

A NOVEL AND HIGHLY SENSITIVE CATALYTIC METHOD FOR THE DETERMINATION OF ULTRA TRACE AMOUNTS OF CERIUM WITH SPECTROPHOTOMETRIC DETECTION

A.A. Ensafi* and M. Hashem

*College of Chemistry, Isfahan University of Technology, Isfahan, Islamic Republic of Iran
Department of Chemistry, Azad University of Yazd, Yazd, Islamic Republic of Iran*

Abstract

Cerium (IV) has a catalytic effect on the very slow redox reaction between galloxyanine and bromate in acidic media. The reaction was monitored spectrophotometrically at 525 nm by a fixed time method of 4.0 min from initiation of the reaction. The decrease in absorbance at 525 nm is proportional to the Ce (IV) concentration in the range of 0.005-1.000 and 1.00-10.00 $\mu\text{g. ml}^{-1}$. The limit of detection is 2.0 ng. ml^{-1} . The relative standard deviation for ten replicate analyses of 0.100 $\mu\text{g. ml}^{-1}$ is 1.5%. The method is used for the determination of cerium in synthetic and in real samples, with good accuracy. The effect of interfering cations and anions was also studied.

Introduction

The addition of small amounts of the rare earth element cerium to steel significantly modified its properties [1]. Therefore, the accurate determination of cerium at ultra trace levels is important industrially.

Many methods such as spectrophotometric [2-5], fluorimetric [6-8], kinetic fluorimetric [9-10] and ICP-AES [11] have been used for the determination of cerium. But most of these [1-8] suffer drawbacks because of many interfering ions [1-10], or because they are very time-consuming or require the use of expensive instrumentation [11].

A few methods for the determination of cerium based on kinetic procedures have been published [12,13], and these have limited linear dynamic range or low precision. This paper describes a sensitive spectrophotometric procedure for the determination of cerium, based on the catalytic effect of Ce (IV) on the oxidation of galloxyanine (GC) by bromate in sulphuric acid medium. The method possesses distinct advantages over the existing methods with respect to sensitivity, selectivity, simplicity and speed.

Keywords: Catalytic; Cerium; Galloxyanine

Experimental Section

Reagents

All reagent chemicals were of analytical-reagent grade and triply distilled water was used throughout. Galloxyanine solution, 3.56×10^{-4} M, was prepared by dissolving 0.01200 g of the compound (Aldrich) in 50 ml of 10^{-5} M sodium hydroxide solution, and the solution was diluted in a 100-ml volumetric flask with water. Potassium bromate solution, 0.100 M, was prepared by dissolving 16.700 g KBrO_3 (Merck) in water and was diluted to 1.00 L in a volumetric flask. Cerium (IV) solution, $1000 \mu\text{g. ml}^{-1}$, was prepared by dissolving 3.8910 g $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (Merck) in water in a 1.00 L volumetric flask and was diluted to the mark with water. Sulphuric acid solution was prepared by its concentrated sulphuric acid (Merck).

Apparatus

A spectrophotometer (Shimadzu, model 256) was used for recording the absorbance spectra at various wavelengths. A spectrophotometer (Shimadzu, model 120-01) with a 1.0 cm glass cell was used for absorbance measurements at a fixed wavelength (525 nm). A thermostated water bath, (Gallenkamp Griffine) was used to maintain the solution temperature.

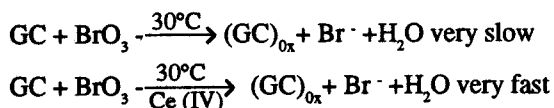
Procedure

All the solutions were equilibrated at 30°C. Into a 10-ml volumetric flask, a known volume of Ce (IV) solution (0.050-10.00 µg) was placed and 1.0 ml of 0.20 M H₂SO₄ solution and 4.0 ml of 0.100 M bromate was added. The solution was diluted to ca. 8 ml with water. Then 1.0 ml of 3.56×10⁻⁴ M GC solution was added, and the solution was diluted to the mark with water and mixed well. A portion of the solution was transferred into a cell and the decrease in absorbance was measured during the 0.5-4.0 min from initiation of the reaction. The time was measured from when the last drop of GC was added. The decrease in absorbance for a range of cerium concentrations was plotted as a function of cerium concentration to prepare a calibration graph.

