2EHPA) are commonly applied for the light rare earths separation. In the present study, the extraction behaviors of Pr(III) with D2EHPA in the presence of two complexing agents H3cit and LA have been investigated.

1,4-dihydroxyanthraquinone is a chromogenic and fluorogenic agent of metallic ions that shows high selectivity in its reactions since the O-donors are blocked by two strong intramolecular hydrogen bondings; therefore, few spectrophotometric methods using this reagent are known. This reagent has been applied for the determination of Mg^{2+} and UO_2^{2+} (Gracia, L.G., et al., 1997)

In the present study, the ability to determine Pr spectrophotometrically in the produced rare earth concentrates by 1,4-dihydroxyanthraquinone dye after separation. Optimum factors affecting formation of the complex such as maximum wavelength, pH, initial concentration of dye, molar ratios, effect of duration time, and calibration curve were investigated.

1. EXPERIMENTAL

1.1 Apparatus

A double beam Unicam spectrophotometer (England) equipped with 1cm cell path length was used for all absorbance measurements. The pH values were determined with NEL pH meter where daily calibration was performed using two successive pH standard buffers either 4 and 7 or 7 and 10.

1.2. Reagents

All the reagents employed were analytical grade. Standard rare earth elements (REEs), di-(2-ethylhexyl)phosphoric acid (Merck), lactic acid (Merck), citric acid (Merck), 1,4-dihydroxyanthraquinone (Merck), methanol (Merck) and mineral acids (Sigma-Aldrich) were used in the present work.

1.3. Preparation of Rosetta monazite rare earth concentrate

A rare earth concentrate was prepared after alkali treatment of Egyptian Rostta monazite followed by dissolution of hydrous cake in concentrated HCl where rare earth concentrate precipitate at pH 9.

1.4. Separation of cerium by air oxidation method

Cerium was separated by dissolve known amount of monazite concentrate in 1M HCl at 70° with stirring till complete dissolution, adjust pH to 9.5 then filter and wash well. The precipitate after that was dried at 200°C for six hours to oxidize Ce(III) to Ce(IV), the precipitate was ground and then dissolved in double distilled water; adjust pH to 3.5 using HNO₃ with stirring for four hours. From the obtained filtrate, the REEs were then precipitated by oxalic acid followed by calcination to a mixed REO concentrate (miodusk, T., et al., 1989).

1.5. Preparations of stock solutions

All solutions were prepared using dionized water. A stock standard of praseodymium solution 1000 ppm was prepared by dissolving 0.121 g of Pr₆O₁₁ in the least amount of 6M HCl and then completed up to the mark of 100 ml volumetric flask with double distilled water. A 10⁻³ M 1,4-dihydroxyanthraquinone solution was prepared by dissolving 0.012g of 1,4-dihydroxyanthraquinone using absolute methanol in 50 ml volumetric flask. A 0.1 M stock solution of citric acid was prepared by weighing 1.92g of citric acid and dissolved in the double distilled water and complete up to volume in 100 ml volumetric flask. A volume of 8.77 ml of lactic acid (11.4 M) was mixed with double distilled water in 100 ml volumetric flask and completed to the mark to have 1 M solution of lactic acid. Buffer solution of pH 9.5 was prepared by dissolving 6.7g ammonium chloride in 30 ml water followed by addition of 8.4 ml ammonia and then up to the mark of 50 ml volumetric flask using bidistilled water.

1.6. Procedure

An aliquot of sample solution containing (not more than 25µg ml⁻¹ Pr) mixed with a 0.05 M of lactic acid (LA) and 0.005 M citric acid (H₃cit) and adjust the pH of the solution to 1.0 then complete up to volume in 10 ml volumetric flask using double distilled water (DDW). Extract praseodymium by shaking with 10 ml of di-(2-ethylhexyl)phosphoric acid(0.5 M) in purified kerosene for 15 min. After separation of the phases, the organic phase loading praseodymium was stripped with 6 mol L⁻¹ HCl.

The purple colored Pr-(1,4-Dihydroxyanthraquinone)-methanol complex were prepared by add 4 ml of (1,4-diOH-AQ)solution, a sample solution (pH 4.5-6.5) of praseodymium ion (≤ 0.2 ml) by micropipette, 0.8 ml buffer solution (pH 9.5), 5.0 ml of methanol , and complete up to volume in 10 ml volumetric flask

using double distilled water, then measure the absorbance of the complex formed in a 1cm cell against a reagent blank at 560 nm.

