Journal of Fluorescence, Vol. 16, No. 1, January 2006 (© 2006)
DOI: 10.1007/s10895-005-0028-x

Fluorimetric Determination of Cerium(IV) with Ascorbic Acid

Mohammad Mainul Karim,[1] Sang Hak Lee,[1,3] Young Sun Kim,[2] Hyun Sook Bae,[2] and Sang Beom Hong[2]

Received August 14, 2005; accepted October 26, 2005
Published online: February 23, 2006

A simple, sensitive, and selective method for the determination of cerium(IV), based on the oxidative reaction between cerium(IV) and ascorbic acid, has been described. The fluorescence comes from Ce(III) at $\lambda_{excitation}$ 298 nm and $\lambda_{emission}$ 358 nm, which, in turn, is obtained from the oxidation of ascorbic acid by Ce(IV) in the presence of sulfuric acid. The optimum conditions such as concentrations of ascorbic acid, sulfuric acid media and pH of the buffer solution were investigated. The fluorescent intensity of the system is linear over the range 0.0531 μg/ml to 0.3322 mg/ml Ce(IV) and detection limit and correlation coefficient are 0.0145 μg/ml and R=0.99987, respectively.

KEY WORDS: Fluorescence; emission spectra; cerium; ascorbic acid.

INTRODUCTION

Cerium is a silvery metallic element, belonging to the lanthanide group. It is used in some rare-earth alloys. In metallurgy, cerium is used in making aluminum alloys and in stainless steel as a precipitation hardening agent. It is added to cast irons which oppose graphitization and produce a malleable iron. In steels, cerium degasifies and can help reduce sulfides and oxides. Therefore, with the extensive application of cerium in metallurgical and functional materials areas, the development of quick and sensitive analysis methods for the determination of cerium is required.

Cerium has two common oxidation states, +3 and +4 but most common state of cerium is cerium(IV). It was determined by spectrophotometric method using phenothiazine derivative [1], sulphanilic acid [2], and by chemiluminescence using cypridina luciferin analog (CLA) [3]. The determination of lanthanide is normally carried out by various spectrophotometric methods but as an analytical technique, fluorimetry has the basic advantage of considerably greater sensitivity over the spectrophotometry. Spectrofluorimetric methods [4,5] were also reported for the determination of cerium.

Cerium(IV) has been used as an oxidizing agent for the determination of carbohydrates [6] and certain antiviral drugs [7]. It can be easily reduced to Ce(III) that shows a characteristic fluorescence in dilute sulfuric acid [8].

Our study shows that Ce(IV) is reduced by ascorbic acid to Ce(III), which emits natural fluorescence in sulfuric acid media and the light intensity is linearly related to the concentration of Ce(IV). Up to now nothing has been published concerning the determination of Ce(IV) using ascorbic, and this method can become a leading analytical tool in material science because of its simplicity, fastness, and sensitiveness.

EXPERIMENTAL

Reagents and Solutions

Cerium(IV) sulfate was used as standard (Aldrich, USA). All reagents were of analytical-reagent grade. A

[1] Department of Chemistry, Kyungpook National University, Taegu, 702-701, Korea.
[2] Department of Sensor and Display Engineering, Kyungpook National University, Taegu, 702-701, Korea.
[3] To whom correspondence should be addressed. E-mail: shlee@knu.ac.kr

5×10^{-2} M cerium(IV) sulfate solution was prepared by dissolving 1.6612 g of $Ce(SO_4)_2$ in 100 ml of 0.5 M sulfuric acid (Duksan Pure Chemical Co Ltd., Korea). L-Ascorbic acid ($C_6H_8O_6$) was purchased from Aldrich, USA. A 0.01 M ascorbic acid was prepared in deionized water. CH_3COOH-NaOAc buffer solution (pH 3.4) was prepared as follows: 0.50 ml of 2 M NaOAc and 9.5 ml of 2 M CH_3COOH were transferred into a 100 ml standard flask and diluted to the mark with water.

Instrument

SPEX Fluorolog-2 spectrofluorimeter equipped with a 150 W xenon lamp was used for all measurements. The fluorescence intensities of solutions were obtained using 1 cm quartz cells. The excitation and emission monochromators were fixed with 0.25 mm slits. Fluorescence was collected and detected by photomultiplier tube. All spectral data are obtained by SPEX DM 3000F spectroscopy computer. A pH meter (Model Orion 520A, USA) was used for monitoring pH adjustment. Origin version 6.0 professional software was used for data processing.