Large amounts of Ce (IV) can be determined by the proposed method with larger amounts of GC and small amounts of bromate concentration.

Results and Discussion

The reaction of GC with bromate is very slow and can not proceed at room temperature [14]. In the presence of trace amounts of Ce (IV) in acidic media, fast reaction occurred. The rate of reaction monitored spectrophotometrically is related to Ce (IV) concentration (Fig. 1). This catalytic reaction can occur in two steps:



In this work, Ce (IV) was measured by using a fixed time method by measuring the decrease in absorbance of gallocyanine, ΔA, for various amounts of Ce (IV).

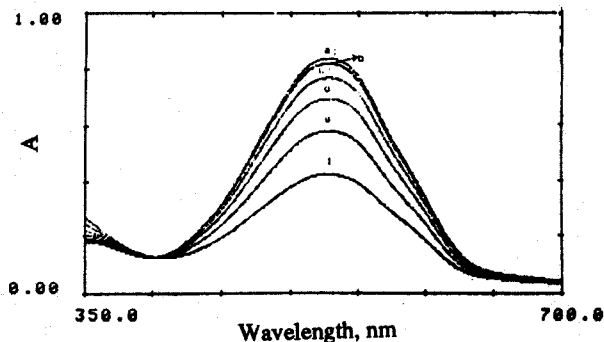


Figure1. Variation of absorbance with time for the system; (conditions: H₂SO₄, 0.020 M; BrO₃⁻, 0.040 M; GC, 3.5×10⁻⁵ M; Ce (IV), 0.100 µg. ml⁻¹, temperature, 30 °C); a) 30, b) 60, c) 120, d) 240, e) 300, and f) 360 sec from initiation of the reaction.

Effect of Variables

Figure 2 shows the effect of sulphuric acid concentration on the reaction rate. The rate of catalytic reaction increased up to 0.020 M sulphuric acid concentration, whereas greater amounts of the reagent decreased the reaction rate. This effect is due to the fact that the protonation of GC occurred at high acidic media, and thus decreased the activity of GC. From the results, 0.020 M H₂SO₄ concentration was selected for the study.

The effect of bromate concentration on the rate of uncatalyzed and catalyzed reaction was studied for the range of 0.0050-0.060 M bromate concentration (Fig. 3). The results show that in 0.040 M bromate concentration the catalyzed reaction was increased. Thus 0.050 M bromate concentration was selected.

Figure 4 shows the effect of GC concentration on the catalyzed and uncatalyzed reaction. The results show that the sensitivity increased when GC concentration was increased from (0.119-3.56) ×10⁻⁵ M, whereas higher concentrations of the reagent caused a decrease in the reaction rate. This effect may be due to the change of mechanism of the reaction or deviation from Beer's law. From the results, 3.56 ×10⁻⁵ M GC concentration was selected.

The effect of temperature on the catalyzed and uncatalyzed reaction was studied for the range of 5-60°C with optimum reagents concentration (Fig. 5). The results show that by increasing the temperature to 40°C, the change in absorbance was increased, while at higher temperatures it decreased. This effect is due to the fact that at higher temperatures, the catalyzed reaction is so fast that

