SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF CERIUM AS CERIUM (IV) ASSISTED BY NUCLEOPHILIC COUPLING OF *P*-ANISIDINE WITH CATECHOL STABILIZED THROUGH ION-PAIR FORMATION

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ABSTRACT

A simple sensitive spectrophotometric method for the determination of cerium (IV) involving ion-pair complexation. It starts with the introduction to cerium, literature survey regarding the various methods reported for cerium including spectrophotometric methods. In this method, cerium (IV) oxidizes catechol to quinone, which is quite reactive and can be attracted by a variety of nucleophiles, which prompted to use p-anisidine to attack the quinone formed via the oxidation of catechol by cerium (IV) in acidic medium producing coloured compound having maximum absorbance at 565nm and stabilized through an ion-pair formation with $[Ce(OH_2)_2Cl_4]$. The method obeys the Lambert – Beer's law in the range 1.732-173.285μg ml^{-1} with a straight line having slope 0.0020 and intercept 0.0594. Molar absorptivity, correlation coefficient and Sandell's sensitivity values were calculated and found to be 2.77 x 10^{3}Lmol^{-1}cm^{-1}, 0.992 and 0.0505μgcm^{-2} respectively. A probable reaction mechanism along with experimental stoichiometry of the ion-pair are indicated. The proposed method was applied for the determination of cerium in high purity rare earth carbonates and synthetic mixtures.

KEYWORDS

Cerium as cerium (IV), Redox reaction, Spectrophotometry, *p*-anisidine and Catechol.

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INTRODUCTON

Cerium can rarely be found in nature, as it occurs in very small amounts. Cerium is found in a number of minerals including allanite (also known as orthite), monazite, bastnasite, cerite and samarskite. Monazite and bastnasite are presently the more important sources of cerium[1]. Rare earth element geochemistry has been established as one of the most powerful tools for petrogenic studies of rocks.

Rare earth elements are of growing importance because of their chemical[2], industrial[3] and biochemical and medicinal[4] applications. Among the rare earths, cerium is considered to be industrially more important[5] because it is used in nuclear reactors, its alloys with nickel and chromium are used in microwave devices and as fluorescing surfaces in television screens[6]. Due to the increasing industrial use of cerium coupled with reports on cerium toxicity as it is found in edible sea products, oyster clams[7], much attention is now been given to develop analytical procedures for monitoring cerium in environment[8]. Cerium is mostly dangerous in the working environment, due to the fact that damps and gases can be inhaled with air. This can cause lung embolisms, especially during long-term exposure. Cerium can be a threat to the liver when it accumulates in the human body[9]. Cerium is dumped in the environment in many different places, mainly by petrol-producing industries. It can also enter the environment when household equipment is thrown away. Cerium will gradually accumulate in soils and water soils and this will eventually lead to increasing concentrations in humans, animals and soil particles[10]. With water animals cerium causes damage to cell membranes, which has several negative influences on reproduction and on the functions of the nervous system[11].