2. RESULTS AND DISCUSSIONS

2.1. Composition of monazite rare earth oxides concentrate

The chemical composition of the rare earth oxides (REO) was first treated to prepare a pure REO concentrate. ICP-EOS analysis and ESEM analysis are shown in Table (1).

Table (1): Chemical composition of rare earth oxides (REO) using ICP- EOS analysis.

RE ₂ O ₃	Wt.,%
La ₂ O ₃	23.00
Ce ₂ O ₃	44.20
Pr ₆ O ₁₁	05.91
Nd ₂ O ₃	16.94
Sm ₂ O ₃	02.20
Eu ₂ O ₃	01.70
Gd ₂ O ₃	01.40
Dy ₂ O ₃	01.30
Y ₂ O ₃	03.10
Total	99.75

It was shown from the Table (1) that the presence of light rare earth elements (LREEs) in the prepared monazite concentrate; lanthanum, cerium, praseodymium and neodymium about 90%, where a cerium alone assaying about 44.20%. The remaining 10% involve Sm 2.2%, Eu 1.7%, Gd 1.4%, Dy 1.3% and Y about 3%. Monazite REO concentrate is composed of eight lanthanide in addition to yttrium. Through these results could be obtain of praseodymium preconcentration by removal cerium where highest content in the mixed REO concentrate.

2.2. Removal of cerium from rare earth (RE) concentrate

Separation of cerium from rare earth (RE) concentrate as it was the highest content. Cerium(III) was separated by oxidation to cerium(IV) . As cerium trivalent was oxidized into cerium tetravalent, it was easily separated from RE concentrate by leaching (REE³⁺) with nitric acid. The undissolved portion contained ceric hydroxide. The dissolved portion to obtain rare earth (RE) without cerium were precipitated using oxalic acid,

then ignited. The chemical composition of the rare earth oxides (REO) after removing of cerium are shown in Table (2).

Table (2): Chemical composition of rare earth oxides (REO) concentrates after separation of cerium using ICP-EOS analysis.

RE ₂ O ₃	Wt.,%
La ₂ O ₃	42.13
Ce ₂ O ₃	0.31
Pr ₆ O ₁₁	13.04
Nd ₂ O ₃	29.10
Sm ₂ O ₃	03.86
Eu ₂ O ₃	02.73
Gd ₂ O ₃	01.86
Dy ₂ O ₃	01.70
Y ₂ O ₃	05.20
Total	97.82

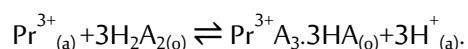
It was shown from the Table (2) cerium(III) oxidized to cerium(IV) and separated by 99.7% while 0.31% cerium(IV) was dissolved in hydrochloric acid. Accordingly preconcentration of the other rare earth elements in the prepared pure mixed rare earth oxides (REO) concentrate lanthanum, neodymium and praseodymium about 43.83%, 28.04% and 12.04% respectively.

2.3. The praseodymium separation for determination by Solvent extraction

Di-(2-ethylhexyl)phosphoric acid (D₂EHPA) are commonly applied for the light rare earths separation. In D₂EHPA-HCl system, the separation factors of light rare earths elements are low when adding complexing agent lactic acid and citric acid were improve separate rare earth chlorides (RECl₃) (Shaohua, Y., et al., 2013).

2.3.1. Influence of D₂EHPA concentration on percent extraction of praseodymium

The influence of D₂EHPA (cation-exchange) on the extraction of praseodymium was very important due to exchanged hydrogen ions of the extractant with REE³⁺ from the aqueous phase. The Pr³⁺ locates in the center of the extracted complex which is formed by the chemical bond (Shaohua, Y., et al., 2013). Also, the extraction mechanism could be expressed by the following equation:



The different concentrations of D₂EHPA studying in D₂EHPA-HCl-LA-H₃cit extraction system at fixed time and concentrations of LREEs, lactic acid (0.03M) and citric acid (0.003M). The influence of D₂EHPA concentration on percent extraction of LREEs were given Fig. (1). It was shown from the Fig. (1) Indicated that 0.4 M of D₂EHPA gave the maximum percent extraction of LREEs.