Procedure

The fluorescence intensities were measured at room temperature and optimum excitation and emission wavelengths were found from these spectra. A known amount of Ce(IV) and 1 ml of 1×10^{-2} M ascorbic acid and 1 ml buffer solution of pH 3.4 were pipetted into a vial, mixed well and stood for 30 min. The content of the vial was made up to 10 ml with distilled water. The fluorescence intensity of the system was measured in 1 cm quartz cell. The fluorescence intensity of the solution was measured at 358 nm with excitation at 298 nm against a reagent blank prepared with the reagent concentrations but no cerium(IV).

RESULTS AND DISCUSSION

Excitation and Emission Spectra of Cerium

The excitation and emission spectra of cerium(IV) in presence of ascorbic acid and of the reagent alone were obtained with pH 3.4 buffer solution and are shown in Fig. 1. In sulfuric acid media, Ce(IV) can be reduced by ascorbic acid to Ce(III), which causes fluorescence. The excitation and emission peaks of Ce(III) appeared at 298 and 358 nm, respectively. The excitation spectrum shows two peaks at 270 and 298 nm. Therefore, λ_{ex} 298 nm and λ_{em} 358 nm were selected as operating wavelengths during the whole experiments. The reagent blank is very low in this work which benefits determining Ce(IV).

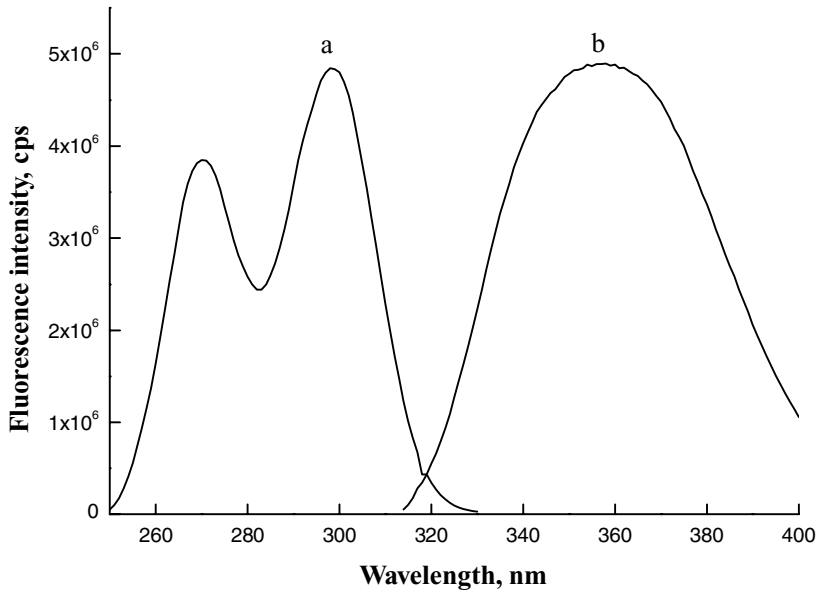

Fig. 1. Excitation (λ_{em}= 358 nm) (a) and emission (λ_{ex}= 298 nm) (b) spectra of the reaction product formed by the oxidation of ascorbic acid with Ce(IV). Conditions: [ascorbic acid]=1×10^{-2} M; [Ce(IV)]=5×10^{-2} M; [CH_3CO_2H-NaOAc] (pH=3.4)=2 M; [H_2SO_4]=0.5 M.