Cerium is the only rare earth which can exist in aqueous solution in the quadrivalent state finding applications[12] and this property is made use in separating cerium from the other lanthanides. Cerium could also be determined selectively in presence of other lanthanides by oxidizing cerium (III)[13]. Though, cerium (III) forms chelate complexes with number of ligands[14] whereas cerium (IV) does not form such a large number of colored complex due to the facile reduction and the heat of formation[15]. However, some cerium (IV) chelate complexes are known to undergo kinetically controlled reduction to cerium (III) with reducing agents like As (III)[16] which are finding importance in analytical chemistry[17]. Cerium is the only lanthanide that can be determined selectively in the presence of other rare earths by oxidation of cerium (III) to cerium (IV), which is a versatile oxidizing agent[12]. This necessitated the development of convenient and reliable analytical methods for the determination of cerium. Analytical techniques, such as ICP-AES[18-20] or electrothermal vaporization ICP-AES after HPLC separations[21,22], chromatography[23], spectroflurometry[24,25], stripping voltammtry[26,27] reported for the determination of cerium but instruments involved are of high cost and may not be available in common laboratories. Hence it was planned to develop a reasonably sensitive and economically viable spectrophotometric procedure for cerium (IV). Various analytical reagents viz., o-iodobenzoyl-o-tolylhydroxyl amine[28], 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone[29], diantipyrylvinylphenyl methane[30], 2, 4-dihydroxybenzo-phenonebenzoichydrazone[31], o-phenylenediamine[32], p-aminophenylmercaptoacetic acid[33], 2-thenolyl-trifluroacetone[34], 8-hydroxyquinoline[35], N-p-chlorophenyl-2-furylacrylo-hydroxamic acid[36], hydroxamic acids[37] and pyrogallol red[38], have been proposed for the determination of cerium. However most of these methods suffer from number of limitations, such as interference by a large number of ions, low sensitivity, need for extraction[28,29,34-36] or applicable only at higher concentration of cerium. Concerning the present investigation, a simple, rapid and sensitive spectrophotometric method for the determination of cerium (IV) using p-anisidine is developed. The new method is based on oxidative coupling reaction in that cerium (IV) which oxidize catechol to quinone, which is quite reactive and can be attracted by a variety of nucleophiles, which prompted to use p-anisidine to attack the quinone formed via the oxidation of catechol by cerium (IV) in acidic medium producing coloured compound having maximum absorbance at 565nm. Therefore, the intensity of the colour produced is proportional to the concentration of cerium (IV). The proposed method was applied for the determination of cerium in high purity rare earth carbonates and simulated Ce (IV) alloys.

EXPERIMENTAL
MATERIAL AND METHODS

From Sigma-Aldrich Chemicals we were purchased all the reagents for synthesis. All chemicals used in the experiments were of analytical reagent grade and the water used was distilled water. Elico spectrometer, model SL171 (Hyderabad India) with 1cm matched quartz cells, UV-visible-spectrophotometer (Shimadzu), Acculab digital balance readable 0.0001g and UV spectrophotometer (Jena, Germany) were used.

Procedure

A series of labeled 10ml volumetric flasks were arranged. To each flask, 0.6ml of 0.1M hydrochloric acid, 2ml of 0.0081M *p*-anisidine, 2ml of 0.005M catechol, aliquots of the solution containing 1.732-173.285μg ml^{-1} of cerium (IV) were added. The solutions were made upto 10ml with distilled water and mixed well. The absorbance of each solution was measured at 565 nm against corresponding reagent blank but not containing cerium (IV).

Analysis of simulated cerium (IV) alloys

Synthetic mixtures of various cerium alloys, misch metal, flint and aircraft alloy[39] were prepared by mixing a known quantity of cerium and other metal salts, lanthanum carbonates, ferrous ammonium sulphate and magnesium sulphate equivalent to that in the corresponding alloy in 100ml volumetric flask. The amount of cerium present in each alloy was determined by taking suitable amount of the stock solution, 0.1-1.5ml (3.46-51.985μg ml^{-1}) and measuring the absorbance at 565nm after developing colour through the procedure described before for cerium (IV). The results obtained are given in Table No.1.

Estimation of Ce (IV) in rare earth carbonates

A stock solution of each rare earth was prepared by dissolving 0.2g of the respective rare earth carbonate with 1ml of 2M hydrochloric acid and the solution so obtained was diluted to 50ml with water. To the aliquot solution, 0.1ml of each rare earth, 0.2ml of Ce (IV) solution was added and the solution was left at room temperature for about 20 min. Then the amounts of Ce (IV) present in those solutions were determined following the procedure as described under the general procedure for Ce (IV).