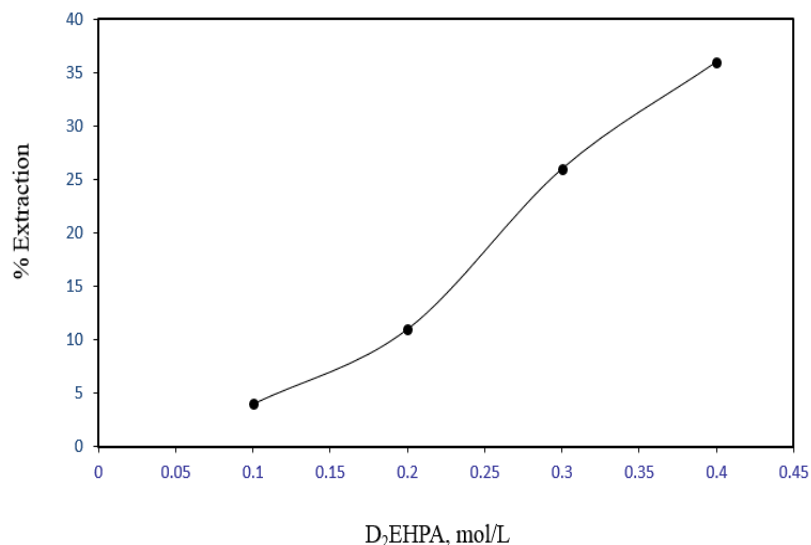


Fig. (1). the influence of D₂EHPA concentration on extraction of LREEs

2.3.2. Influence of complexing agents concentration on percent extraction of LREEs

The extraction behaviors of LREEs with D₂EHPA in the presence of two complexing agents lactic acid (LA) and citric acid (H₃cit) have been performed. The ratio of [H₃cit]:[LA] in the D₂EHPA-HCl-LA-H₃cit extraction system is 1:10 (Shaohua, Y., et al., 2014).

The influence of complexing agents concentration on percent extraction of LREEs were given in Fig. (2). It was shown Indicated that 0.05 M of LA gave the maximum percent extraction of light rare earths (LREEs).

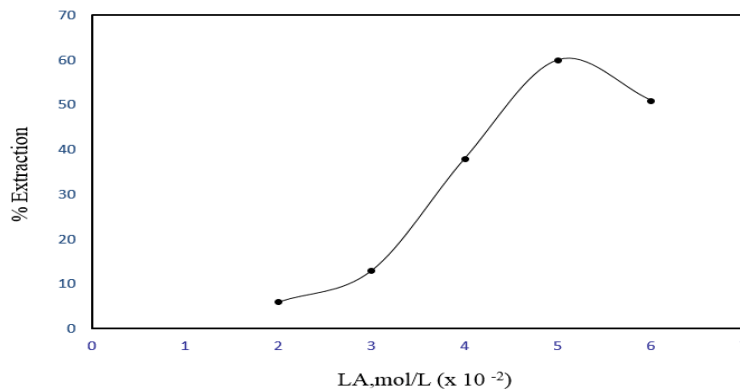


Fig. (2). the influence of lactic acid concentration on extraction of LREEs

2.3.4. Influence of acidity on percent extraction for LREEs

The influence of acidity on percent extraction for light rare earths (REEs) were given in Fig. (3).

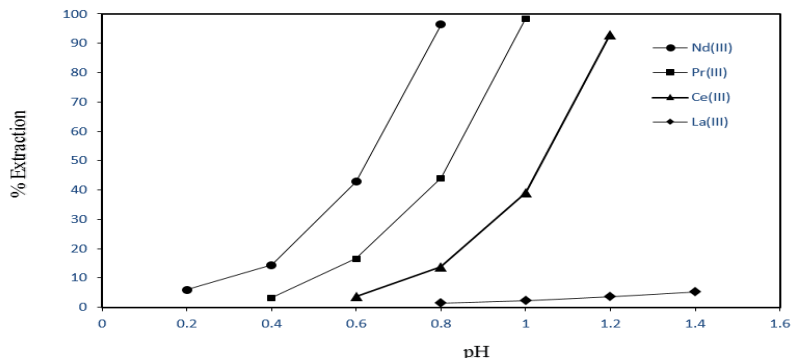


Fig. (3). the influence of acidity on extraction of LREEs

From the obtained results, in Fig. (3), it was found separation of praseodymium from neodymium and lanthanum at pH (1.0). While 39.0 % cerium separated at the same conditions. Through these results must removal cerium for determination of praseodymium.

