Available online at **www.joac.info**

ISSN: 2278-1862

Journal of Applicable Chemistry

2021, 10 (5): 628-637

(International Peer Reviewed Journal)

Derivative Spectrophotometric Determination of Neodymium (Nd) in rare Earth concentrates using 2-Hydroxymethyl-5-hydroxy-γ-pyrone

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Accepted on 4th September, 2021

This Paper is dedicated to Journal of Applicable Chemistry during first Decadal Publication Celebrations

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ABSTRACT

Utilizing third derivative spectrophotometry, a sensitive and selective spectrophotometric technique using 2-Hydroxymethyl-5-hydroxy-γ-pyrone was investigated for the detection of neodymium (Nd) from rare earth concentrates (xenotime and monazite concentrates). The complex of neodymium (Nd) with 2-Hydroxymethyl-5-hydroxy-γ-pyrone (Koj) was studied in acidic and alkaline solutions (in the presence of cationic surfactant). The effect of different factors and reaction circumstances on the complex formation was studied. The calibration curve was linear for neodymium concentrations of 1 to 100 μgmL^{-1}*. After five consecutive measurements, the relative standard deviation for determining 1* $\mu g\ mL^{-1}$ *neodymium was determined to be 1.5. The method has been applied to Nd determination from xenotime and monazite concentrates, and the acquired findings were found to be highly equivalent to those obtained using traditional techniques. The Nd determination from xenotime and monazite concentrates had percentage errors of 4.48 and 3.4 percent, respectively. The molar absorptivity of the conventional and third derivative spectrum was* 0.12×10^{3} *and* $0.625\times10^{2}\ M^{-1}\ cm^{-1}$*, respectively. The detection limit of the present method was* $1\mu g\ mL^{-1}$*.*

Highlights

- Third-derivative spectrum for the determination of neodymium complex with Koj in the presence of CPC.
- The effect of different factors and reaction circumstances on the complex formation was studied.
- The method was highly selective for measuring of neodymium in rare earth concentrates in the presence of other REEs.
- The calibration curve was linear for neodymium concentrations of 1 $\mu g\ mL^{-1}$ to $100\mu g\ mL^{-1}$.
- The relative standard deviation for determining 1 $\mu g\ mL^{-1}$ neodymium was determined to be 1.5.
- The molar absorptivity of the conventional and third derivative spectrum was 0.12×10^{3} and $0.625\times10^{2}\ M^{-1}\ cm^{-1}$, respectively.

Keywords: Derivative, Spectrophotometric determination, Neodymium, Monazite, Xenotime.

INTRODUCTION

Spectrophotometry is widely used due to its simplicity, low cost and adaptability [1-5]. 2-Hydroxymethyl-5-hydroxy-γ-pyrone or Kojic acid, a γ-pyrone derivative, is a natural heterocyclic chelating agent found in fermented foods. It forms stable, water-soluble chelates with several cations, such as Nd [6]. The Neodymium was discovered by the Austrian chemist Baron Carl Auer Von Welsbach in Vienna in 1885[7]. Its abundance is about 38 parts per million (ppm) in the Earth's crust. It is the 27th among the chemical elements in terms of abundance. The most bearing minerals of neodymium are monazite (18.4%) and bastnasite (13.5%) [8]. $Nd_2Fe_{14}B$is used in the strongest permanent magnets known [9]. Neodymium: YAG laseris widely used in medical applications, especially for ophthalmology treatments [10]. Scanning for neodymium isotopes can predict the size and strength of volcanic eruptions [11]. Neodymium is a partof didymiumcompound be used for coloring glass to make glass-blower's goggles andwelder's [12]. Neodymium oxide used in manufacturing of TV face plate glass [13]. Probably because of similarities to Ca^{2+}, Nd^{3+} has been reported to promote plant growth as a fertilizer [14].