RESULTS AND DISCUSSION

Oxidation coupling reactions are frequently used in analytical determination of some important compounds[40-44]. Accordingly, there are many compounds subjected to such kind of reactions, for example, an oxidative coupling of 3-methyl-2-banzo- thiazolinone hydrazone with N,N - dimethylaniline by hydrogen peroxide[45], amino phenol and p - phenyl enediamine[46], N - phenyl - p - phenylene diamine with N,N - dimethyl aniline in the presence of an oxidant[47,48], p-anisidine[49,50], 4–aminoantipyrine[51] with N-N-dimethyl aniline in the presence of hydrogen peroxide. Based on the literature survey about oxidative coupling reactions[40-51], the developed method that exploited this type of reactions[40-51] for determination cerium (VI) which oxidise catechol to quinone[52-54], which is quite reactive and can be attracted by a, variety of nucleophiles[52], which prompted to use p-anisidine to attack the quinone formed via the oxidation of catechol by cerium (IV) in acidic medium producing coloured compound having maximum absorbance at 565nm. Therefore, the intensity of the color produced is proportional to the concentration of cerium (IV)

Optimization of Conditions

Optimization and stoichiometry experiments for catechol and p-anisidine have already been given under chromium chapter under fixed concentration of chromium (VI). However, the same experiments have been repeated since the experiments were carried out in presence of cerium (IV) oxidant. The spectrophotometric properties of the coloured product as well as the various experimental parameters affecting the development and stability of the coloured product have been carefully optimized; those variables that include different volumes of catechol (0.005M), different volumes of 0.1M hydrochloric acid different volumes of p-anisidine (1000μg ml^{-1}) and order of the reagents addition.

Effect of the different volumes of catechol
A series of labeled 25ml volumetric flasks were arranged. To each flask 1ml of 0.1M hydrochloric acid, 0.5ml of 1000μg ml^{-1} p-anisidine, but various volumes 0.1, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0ml of 0.005M catechol and 0.5ml of (0.0025 M) cerium (IV) were added. Solution of the each flask was then diluted to the mark with water. Absorbance of each solution and the blank (same as the test solution but not containing cerium (IV) were measured against water at 565nm. The absorbance of the solutions were 0.81, 0.089, 0.092, 0.098, 0.106.0.110 and 0.108 for 0.1, 0.5, 1, 0, 1.5, 2.0 and 3.0ml of catechol. Based on the highest absorbance of the solution obtained under the specified conditions, 2ml of this reagent was selected for the construction of the calibration graph to determine cerium (IV).

Effect of different volumes of 0.1M hydrochloric acid
The effect of concentration of hydrochloric acid on absorbance was investigated to achieve high absorbance via taking various volumes (0.2-1.0ml) of 0.1M hydrochloric acid, 2ml of 1000μg ml^{-1} *p*-anisidine, 2ml of (0.005M) catechol and 1.0ml of (0.0025M) cerium (IV) were added to the 10ml volumetric flasks. Then, the solutions were diluted to the mark with water. Absorbance of each solution was measured at 565nm. The absorbance of the solutions was 0.092, 0.092, 0.122 and 0.089 respectively for 0.2, 0.4, 0.6 and 1.0ml of 0.1M hydrochloric acid. The absorbance values indicated that the solution containing 0.6ml of 0.1M hydrochloric acid appeared to be more sensitive than other solutions. Therefore, 0.6ml of 0.1M hydrochloric acid per 10ml used throughout the experiment to determine the cerium (IV).