2.4. Determination of praseodymium

2.4.1. Spectrum of ligand (1,4-diOH-AQ) and its praseodymium complex

The absorption spectra of the ligand (1,4-diOH-AQ) and its praseodymium complex shown in Fig. (4) Were scanned in the region between (400 to 600 nm). The results showed that, there was a maximum absorption of the free ligand at λ_{max} 480 nm against methanol as blank, and there were a formation of “ Pr-(1,4-diOH-AQ)-methanol ” complex against reagent blank due to shift in wavelength at λ_{max} 560 nm. Methanol is the best solvent (Sanchez, F., et al., 1987).

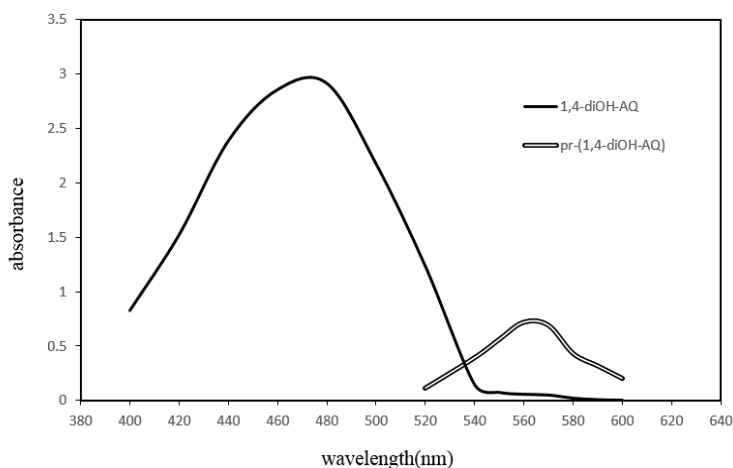


Fig. (4): spectrum of ligand (1,4-diOH-AQ) and its praseodymium complex in methanol, [Pr] = $8 \mu\text{g ml}^{-1}$ and [dye] = 4×10^{-4}

2.4.2. Effect of the pH variation on the absorption of the studied dye

The pH value plays an important role in the colour of the dye and the formed complex. Therefore, the effect of different pH values on the absorption spectrum of free 1,4-Dihydroxyanthraquinone dye was first studied using ammonium hydroxide. The absorption values of 1,4-Dihydroxyanthraquinone in methanol media of various pH values were given in Fig. (5). Absorbance spectrum in the range from pH 5.0 to 7.5 where the maximum absorption of the free 1,4-Dihydroxyanthraquinone was constant.