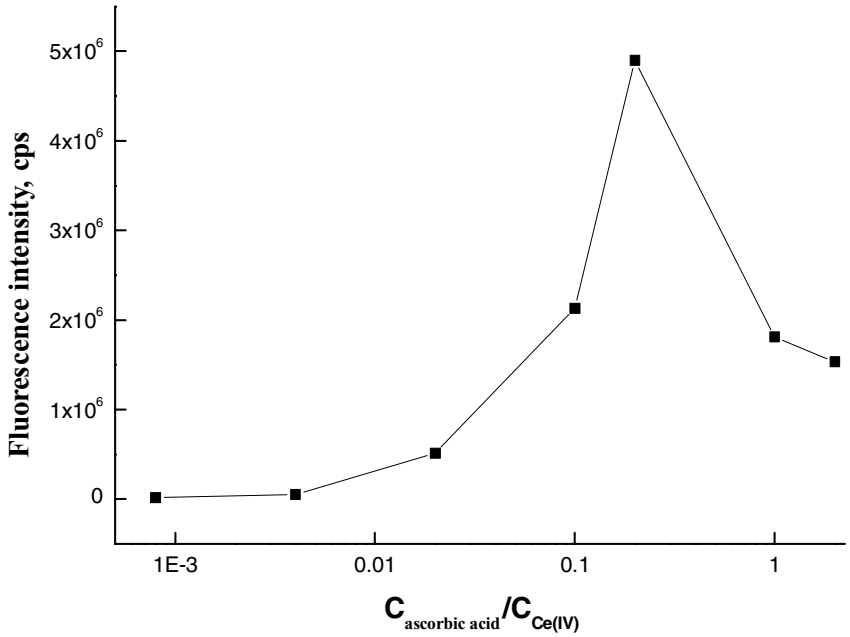

Fig. 2. Effect of ascorbic acid concentration on the fluorescence intensity of cerium(IV). Conditions: [Ce(IV)]=5×10^{-2} M; [CH_3CO_2H-NaOAc] (pH=3.4)=2 M; [H_2SO_4]=0.5 M.

Effect of Ascorbic Acid on the Intensity

Effect of ascorbic acid concentration on intensity (peak height) was studied over the range 4×10^{-5} to 1×10^{-1} M of ascorbic acid, while the concentration of Ce(IV) was kept constant in a solution of pH 3.4. The peak height increased with increasing ascorbic acid concentration range 4×10^{-5} up to 1×10^{-2} M and fluorescence intensity reached a maximum at the AA:Ce(IV) ratio of 1:5. The enhancement of the fluorescence intensity was a result of an increase in the reduction rate of Ce(IV) to Ce(III) with sufficient ascorbic acid concentration. The fluorescence intensity decreased on further addition of ascorbic acid and background signal quickly increased. Therefore, 1×10^{-2} M ascorbic acid solution as shown in Fig. 2 was selected in the work.

Effect of pH on the Intensity

The pH effect of the standard solution on the fluorescence intensity of Ce(IV)–ascorbic acid was conducted following the procedure mentioned earlier. The result is shown in Fig. 3. The rate of reduction of Ce(IV) to Ce(III) by ascorbic acid in sulfuric acid media is pH dependent. The pH of the system was studied in the range 1–12.0. The peak height was increased from pH 1.0 and reached maximal at pH 3.4, and decreased outside this range. The decrease of fluorescence with increase of pH seems to be related with decrease of protonated forms of Cerium sulfates, which are more oxidant because the net charge is increased. Therefore, acetate buffer of pH 3.4 was used for subsequent experiments.

The effect of the concentration of acetic acid over the range of 0.1–5 M was further studied. The fluorescence intensity was increased with acetic acid concentration in the range of 0.1–2 M, decreased from 2 to 5 M. The lower detection limit was obtained for the highest S/N ratio at the concentration of 2 M acetic acid. Therefore, 2 M CH_3CO_2H-NaOAc buffer (pH 3.4) was selected as the optimum condition.

Effect of H_2SO_4 on the Intensity

The fluorescence emission depends on the concentration of H_2SO_4. The experiment was performed in the range of 0.08 to 1 M H_2SO_4 under the standard conditions mentioned. The maximum intensity reached at 0.5 M H_2SO_4. When the H_2SO_4 concentration was above this level, fluorescence intensity decreased (Fig. 4). In the range of the used H_2SO_4 concentration, the Ce(IV) species exist as sulfated complexes, such as, $Ce(SO_4)^{2+}$, $Ce(OH)(SO_4)^{1+}$, $Ce(SO_4)_2$, $Ce(SO4)_3{}^{2-}$, $HCe(SO_4)_3{}^{-}$, $HCe(SO_4)_4{}^{3-}$, and $Ce(SO_4)_4{}^{4-}$ [9], and these species are in a series of equilibria with $HSO_4{}^{-}$. It has already been pointed out that the reactive species of the oxidants are Ce(IV), $Ce(SO_4)_2$, and $HCe(SO_4)_3{}^{-}$ [10]. So, the reactive species of Ce(IV)