For the detection of neodymium, various spectrophotometric approaches have been utilized with many chromophoric reagents, such as 8-hydroxyquinoline with nonionic surfactant Triton X-100, which was investigated using conventional and third-derivative spectrophotometry [15]. Neodymium can form stable ternary complexes with 8-hydroxyquinoline-5-sulphonic acid with cationic surfactant cetylpyridinium chloride, but it is not sensitive and it is subjected to interference by cerium [16]. The complex of neodymium/ferron (5-sulpho-7-iodoquinolin-8-ol) was studied in the presence of diethylamine. Their molar absorptivitywas about greater than that in the absence of the complexing agents (at λ_{max} 574.2 nm) [17]. Simultaneous quantification of neodymium in nitric acid solutions using spectrophotometry was studied [18]. The neodymium/fleroxacin complex in the presence of cetylpyridinium chloride was studied by normal and derivative spectrophotometry[19]. An investigation into the complexation reactions between neodymium and nitrate ions in aqueous methanol was carried out using visible spectroscopy [20]. Neodymium was measured spectrophotometrically in chloride [21]. Normal and derivative spectrophotometrical study were applied forthe formed colored complex of neodymium with 2-(diphenylacetyl) indan-l,3-dione and dodecylbenzenesulfonic acid sodium salt [22]. Nd-PAN complex was studied Spectrophotometrically in micellar media [23]. Measurement of neodymium using derivative spectrophotometry by forming a colored complex ofneodymium with semi-xylenol orange and cetyl pyridinium chloride have been studied [24]. The neodymium/benzoyl-indan-1,3-dione complex with cetyltrimethylammonium bromide has been studied by normal and derivative spectrophotometry. The molar absorbitivity of the 4f electron transitions at the maximum absorption bands is 84.7 [25]. The characteristic absorbance of the neodymium complex with 2-phenyltrifluoroacetone (PTA) in the presence of the nonionic surfactant Triton X-100 has been reported [26].

In the present work, the studied REE concentrates have been extracted from karest laterites which are mainly associated with clastic sediments in the Abu Mogheirate area, South Eastern Sinai. Laterites are residual deposits formed by intense subtropical weathering of pre-existing rocks. REE distribution in laterites depends on its concentration in the parent rocks and the weathering processes carried out on studied REE distribution in two types of laterites (karest and blanket). They concluded that total REE content in these ores varied between 1800 and 11709 ppm and that there was an expression of enrichment in the MREE (middle rare earth elements) [27]. The ability to detect neodymium in rare earth concentrates was investigated using Kojic acid (Koj) dye in the presence of cationic surfactant (cetyl pyridinium chloride, CPC). Optimal factors impacting complex formation and measurement, such as wavelength, pH, dye and surfactant concentrations, calibration curve, molar ratios, and interference metal ions effects were tested and discussed.

MATERIALS AND METHODS

Apparatus and reagents: A double beam spectrophotometer Unicam (England) equipped with a 1cm cuvette cell was used for all absorbance measurements. A pH-meter model from SCHOTT GERATE, Germany was used for all experiments in the present work. Kojic acid and cetylpyridinium chloride are Merck products. Standard rare earth elements and other chemicals are Sigma-Aldrich.

Preparation of stock solution: All stock solutions were prepared using double distilled water. A stock standard neodymium solution (1µg mL^{-1}) was prepared by dissolving 0.1166g of neodymium in the least amount of hot 6M HCl and diluting it to 100 mL with double distilled water. A 0.2M kojic acid solution was prepared by dissolving 1.414g of kojic acid (koj) using double distilled water in a 50 mL volumetric flask. Surfactant stock solution, 0.15M, was prepared by dissolving 3.58g of Cetyl pyridinium chloride (CPC) in a 100 mL volumetric flask using double distilled water.By using double distilled water, dissolve 6.75gof ammonium chloride, add 57 mL of ammonia solution and then up to volume in a 100 mL volumetric flask to obtain buffer solution of pH 9.3.

Procedure: To a standard neodymium sample solution (containing less than 150 µg mL^{-1} Nd) in a 10 mL volumetric flask, 1mL of 0.15 MCPC solution, and 4mLof 0.05M Koj solution were added. The pH was adjusted to 9.3 using a 2 mL of buffer solution. The mixture was then completed to the mark using double distilled water, mixed well and the third-derivative spectrum was recorded against a reagent blank using 1cm glass cells.