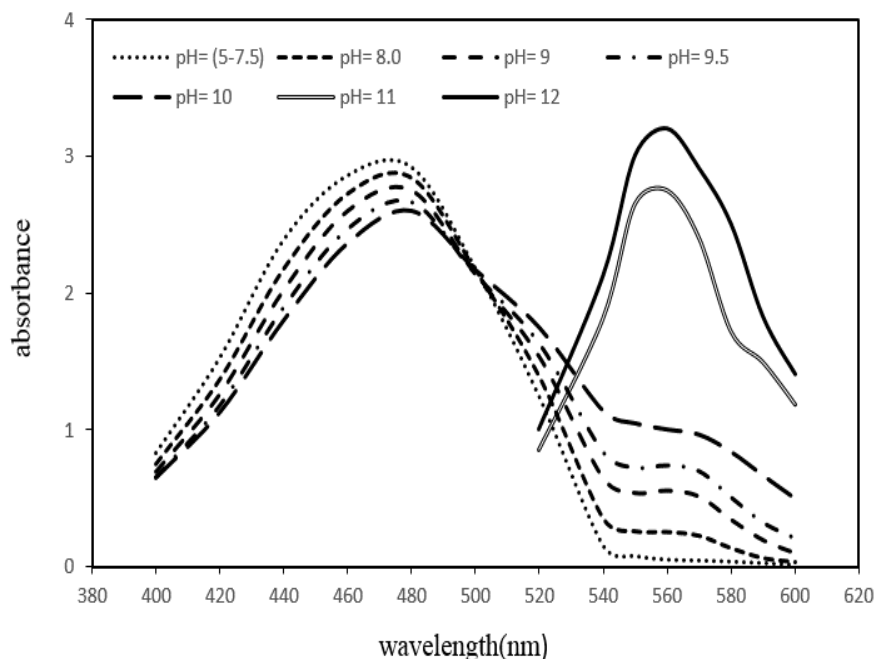


Fig. (5): Effect of pH on 1,4-dihydroxyanthraquinone at different wavelengths

The results showed that, there was an absorption bands in the range from pH 5.0 to 7.5 only at λ_{\max} 480 nm against methanol as blank, in the range from pH 8 to 10 at λ_{\max} 480 nm with λ_{\max} 560 nm and in the range from pH 11.0 to 12.0 only at λ_{\max} 560 nm due to the colour change of 1,4-Dihydroxyanthraquinone from its molecular form yellow, purple and blue respectively

2.4.3. Optimization of the suitable pH on “Pr-(1,4-diOH-AQ)-methanol” complex formation

The first step in the development of the analytical method was to investigate the effect of varying pH values on “Pr-(1,4-diOH-AQ)-methanol” complex. Thus, the choice of a suitable pH value of “Pr-(1,4-diOH-AQ)-methanol” complex formation were studied by using ammonium hydroxide of pH value from 8.0 to 10.0. The absorption of each solution was measured against the same amount of the reagent blank at 560 nm for praseodymium. From the obtained results, in Fig. (6) Indicates that pH 9.5 gave the highest absorbance.

Accordingly this pH represents the optimum value for the formation of “ Pr-(1,4-diOH-AQ)-methanol ” complex.

2.4.4. Optimization of methanol solvent concentration

The optimum solvent concentration of methanol was studied by using a series of methanol concentrations with $[4 \times 10^{-4}]$ ligand and $(8 \mu\text{g ml}^{-1})$ Pr at pH 9.5, then measure absorbance at different wavelength. Fig. (6) Indicates that the optimum concentration of methanol was 90% due to present absorption band at λ_{max} 560 nm.

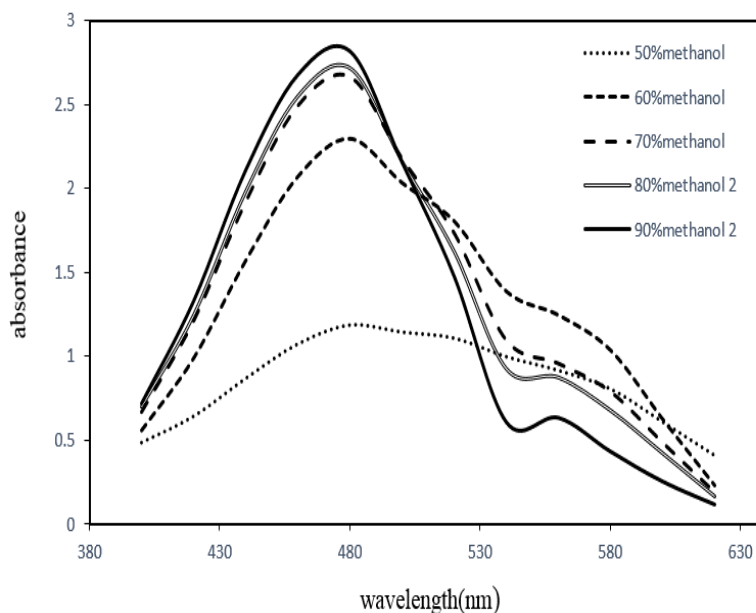


Fig. (6): Optimization of methanol solvent concentration

2.4.5. Optimization of 1,4-Dihydroxyanthraquinone dye concentration

It was evidently known that the concentration of 1,4-diOH-AQ dye should be optimized since any amount less or higher than optimum would cause deviation from Beer's law in praseodymium calibration curve. In these experiments different concentrations of 1,4-diOH-AQ solution were added to a series of 10 ml volumetric flasks containing fixed concentrations of Pr in 90% methanol media and fixed amount of buffer solution. Then the absorbance of each solution was then measured at different wavelength. Fig. (7) Showed the obtained results.