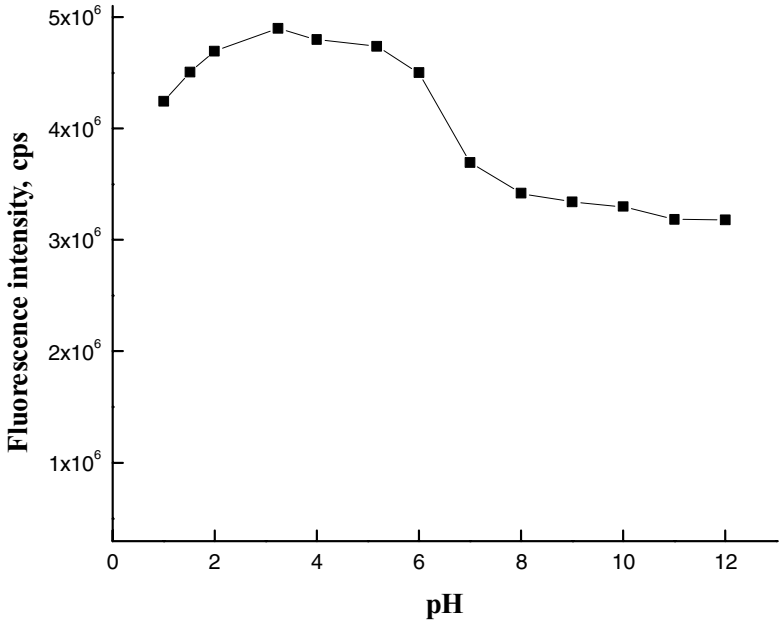

Fig. 3. Effect of pH on the fluorescence intensity of cerium(IV). Conditions: [ascorbic acid]=1×10^{-2} M; [Ce(IV)]=5×10^{-2} M; [H_2SO_4]=0.5 M.

decrease with increasing H_2SO_4 concentration, and the intensity decreases. The effect seems related with competition of Ce complexation between the ascorbic acid and sulfate ions. Furthermore, the rate of reaction is inversely proportional to the concentration of H_2SO_4 [11]. For this reason, 0.5 M H_2SO_4 solution was used in the work.

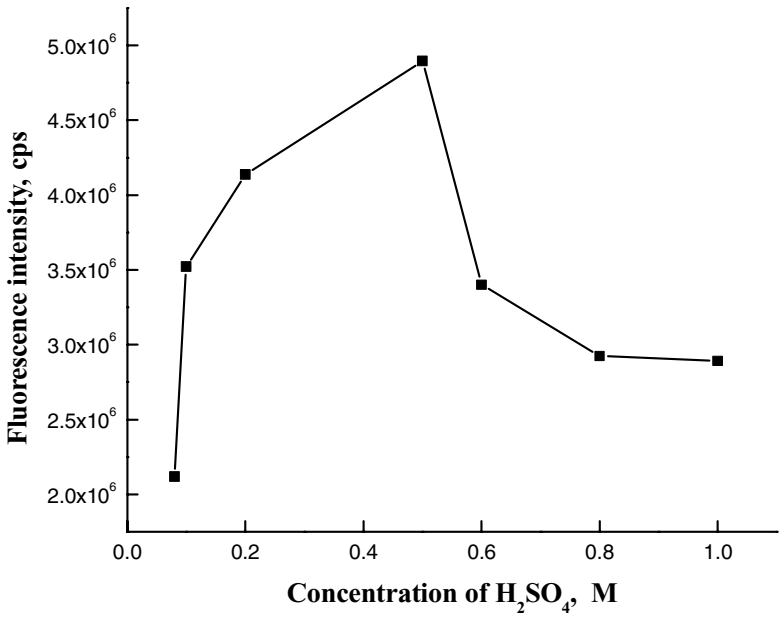

Fig. 4. Effect of H_2SO_4 on the fluorescence intensity of cerium(IV). Conditions: [ascorbic acid]=1×10^{-2} M; [Ce(IV)]=5×10^{-2} M; [CH_3CO_2H-NaOAc] (pH=3.4)=2 M.

Analytical Parameters

Calibration curve for Ce(IV) run under the aforementioned optimum conditions such as [ascorbic acid]=1×10^{-2} M; [Ce(IV)]=5×10^{-2} M; [CH_3CO_2H-NaOAc] (pH=3.4)=2 M; [λ_{ex}]=298 nm was obtained by using a series of 10 standard solutions. The calibration curve was found to be linear in the range of 0.0531 μg/ml to 0.3322 mg/ml. The equation for calibration graph is x=0.00000189101y−0.022503 (R=0.99987), where x is the concentration of Ce(IV) expressed in μg/ml and y is the fluorescence intensity (cps unit). The limit of detection as defined by IUPAC, $C_{LOD}=3\ S_b/m$ (where S_b is the standard deviation of the blank signals and m is the slope of the calibration graph) was found to be 0.0145 (μg/ml. The relative standard deviation (RSD) for five repeated measurements of 0.0531 μg/ml Ce(IV) was 2.75%.

Interference Studies

In order to apply the proposed method to the determination of the concentration of Ce(IV) in the real sample, the effect of some coexisting species was investigated using the solution containing 13.289 (μg/ml Ce(IV) and only one coexisting species. The tolerance concentrations of each species was taken as the largest amount yielding an error less than 5% of the analytical signal of Ce(IV). The results are summarized in Table 1. From the table it is indicated that many diverse cations, especially lanthanides did not interfere with the determination of Ce(IV).