RESULTS AND DISCUSSION

Neodymium formed a ternary complex with kojic acid dye and Cetyl pyridinium chloride (Nd-Koj-CPC). Cetyl pyridinium chloride (CPC) play important role in manner of increasing the molar absorptivity (Ɛ). Optimum conditions of the Nd-Koj-CPC complex formation were studied. These parameters include optimum wavelength λ_{max}, pH of dye and Nd-Koj-CPC complex, initial concentration of dye and surfactant, sequence of addition to the formation and stability of the Nd-koj-CPC complex against time, Nd:Koj:CPC molar ratios, calibration curve, and interfering effect of REEs.

Optimum wavelength selection: The absorbance of koj (10^{-2}M), koj-CPC (10^{-2}M) against water as blank and Nd-koj-CPC (10^{-3}M) complex against reagent blank were measured using zero order in scan range from 250 to 600 nm. Figs. (1 and 2) showed that kojic acid dye give a peak at (λ_{max} 320 nm), Koj-CPC give another peak at (λ_{max} 370 nm) and showed a significant peak for Nd of the formed Nd-koj-CPC complex at λ_{max} 580 nm.

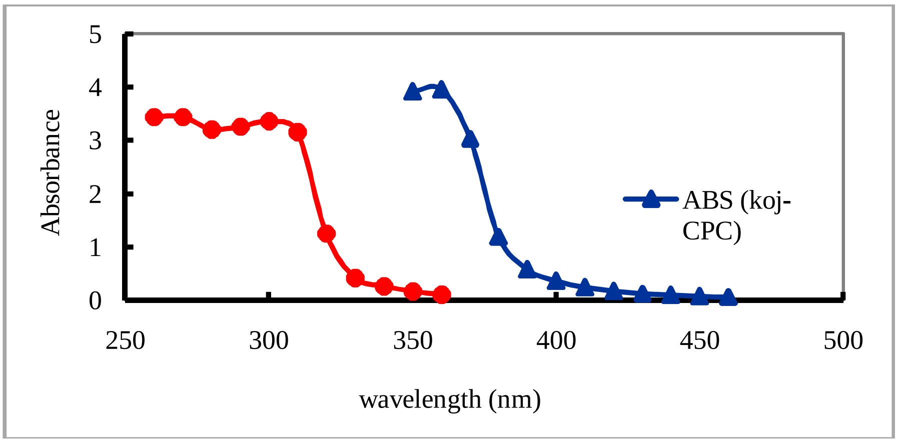

Figure 1. Absorption spectra of kojandkoj-CPC at different wavelengths.

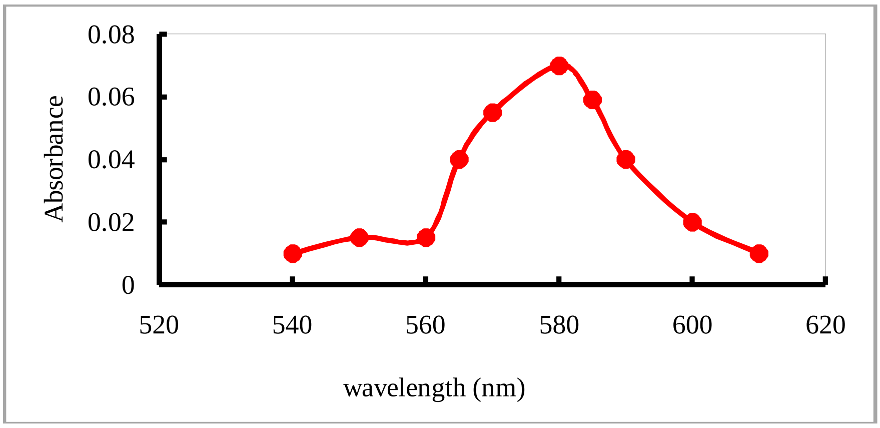

Figure 2. Absorption spectrum of Nd -koj –CPC complex at different wavelengths.