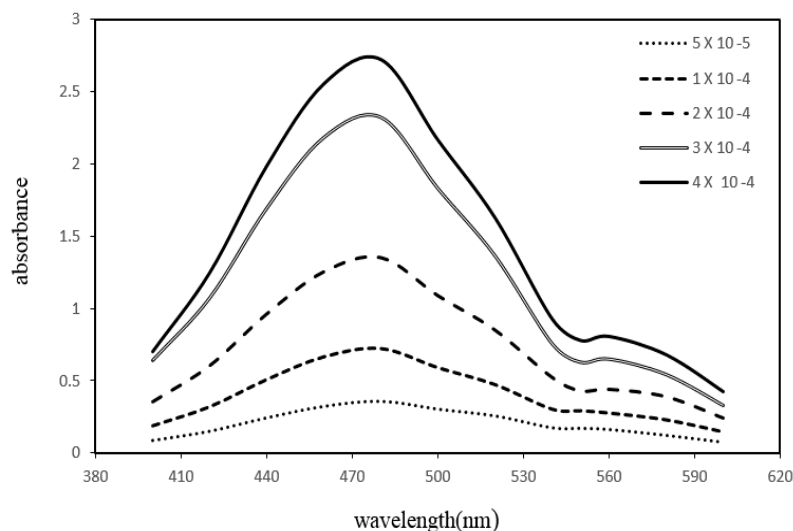


Fig. (7): Optimization of (1,4-diOH-AQ) dye concentration

2.4.6. Effect of duration time on the formation and stability of the “Pr-(1,4-diOH-AQ)-methanol ” complex

The effect of duration time on the formation and stability of the studied praseodymium complex were studied by measuring the absorbance of “ Pr-(1,4-diOH-AQ)-methanol ” complex under the optimum conditions previously studied, using proper reagent blank with time intervals for a period of five hours. It was found experimentally from Table (3) that the complex was formed very rapid and was stable for four hours then the complex began to dissociate.

Table (3): Effect of duration time on stability of Pr complex.

Time (min)	Pr absorbance
1	0.558
5	0.555
10	0.555
30	0.538
60	0.536
90	0.532
120	0.528
240	0.518
250	0.403
260	0.315

2.4.7. Effect of sequence of addition on the formation and stability of the “Pr-(1,4-diOH-AQ)-methanol ” complex

It was necessary to optimize the sequence of addition of the complex species that gave the optimum absorbance values; in this manner a series of six different sequences of addition of the complexes components; (the dye, metal ion, methanol and buffer solution) were mixed and recording the absorbance of each series was recorded at λ_{\max} 560 nm for praseodymium. It was found from Table (4) that the optimum sequence was the addition of Pr ion on the (1,4-diOH-AQ) then methanol and finally adjusting pH.

Table (4): Effect of sequence of addition on the absorbance of “Pr-(1,4-diOH-AQ)-methanol ” complex of at 560 nm

sequence of addition	Pr absorbance
(1,4-diOH-AQ)-Pr-buffer-methanol	0.181
(1,4-diOH-AQ)-Pr-methanol-buffer	0.291
(1,4-diOH-AQ)-methanol-Pr-buffer	0.168
(1,4-diOH-AQ)-methanol-buffer-Pr	0.099
(1,4-diOH-AQ)-buffer-methanol-Pr	0.101
(1,4-diOH-AQ)-buffer-Pr-methanol	0.044

2.4.8. Stoichiometry of “ Pr-(1,4-diOH-AQ)-methanol ” complex

In the present work, the compositions of “Pr-(1,4-diOH-AQ)-methanol” complexes under the operating conditions were determined by using the mole ratio method. In this method, was applied to investigate the metal to dye ratio [Pr]:[ligand] by absorbance of purple color at λ_{\max} 560 nm for praseodymium. Fig. (8) Showed the obtained results. It was shown the mole ratio method suggest a 2:3 metal-ligand stoichiometry.