Effect of the different volumes of *p*–anisidine
The effect of various volumes of (0.5 - 3.0ml) of 1000μg ml^{-1} p-anisidine on absorbance was investigated to achieve higher absorbance. The study was performed following the optimized variables achieved in the earlier studies. A series of labeled 10ml volumetric flasks were arranged. To each flask 0.6ml of 0.1M hydrochloric acid various (0.5-3.0) ml of 1000μg ml^{-1} p-anisidine, 2ml of 0.005M catechol, followed by 1.0ml (0.0025 M) of cerium (IV) were added. The solution of each flask was diluted to the mark with water. Absorbance of each solution and the blank (same as the test solution but not containing cerium (IV) were measured against water at 565nm. The absorbance of the solutions were 0.116, 0.130, 0.138, 0.154, 0.140 respectively for 0.5, 1.0, 1.5, 2.0 and 2.5ml of 1000μg ml^{-1} p-anisidine. The absorbance values which were found to be increasing with the increasing volume of p-anisidine up to 2.0ml, after that the absorbance values were found to be decreasing with the increasing volume of p-anisidine, therefore, 2ml of 1000μg ml^{-1} p-anisidine per 10 ml was selected as optimized value for the construction of the calibration graph for the determination of cerium (IV).

Effect of order of addition of the reagents
Different orders of the reagent addition were studied using optimized amounts of reagents following the recommended procedure. The results obtained have shown that the order of reagents addition do not affect absorbance values. But for maintaining the uniformity of the order of the reagents addition as mentioned in the recommended procedure was followed throughout course of the determination of cerium (IV).

Calibration graph
Under the optimum condition, a good linear relationship Figure No.1 was found to be existing between the absorbance of the system and the concentration of cerium (IV) 1.732-173.285μg ml^{-1} with a straight line having slope 0.00205 (cal.) and intercept 0.0594. Molar absorptivity, correlation coefficient and Sandell's sensitivity values were calculated and were found to be 2.77 x 10^{3}mol^{-1}cm^{-1}, 0.992 and 0.0505mg cm^{-2} respectively. The precision and accuracy of the method were studied by analyzing a series of solutions containing known amount of cerium (IV) (3.465, 86.642 and 155.956μg ml^{-1}) by using recommended volumes and concentration of the reagents. The precision of the method as expressed by relative standard deviation was less than 3.7 % whereas the accuracy expressed by the calculated relative error was 3.2%.

Stiochiometry

Composition of coloured product of the system involving p-anisidine was studied by Job's method of[55] continuous variation as well as mole ratio method. The procedures were carried out as shown below.

Job's method of continuous variation

The study was carried out using a series of solutions of 0.002M catechol and 0.002M p-anisidine which were prepared by mixing complementary proportions to a fixed total volume of 5ml. The procedure performed was 0.6ml of 0.1M hydrochloric acid, (5-0ml) of 0.002M *p*-anisidine but various volume (0-5ml) of 0.002M catechol, 3ml of 0.002M cerium (IV) were transferred into a series labeled 10ml volumetric flasks and then the solution of each flask was diluted to the mark with water. The absorbance of each solution was measured at 565nm. The results obtained were used in plotting the graph which is shown in Figure No.2 that accounts for 1:1 stoichiometry between catechol and *p*-anisidine.

Mole ratio method

Equimolar solutions of 0.002M catechol and 0.002M *p*-anisidine were used. A series of solutions were prepared keeping the concentrations of the volume of catechol, 2.5 ml with varying p-anisidine volumes (0 - 5ml). This procedure carried out a 0.6 ml of 0.1 M hydrochloric acid, various volumes (0-5 ml) of 0.002 M p - anisidine, constant volume 2.5 ml of 0.002 M catechol and 3.0 ml of 0.002 M cerium(IV) were transferred into 10 ml volumetric flasks and diluted to the mark with water. The absorbance of each solution was measured at 565 nm. The results obtained were used to construct the graph as it shown in Fig. 3, which also accounts for 1:1 stoichiometry between catechol and p-anisidine. The stability constant of the dye product was also calculated which was found to be ^{1} mol^{-1}. A tentative mechanism for the formation of the dye has been proposed the scheme 1, which is agreeing with experimental stoichiometry as well as the literature information on the formation of similar such dyes[53-54, 56-57].