Effect of pH on the absorption spectrum of kojic acid: The pH value plays an important role in the colour intensity of the dye itself and the formed complex. Accordingly, the effect of pH on the absorbance of 10^{-2}M kojic acid dye using ammonium hydroxide from4.5 to 9.5 was studied. Figure 3 Shows that the maximum absorbance noticed for the pH range (8-9.5) indicating that Nd-Koj-CPC complex formation in the alkaline media.

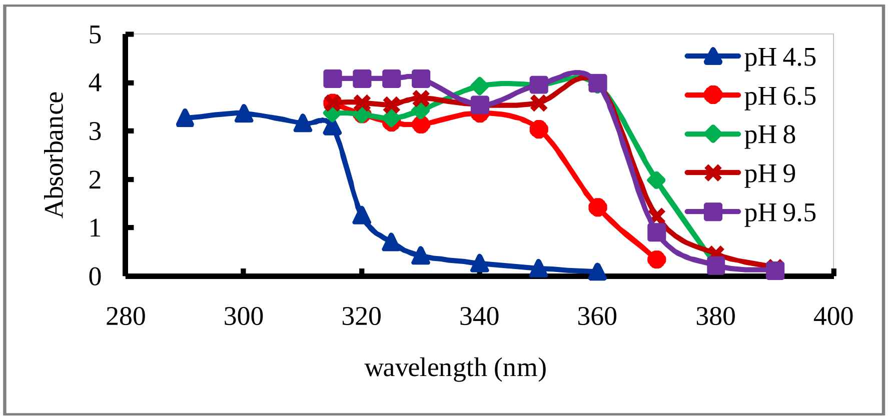

Figure 3. Impact of pH on the absorption spectrum of Koj.

Effect of pH on the Nd–Koj-CPC complex formation: The optimum pH of Nd-Koj-CPC complex was studied in alkaline media in range 6-10 using sodium hydroxide. Accordingly, 1 mL of (10 µg mL^{-1}) Nd solution, 5 mL of 10^{-2}M Koj dye and 1 mLof10^{-2}M CPC solution were mixed in a 10 mL

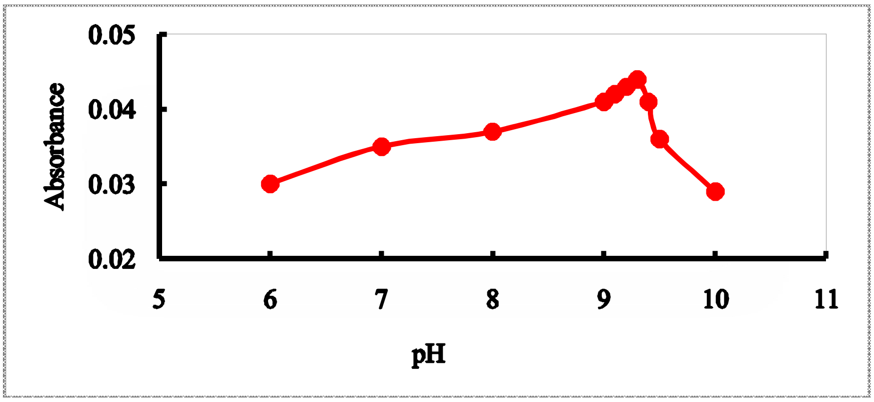

Figure 4. Effect of pH on the absorption of the Nd-koj-CPC complex at λmax = 580 nm.

volumetric flask and the solution was brought up to volume with double distilled water, then the absorbance of the formed complex was measured at λ_{max}580 nm. Figure 4 show that the maximum absorbance value was found at pH 9.3 and indicated that Nd-Koj-CPC complex formation takes place in the alkaline media.

Effect of kojic acid dye concentration: It obviously known that the concentration of dye affect on absorbance of the formed complex. Accordingly, a series of Koj concentrations were prepared with 1 mL of 10µg mL^{-1} Nd, 1 mL of 10^{-2} M CPC and pH 9.3 then measure at λ_{max} 580nm against reagent blank figure 5shows that the optimum dye concentration is 2X10^{-2}M of koj acid.