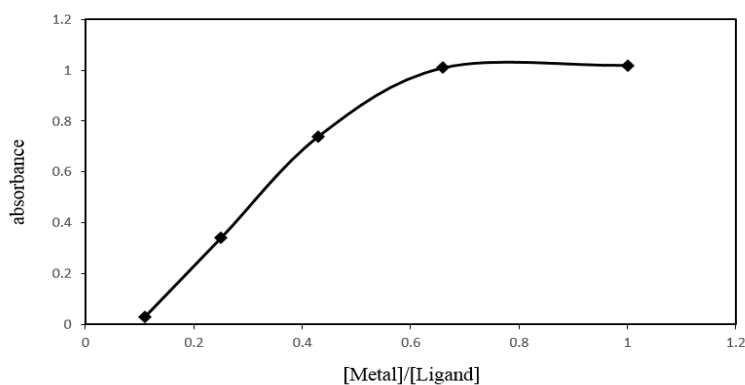


Fig. (8): molar ratio between Pr³⁺ and 1,4-diOH-AQ

2.4.9. Calibration curve of praseodymium by the studied dye

The linear part of the calibration curve of praseodymium represent the concentration range through which praseodymium could be determined spectrophotometrically with good accuracy. The absorbance of “ Pr-(1,4-diOH-AQ)-methanol ” complexes were measured against a reagent blank solution (under the optimum previous conditions) at wavelengths λ_{max} 560 nm for praseodymium then the absorbance was plotted versus a series of different metal ion concentrations. Fig. (9) Showed the obtained results. Figure (9) showed that the calibration curve was linear over the range $0.1 \mu\text{g ml}^{-1}$ to $12 \mu\text{g ml}^{-1}$ for Praseodymium with molar absorptivity (ϵ) value of $1.23 \times 10^6 \text{ M}^{-1} \text{ cm}^{-1}$ for Praseodymium.

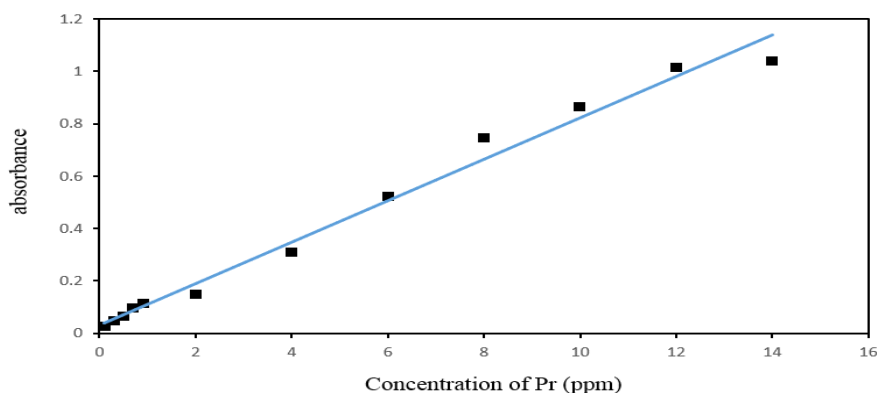


Fig. (9): Calibration curve of praseodymium at λ_{max} 560 nm

2.5. Application of the studied

To test the utility of the suggested method, synthetic sample (were prepared according to the composition of monazite concentrate without Ce) and measured sample was extracted of monazite concentrate free Ce. Table (5) gives the composition of the investigated samples. The suggested method was applied and the results are listed in table (6), indicated that for synthetic and sample could be measured with good accuracy (percent error 5.02%).

Table (5): Chemical analysis of investigated samples

Element	Concentration of Synthetic (ppm)	Concentration of sample (ppm)
La	400	359201
Ce	12	10240
Pr	100	91319
Nd	270	242738
Sm	30	33278
Eu	15	12103
Gd	10	10134

Element	Concentration of Synthetic (ppm)	Concentration of sample (ppm)
Dy	10	9329
Y	45	40723

Table (6): Results of analyzed samples

Sample	Conc. present (ppm)	Conc. Measured (ppm)
Synthetic	5	4.74
sample	91319	86743

CONCLUSION

The proposed method involves the use of Spectrophotometric for the determination of praseodymium complex with 1,4-dihydroxyanthraquinone after solvent extraction by using di-(2-ethylhexyl)phosphoric acid (D₂EHPA). The method proved to be high selective in the presence of other REEs and successfully used with good accuracy for the determination of praseodymium in rare earth concentrate.

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