Effect of diverse ions

In order to assess the analytical potential of the proposed method, the effect of some diverse ions, which often accompany cerium (IV), were examined by carrying out the determination of 17.328μg ml^{-1} of cerium (IV) in the presence of a number of other ions. The tolerance limits of interfering species were established at those concentrations that do not cross more than 4 % error in absorbance values of cerium (IV) at 17.328 □g ml^{-1}. The oxidizing agents such as Fe (III), Cr(VI), V(V) interfere severely. However, the tolerance level for these ions may be increased by the addition of 2ml of 2% EDTA. The results presented in Table No.1 indicate that many diverse cations especially lanthanides did not interfere with the determination of cerium (IV).

Analytical application

The applicability of the developed method for the determination of Ce(IV) was checked by analyzing the synthetic mixtures corresponding to the composition of some cerium alloys, namely misch metal, flint, aircraft alloys and its determination in some rare earth carbonates. For the comparison of the results, Ce(IV) present in those samples were also determined separately using an official method[58]. When the concentration of Ce(IV) in rare earth carbonate test solutions was below the detection limit (<1.732μg ml^{-1}) of the developed method, it was determined by standard addition . The results obtained are given in Table No.2 and Table No.3.

Table No.1: Interference of foreign ions in the determination of 17.3285mgml^{-1} of cerium (IV)

S.No	Ion added	Tolerance limit
1	Ni^{2+}	400
2	Zn^{2+}	400
3	Mo^{6+}	38.4
4	V^{5+}	14.2
5	Fe^{3+}	12.4
6	Cr^{6+}	10.4
7	Po^{4-}	30
8	Cu^{2+}	400
9	Cl^{-}	400
10	F^{-}	400
11	La^{3+}	400
12	Pr^{3+}	400
13	Nd^{3+}	400
14	Gd^{3+}	400
15	Er^{3+}	400

Table No.2: Analysis of Cerium (IV) in various synthetic mixtures

| S.No		%Composition	Ce(IV) taken in/ µg ml^{-1}	Amount[a] found by method/	
				Developed	Official
1	Simulated misch Metal	Ce, 50; La, 25; Nd, 15; Fe, 5; Eu, 1.25 ; Gd, 1.25; Er, 1.25; Pr, 1.25;	44	44.96	45.4
			38	38.85	36.9
2	Simulated flint	Ce, 35; Fe33.5; La, 17.5: Nd, 10.5; Eu, 0.87; Gd, 0.87 ; Er, 0.87; Pr, 0.87;	18	18.98	16.92
			15	14.24	16.4
3	Simulated aircraft alloy	Mg, 94; Ce, 3; Fe, 0.3; La, 1.5; Nd, 0.9; Eu, 0.075; Gd, 0.075; Er, 0.075; Pr, 0.075 ;	4	5.68	6.69
			6	7.44	8.22

a. Average of five determinations

Table No.3: Determination of Cerium (IV) in high purity Rare earth carbonates

S.No	Rare earth carbonates (99.9%)[b]	Ce(IV) added/ µg ml^{-1}	Amount[a] found by Official method µg ml^{-1}	Amount found by Developed method/ µg ml^{-1}
1	La	3.46	3.40	3.42
2	Pr	3.46	3.38	3.36
3	Nd	3.46	3.49	3.44
4	Sm	3.46	3.51	3.49
5	Gm	3.46	3.41	3.48