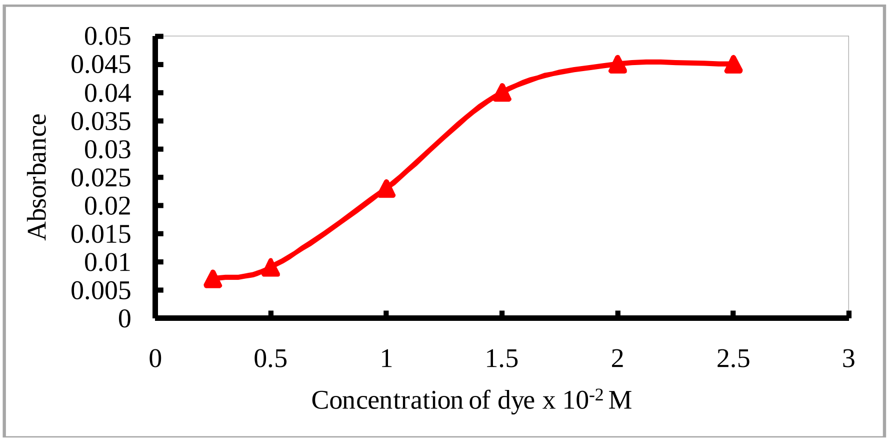

Figure 5. Optimization of Koj acid dye concentration at λ_{max} = 580 nm.

Optimization of surfactant concentration: The optimum concentration of the CPC surfactant was determined by preparing a series of different concentrations of CPC to add to a 1 mL of 10^{-2}M Koj and 1 mL of10µg mL^{-1} Nd solution (at pH 9.3) mixed in a 10 mL volumetric flask. The solution was completed to the mark with double distilled water. The absorbance was measured at λ_{max}580 nm and the results are shown in figure 6 shows that the maximum absorbance was at 1.5X10^{-2}M of CPC

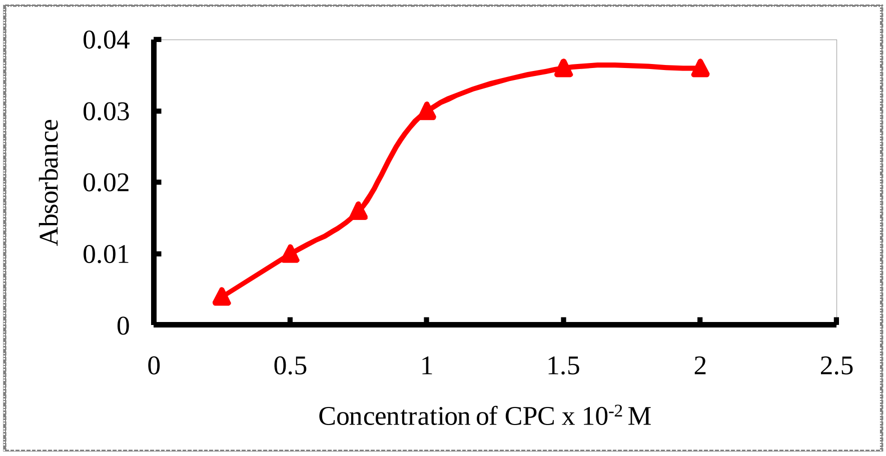

Figure 6. Optimization of CPC concentration at λ_{max} = 580 nm.

Effect of duration time on stability complex formation: The effect of duration time on the formation and stability of the Nd-Koj-CPC complex was studied by recording its absorbance under the previously investigated optimum conditions. Table 1 indicates that the complex was formed instantly and keeps stable more than four hours, then the complex began dissociation.

Table 1. Effect of duration time onstability ofthe Nd-Koj-CPC complex

Time (min)	1	5	10	20	40	60	90	120	240	250	260
Absorbance	0.05	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.08	0.06

Effect of addition sequences: It was found experimentally that the sequence of additions of the complex species affect on absorbance values of neodymium complex, accordingly a series of addition of different sequences of the complex components (the dye, metal ion, buffer solution and surfactant) were mixed well and the absorbance of each series was measured at λ_{max}580 nm for neodymium. Table 2 shows that the sequence of addition Metal-CPC-Koj-Buffer gave the highest absorbance value.