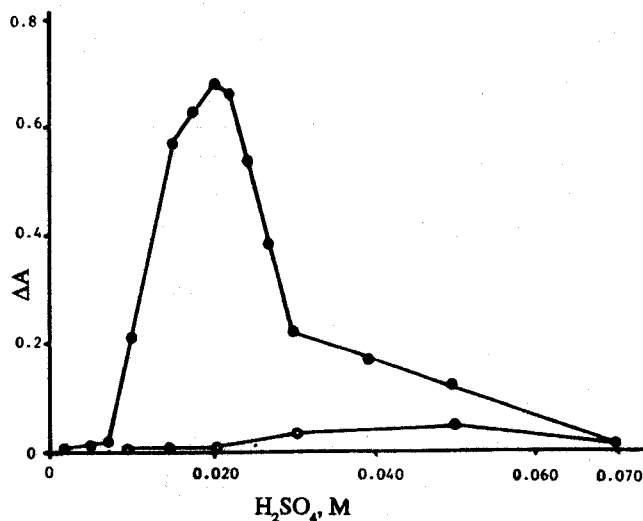


Figure2. Effect of sulphuric acid concentration on the rate of catalyzed (●) and uncatalyzed (○) reaction; (conditions: BrO₃⁻, 0.050 M; GC, 5.94×10⁻⁵ M; Ce (IV), 0.100 µg. ml⁻¹, temperature, 30°C; and measuring time of 4.0 min)

it is completed in the first 0.5 min from initiation and consequently the change in absorbance cannot be measured. Thus for simplicity in routine work, a temperature of 30°C was selected.

A change in ionic strength of the solution had no considerable effect on the rate of reaction up to 0.7 M.

A fixed time of 0.5-4.0 min from initiation of the reaction was chosen, because this provided a good compromise between sensitivity and short analysis time.

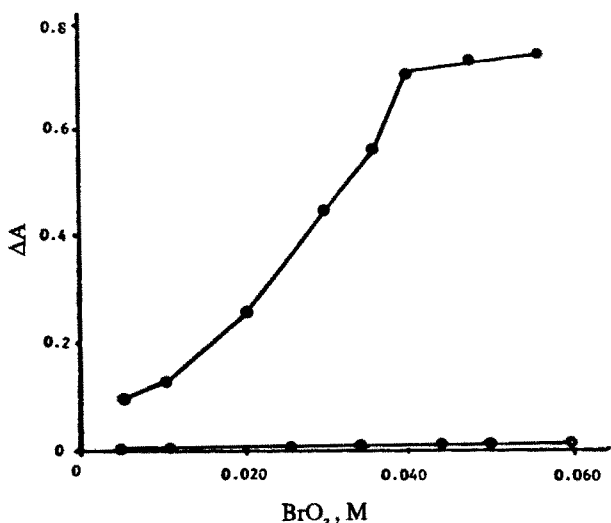


Figure 3. Effect of bromate concentration on the catalyzed (●) and uncatalyzed (○) reaction; (conditions: H₂SO₄, 0.020 M; GC, 5.94×10⁻⁵ M; Ce (IV), 0.100 μg.ml⁻¹; temperature of 30°C; and measuring time of 4.0 min)

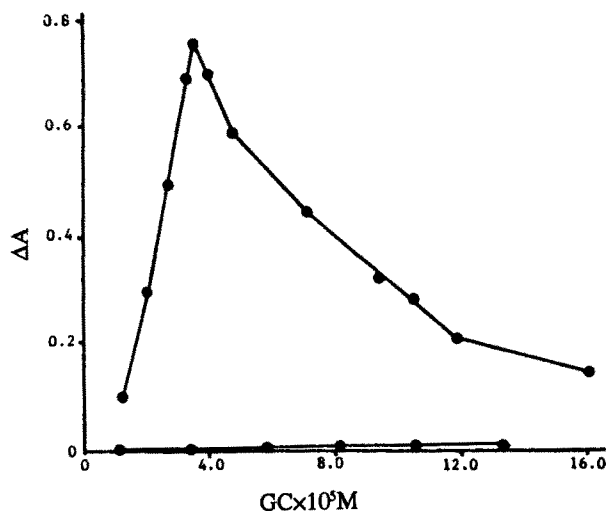


Figure 4. Effect of GC concentration on the rate of catalyzed (●) and uncatalyzed (○) reaction, (conditions: H₂SO₄, 0.020 M; bromate, 0.040 M; Ce (IV), 0.100 μg. ml⁻¹; temperature of 30°C; and measuring time of 4.0 min)