a. Average of five determinations

b. Obtained from Indian Rare Earth Limited Udyogamandalam (S.India)
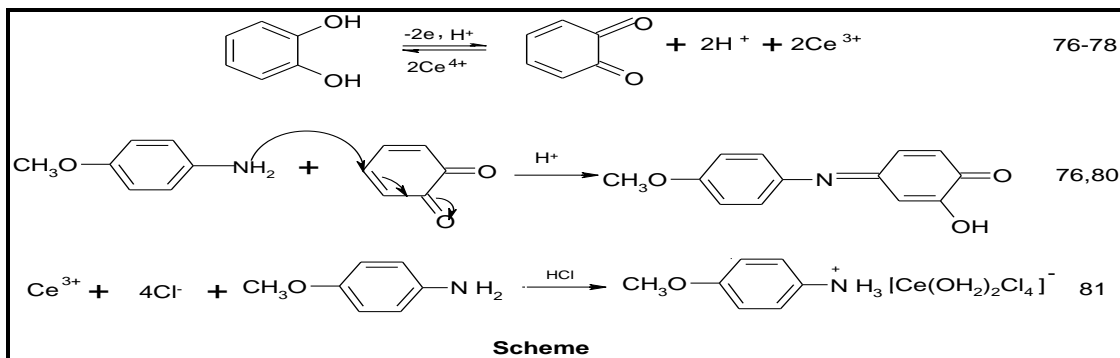
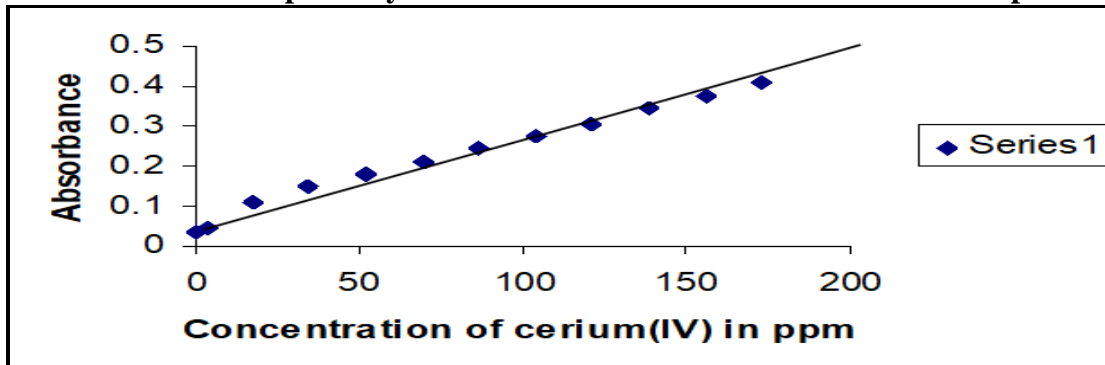**Scheme No.1: Reaction pathway of conversion of catechol into cerium salt of p-anisidine**

Figure No.1: Calibration graph for the determination of Cerium (IV) under the optimum condition
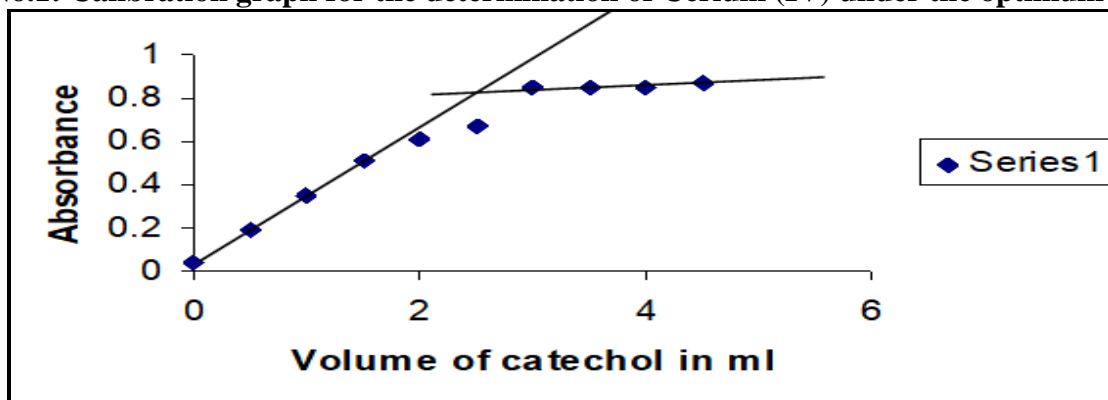