Table 2. Effect of sequence of addition on the absorbance of Nd complex at λ_{max}580 nm

Sequence of addition	**Absorbance**
Metal-Koj-CPC-Buffer	0.06
Metal-Koj-Buffer-CPC	0.03
Koj-CPC- Metal -Buffer	0.03
Metal-CPC-Koj-Buffer	0.09
Metal-CPC-Buffer-Koj	0.04
Koj-CPC-Buffer- Metal	0.01

Composition of Nd-koj-CPC complex: Under the studied optimum conditions, the composition of the ternary Nd-koj- CPC complex was determined by using two methods, the continuous variation method and the molar ratio method.

1. Continuous variation method: This method was applied to determine the ratios of the dye and metal. In this method the molarities of both components (Koj and Nd) were changed continuously meanwhile keeping the total number of moles constant for both components. Then measure the absorbance's of these solutions under the previous optimum conditions at λ_{max}580 nm. The results of the continuous variation method are shown in figure 7. It was found that the molar ratio of the complex Nd:Koj was 1:9 respectively.

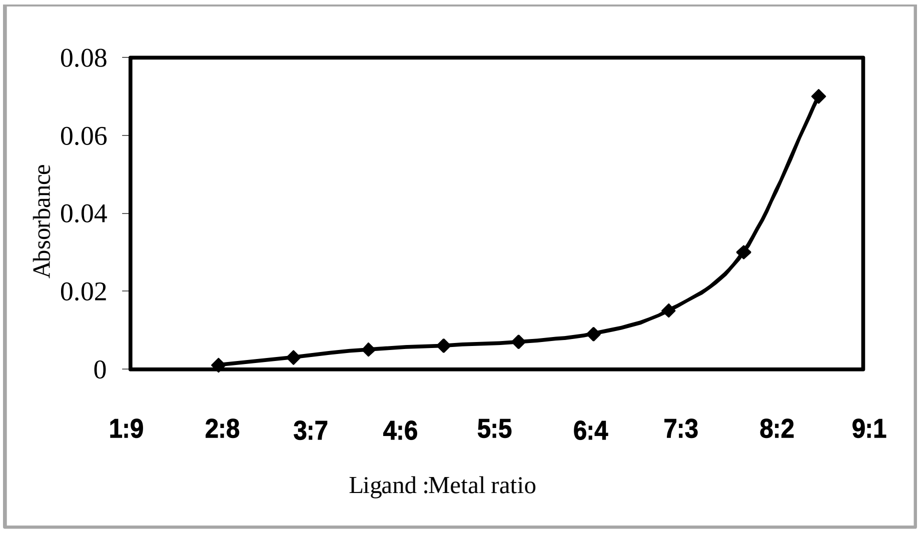

Figure 7. Continuous variation method for estimating the molar ratio between Koj : Nd complex

2. Molar ratio method: In this method, the concentration10^{-3} M of (Nd, koj) components were kept constant while the third one (CPC) was regularly varied. The absorbencies of these solutions were measured at λ_{max} 580 nm for neodymium. The data was illustrated in figure 7, and given in table 3 indicated that the molar ratio of the complex Nd-koj-CPC was 1:9:1.

Table 3. Mole ratio method for estimating the molar ratio of CPC

Concentration of CPC, (10^{-2} M)	Absorbance
0.25	0.007
0.5	0.02
0.75	0.0613
1	0.068
1.5	0.067

Calibration curve of neodymium: The calibration curve of the neodymium complex was shown in figures 8 and 9 at λ_{max}580 nm using conventional and third derivative spectrum. The results showed the performance of the linear calibration graph in the range of 1-100 µg mL^{-1}. Evidentially, the results indicated that the detection limit is 1µg mL^{-1} and the molar absorptivity of conventional and third derivative spectra were found to be 0.12 x 10^3 $M^{-1}cm^{-1}$and 0.625x $10^2 M^{-1}cm^{-1}$ respectively.