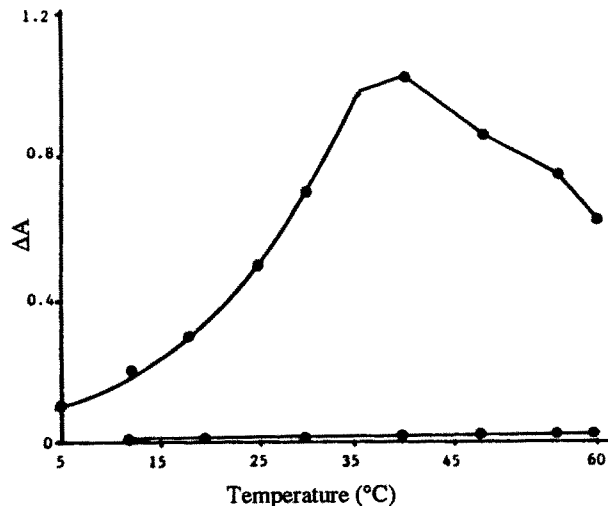


Figure 5. Effect of temperature on the rate of catalyzed (●) and uncatalyzed (○) reaction; (conditions: H₂SO₄, 0.020 M; bromate, 0.040 M; GC, 3.56×10⁻⁵ M; and measuring time of 4.0 min)

Table 1. Accuracy and precision of the method

Ce (IV) present (μg. ml ⁻¹)	Ce (IV) found (μg. ml ⁻¹)	RSD% (n=10)	Relative Error%
0.050	0.050	1.9	0.0
0.100	0.103	1.4	3.0
0.200	0.203	1.4	1.5
0.500	0.496	1.3	-1.0
1.000	1.005	1.0	0.0

Table 2. Tolerance limit of diverse ions for the determination of 0.100 μg. ml⁻¹ of Ce (IV)

Species	Tolerance limit (μg. ml ⁻¹)
Cu (II), Mo (VI), Pb (II), Bi (III), Tl (I), U (VI), Ca (II), Mg (II), Ba (II), Zr (IV), Na ⁺ , K ⁺ , Mn (II), Co (II), Ni (II), W (VI), Sr (II), Rh (III), Zn (II), Th (IV), I, NO ₃ ⁻ , Cl ⁻ , ClO ₃ ⁻ , ClO ₄ ⁻ , NH ₄ ⁺ , C ₂ O ₄ ²⁻ , CO ₃ ²⁻ , SO ₄ ²⁻ , Tartarate, Citrate, Oxalate, EDTA, Hg (I), Cr (III), SO ₃ ²⁻ , Hg (II)	1000*
Fe (III), Se (IV), Cd (II), V(V), Al (III)	500
Fe (III), Cd (II), V (V)	100
	250**

* Maximum amount of the ions tested

** In the presence of 3% EDTA solution

Table 3. Analysis of synthetic mixture and rare-earth ore sample

Sample No.	Composition of solution (%)	% Ce present	% Ce found (n=5)
1	Ce (0.720), Nd (14.71) Eu (25.5), Ho (3.60) Y (3.86), La (14), Ca (14.4), Mg (6.71), Zn (16.50)	0.720	0.724±0.015
2	As in 1+ Pb (10) Mn (10), Co (10), Ni (10)	0.533	0.537±0.016
3	Ore (I)	0.038	0.038±0.002
4	Ore (II)	0.128	0.125±0.009