Table 1. Tolerance Limits of Diverse Ions in Presence of 13.29 μg/ml Ce(IV)

Added substances	Tolerance limit (μg/ml)
La^{3+}, Cd^{2+}	650
Pr^{3+}	530
Nd^{3+}, Eu^{3+}, Sm^{3+}	300
Dy^{3+}	700
Gd^{3+}	450
Ca^{2+}, Ba^{2+}	730
Mn^{2+}, Ni^{2+}, Na^{+}	1000
Cu^{2+}	260
Co^{2+}	800
Cl^{-}, NO_3^{-}, CH_3COO^{-}	1000
Fe^{3+}, Zr^{2+}	65
Al^{3+}	250
Tb^{3+}, Y^{3+}, Ho^{3+}	130

Table 2. Analysis of the Synthetic Mixtures

Mixture number	Mixture composition (μg/ml)	Ce(IV) found[b] (μg/ml)	Error (%)
1[a]	Ce(7.20), La(142), Pr(144), Nd(147.10), Sm(153.2), Eu(155.2), Gd(160.4),Tb(52.4), Ho(10.9), Y(38.6)	7.12	1.11
2[a]	Ce(18.5), La(8.20), Pr(2.30), Nd(7.0), Zr(5.20)	18.32	0.97

[a] 1000 ml, 1 g mixture was prepared on the basis of the composition of cerium alloys.
[b] Average of five measurements.

Application of the Method

The method was applied to the determination of trace amounts of cerium as per specifications in synthetic mixtures reported by Masti *et al*. [1]. The results given in Table 2 indicate that the proposed method is suitable and can be successfully applied.

CONCLUSION

From the results obtained it can be easily concluded that ascorbic acid is a very suitable reducing reagent and that the method could be used as an alternative tool for investigation of trace amount of Ce(IV) in alloy because of the non-interference of associated substances with the determination of Ce(IV).

ACKNOWLEDGMENT

The support of this research by Korea Research Foundation Grant (KRF-2004-005-C00009) is gratefully acknowledged.

REFERENCES

1. S. P. Masti, J. Seetharamappa, and M. B. Melwanki (2002). Spectrophotometric determination of cerium(IV) using a phenothiazine derivative. *Anal. Sci.* **18**, 167–169.
2. P. L. Sarma and L. H. Dieter (1966). Spectrophotometric determination of cerium with sulphanilic acid. *Talanta* **13**, 347–356.
3. A. M. Osman, R. Hilhorst, and C. Laane (2000). Chemiluminescent determination of Ce(IV) using *Cypridina luciferin* analog. *Anal. Chim. Acta* **422**, 81–87.
4. N. Jie, J. Yang, and T. Liu (1994). Fluorimetric determination of cerium with paracetamol. *Talanta* **41**, 415–417.
5. R. Yener and A. Aycicek (1998). New fluorometric reagents, sodium pyrophosphate, sodium tri metaphosphate, and sodium tetra metaphosphate, for the determination of Cerium(III). *J. Fluoresc.* **8**, 45–52.

6. J. Yang, X. Cao, C. Sun, X. Wu, and L. Li (2004). Sensitive determination of carbohydrates by fluorimetric method with Ce(IV) and sodium triphosphate. *J. Fluoresc.* **14**, 275–279.
7. I. A. Darwish, A. S. Khedr, H. F. Askal, and R. M. Mahmoud (2005). Simple fluorimetric method for determination of certain antiviral drugs via their oxidation with cerium(IV). *IL Farmaco* **60**, 555–562.
8. G. F. Kirkbright, T. S. West, and C. Woodward (1996). Some spectrofluorimetric applications of the cerium(IV)–cerium(III) system. *Anal. Chim. Acta* **36**, 298–303.
9. B. S. S. Muhammad and R. K. Vijayachander (1963). Oxidation of alcohols by cerium(IV). II. oxidation of methanol by ceric sulfate. *Bull. Chem. Soc. Jpn.* **36**, 949–953
10. S. Lakshmi and R. Renganathan (1996). Kinetics of oxidation of certain pyrimidines by Ce(IV). *Int. J. Chem. Kinet.* **28**, 713–720.
11. H. Y. Han, Z. K. He, and Y. E. Zeng (1999). A direct chemiluminescence method for the determination of nucleic acids using $Ru(phen)_3{}^{2+}$–Ce(IV) system. *Fresenius J. Anal. Chem.* **364**, 782–785