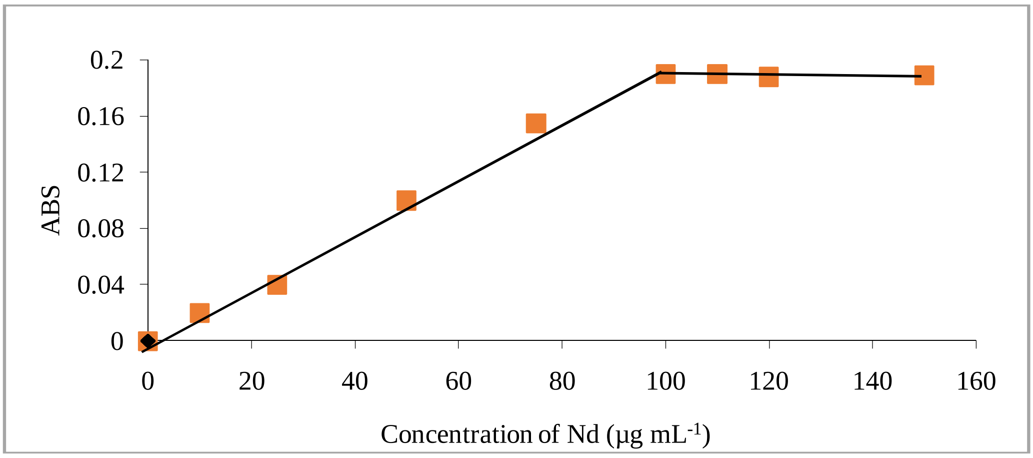

Figure 8. Calibration curve of Nd-koj-CPC at λ_{max} 580 nm.

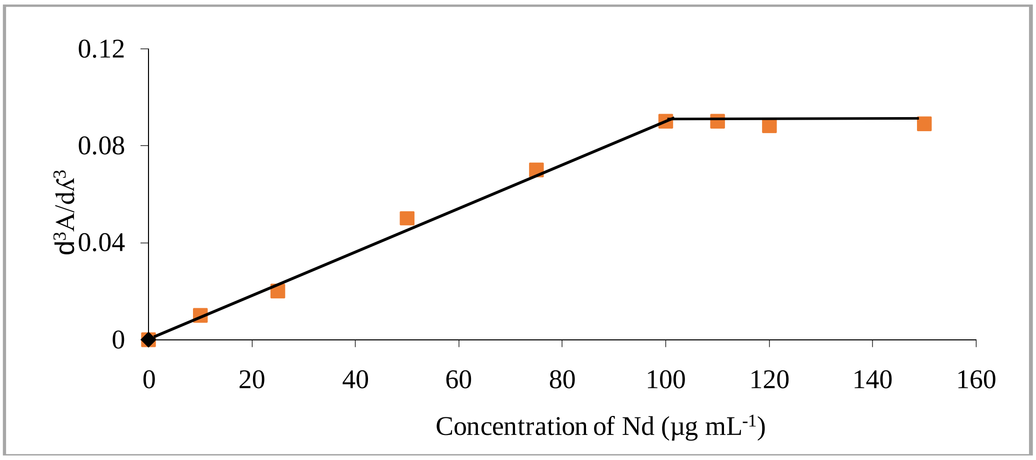

Figure 9. Calibration curve of neodymium using the third derivative method.

Effect of interfering elements: The effect of the accompanying interfering elements La, Ce, Pr, Sm, Eu,Gd, Er, Dy, Ho, Yb, Tm, Tb, Lu and Y on the Nd-Koj-CPC complex was studied. In this manner, and under the previous optimum conditions, a series of variable concentrations of each interfering element were prepared to measure the absorbance of a constant concentration of Nd (1 µg mL^{-1}) Nd against reagent blank at λ_{max}580 nm. The tolerance concentration limit of REEs on Nd determination was shown in table 4, which shows that the determination of neodymium in the presence of REEs will be possible conventionally below the mentioned concentrations. The interference effect causes a systematic error in measuring of neodymium using conventional method. Derivative spectrophotometer method is one of the most applicable solutions to overcome the interfering element effect [28]. Therefore, the first to fourth-derivative spectra were investigated. It was found that the third-derivative spectra eliminated the interference effect and increased the sensitivity for Nd determination; figure 10. The datain table 4 showed the permissibl econcentration limits of REEs where above interference takes place.