Calibration Graph

Under the optimum conditions described above, a linear calibration graph was obtained for the Ce (IV) concentration range of 0.005 -1.000 $\mu\text{g. ml}^{-1}$ with a regression equation of $\Delta A = 5.51 \times 10^{-3} + 0.741C$ ($r=0.9998$) and with 5.94×10^{-4} M GC concentration and 0.0010 M bromate. For the Ce (IV) concentration range of 1.00-10.00 $\mu\text{g. ml}^{-1}$, a regression equation of $\Delta A = 0.172 + 6.10C$ ($r=0.9999$) was obtained, where ΔA is the change in absorbance for 0.5 - 4.0 min from initiation of the reaction and C is the $\mu\text{g. ml}^{-1}$ of Ce (IV), respectively.

The accuracy and precision of the method is given in Table 1. The limit of detection ($3 \times \text{noise}$) was 2 ng. ml^{-1} of Ce (IV).

Effect of Foreign Ions

The effect of more than 40 foreign ions on the catalytic determination of 0.100 $\mu\text{g. ml}^{-1}$ Ce (IV) was examined. The results are summarized in Table 2. The tolerance limit is that giving not more than $\pm 3\%$ error.

Most common ions do not interfere with the determination of Ce (IV). The tolerance limit of Fe (III), Cd (II), and Hg (II) can be increased to 250 $\mu\text{g. ml}^{-1}$ in the presence of 3% EDTA solution.

Determination of Cerium in Synthetic Ore Sample

The weighed ore sample was dissolved in 20 ml of HNO_3 (6 M) and heated gently on a hot plate. Then H_2O_2 was added dropwise until complete dissolution occurred. The solution was cooled and 8 ml of sulphuric acid (18 M) was added. The mixture was heated until white fumes were evolved. The solution was first cooled, 20 ml of water was added, and then it was warmed until the salts were

completely dissolved. The solution was cooled to room temperature and transferred to a 250-ml volumetric flask and diluted to the mark with water. A suitable aliquot of the solution was then analyzed for Ce (IV) by the proposed method. The cerium contents were also determined by atomic absorption spectrometry. The results are presented in Table 3. In addition, the method was tested on a synthetic solution. As can be seen, the results were very satisfactory.

References

1. Wandby, P.F. *Inter. Metals Rev.*, **23**, 74, (1978).
2. Martine, A.C., Hornillos, R.I., Cabeza, A.Q. and Fernandez, J.L. P. *Analyst*, **108**, 1285, (1983).
3. Rahim, S.A., Amin, D. and Bashir, W.A. *Microchem. J.*, **30**, 53, (1983).
4. Zhou, Z. and Chen, Y. *Fenxi Huaxue*, **13**, 289, (1985), (*Chem. Abstr.*, **104**, 14177r, (1986)).
5. Jyothin, A. and Rao, G.N. *Talanta*, **37**, 431, (1990).
6. Cukor, P. and Weberling, R.P. *Anal. Chim. Acta*, **41**, 404, (1968).
7. Pal, B.K., Toneguzzo, F. and Corsini, A. *Ibid.*, **88**, 353, (1977).
8. Jie, N., Yang, J. and Liu, T. *Talanta*, **41**, 415, (1994).
9. Salinas, F., Genestar, C. and Grases, F. *Microchem. J.*, **27**, 32, (1982).
10. Navas, A., Sanchez Rojas, F. and Sanchez, F.G. *Mikrochim. Acta*, **I**, 175, (1982).
11. Grossman, A.M., Ciba, J., Jurczyk, J. and Spiewok, W. *Talanta*, **37**, 815, (1990).
12. Weisz, H. and Pantel, S. *Anal. Chim. Acta*, **116**, 421, (1980).
13. Yan, Y., Ji, Z. and Huang, J. *Fenxi Huaxue*, **21**, 1, (1993), (*Chem. Abstr.*, **118**, 138822, (1993)).
14. Ensafi, A.A. and Shamss-e-Sollaari, E. *Talanta*, **41**, 1651, (1994).