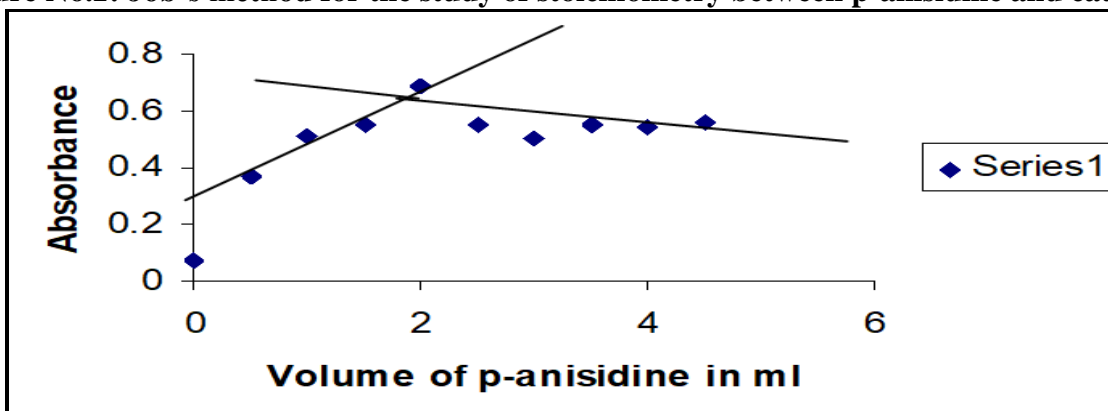**Figure No.2: Job's method for the study of stoichiometry between p-anisidine and catechol**

Figure No.3: Mole ratio method for the study of stoichiometry between p-anisidine and catechol

CONCLUSION

The proposed method is simple, rapid and economical with a wide concentration range of determination of cerium (IV) 1.732-173.285µg ml^{-1}. Cerium is the only lanthanide that can be determined selectively in the presence of other rare earths by oxidation of cerium (III) to cerium (IV), which is a versatile oxidizing agent. This necessitated the development of convenient and reliable analytical methods for the determination of cerium. Analytical techniques, such as ICP-AES, or electrothermal vaporization ICP-AES after HPLC separations, chromatography, spectroflurometry, stripping voltammtry fluorimetric spectrometry, chemiluminescence reported for the determination of cerium but instruments are of high cost and may not be available in common laboratories.

Hence it was planned to develop reasonably sensitive and economically viable spectrophotometric procedure. Various analytical reagents have been proposed for the determination of cerium. However most of these methods suffer from number of limitations, such as interference by a large number of ions, low sensitivity, and need of extraction or applicable only at higher concentration of cerium. In this way the present investigation is simple, rapid and sensitive spectrophotometric method for the determination of cerium as cerium (IV) assisted by nucleophillic coupling of p-anisidine with catechol stabilized through ion-pair formation. The new method is based on oxidative coupling reaction in that cerium (IV) which oxidize catechol to quinone, which is quite reactive and can be attracted by a variety of nucleophiles, which prompted to use p-anisidine to attack the quinone formed via the oxidation of catechol by cerium (IV) in acidic medium producing coloured compound having maximum absorbance at 565nm and stabilized through an ion-pair formation with $[Ce(OH_2)_2Cl_4]$. Therefore, the intensity of the colour produced is proportional to the concentration of cerium (IV). The proposed method was applied for the determination of cerium in high purity rare earth carbonates and simulated Ce(IV) alloys. For the comparison of the results, Ce(IV) present in those samples were also determined separately using an official method[58]. When the concentration of Ce(IV) in rare earth carbonate test solutions was below the detection limit (<1.732µgml^{-1}) of the developed method, it was determined by standard addition. The results obtained are given in Table No.2 and Table No.3.

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CONFLICT OF INTEREST

The authors declares no conflict of interest.

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