Table 4. The tolerance concentration limits of REEs where above interference takes place

Element	La	Ce	Pr	Sm	Eu	Gd	Er	Dy	Ho	Tm	Yb	Tb	Lu	Y
Conc.(µg mL^{-1})	0.12	0.06	0.09	0.1	0.07	0.07	0.12	0.13	0.12	0.16	0.19	0.17	0.1	0.05

Figure 10 shows the third derivative of the Nd-koj-CPC complex free from other rare earth interference effects. Accordingly, itis the most suitable derivative order for the determination of neodymium in Nd-Koj-CPC that eliminate effect of interfering elements. It also indicted the Nd peak at λ_{max}582±2.

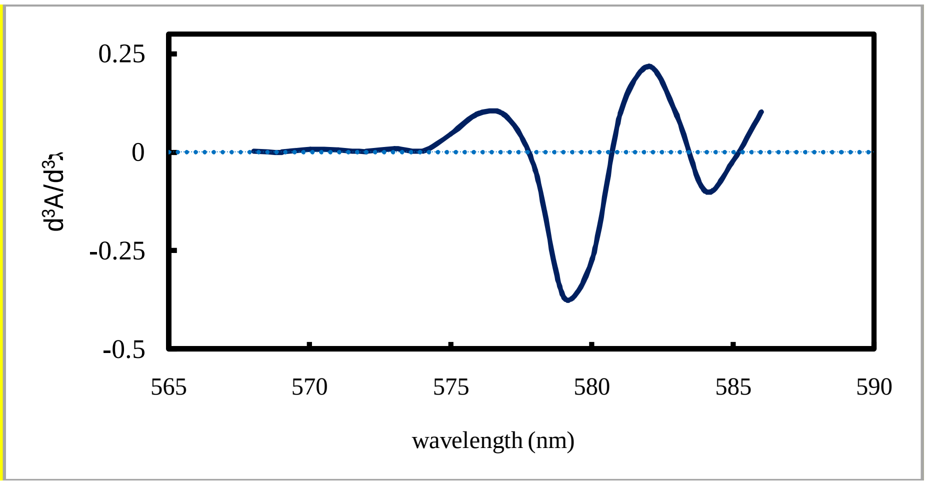

Figure 10. Third order derivative of Nd (100 µg mL^{-1})

APPLICATION

To investigate the applicability of the suggested method, a synthetic sample (of a composition similar to monazite concentrate except Ce as it caused an interfering effect in absorbance of Nd either using conventional or third derivative spectrophotometer) and two geological concentrates, derived from monazite and xenotime, were investigated. The composition of the investigated samples as shown in table 5 was measured using ICP-OES.

The method was applied by adding a definite volume of each investigated sample solution with 1 mL of 0.15 M CPC solution, 4 mL of 0.05 M koj and adjust the pH to 9.3 by adding 2 mL buffer solution. Mix well and up to volume in a 10 mL volumetric flask. Then measure using the third-derivative spectrum against a reagent blank. The results are listed in table 6. The results of the applied samples showed a good accuracy of Neodymium measuring using third derivative and it could be measured without prior extraction.

Table 5. Chemical composition of the studied samples (μg mL^{-1})

Element	La	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Tm	Yb	Tb	Lu	Y
Sample1	240000	21430	662864	1860	70	1530	340	2790	2455	0	260	0	0	61430
Sample 2	1710	310	2610	210	110	1610	2410	55010	27100	3020	14010	0	410	248999
Synth. I	200	40	180	20	20	20	6	2	2	2	1	2	1	20

Table 6. Results of analyzed samples

Sample	Concentration present, (μg mL^{-1})	Concentrationmeasured, (μg mL^{-1})	Nd (% error)
Synth. I	180	186	3.3
Sample 1	662864	640300	3.4
Sample 2	2610	2457	4.48

CONCLUSION

The proposed method involves the use of a third-derivative spectrum for the determination of neodymium complex with Koj in the presence of CPC. The method was highly selective for measuring of neodymium in rare earth concentrates in the presence of other REEs. The method is selective in the presence of other REEs and successfully used for the determination of neodymium in rare earth concentrate

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