

Sensitive Kinetic Spectrophotometric method for Trace determination of Cerium (IV) Based on decolorization of Nile blue by potassium Periodate

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Abstract: A simple and sensitive kinetic spectrophotometric method for the determination of trace amounts of cerium (IV), based on the catalytic effect of Ce (IV) on the oxidation of Nile blue (NB) by potassium periodate is described. The reaction rate was monitored spectrophotometrically by measuring the decrease in absorbance of NB at 636 nm. The detection limit of the method was $0.15 \mu\text{g ml}^{-1}$ and the linear range was between $0.3\text{--}50 \mu\text{g ml}^{-1}$. The effects of acidity, concentration of reactants, reaction time and temperature, and external ions were also discussed. The optimum reaction conditions were fixed and some kinetic parameters determined. The relative standard deviation for the determination of cerium (IV) at the concentration of $10 \mu\text{g ml}^{-1}$ was calculated to be 0.99 % ($n = 11$). The method has been successfully applied to the determination of trace amounts of cerium (IV) in sea, tap, and hat spring water samples. The results are in good agreement with the certified values with the relative standard deviations (RSD) of 0.22–1.47%.

Key words: Cerium (IV), Kinetic spectrophotometry, Nile blue, Potassium periodate, Water samples

Introduction and Experimental

Cerium is an iron-gray lustrous metal. It is malleable, and oxidizes very readily at room temperature, especially in moist air europium cerium is the most reactive of the rare-earth metals. It decomposes slowly in cold water and rapidly in hot water¹.

Cerium is not expected to exist in elemental form in the environment since it is a very reactive metal². Cerium compounds are not expected to volatilize and will exist in the particulate form if released into the air. Cerium will gradually accumulate in soils and water soils and this will eventually lead to increasing concentrations in humans, animals and soil particles. With water animals cerium causes damage to cell membranes, which has several negative influences on reproduction and on the functions of the nervous system¹.

Many methods for determination of cerium are used. These methods are spectrophotometry, spectrofluorimetry, isotope dilution and etc³⁻⁶. Some of these methods needs too time consuming or require complicated, expensive equipment and lack of sensitivity. Kinetic methods of chemical analysis have some advantages including high sensitivity, extremely low detection limits, good selectivity, rapid analysis and inexpensive instrumentation such as a spectrophotometer or a spectrofluorimeter. These advantages are attractive to researchers in the field of the analytical chemistry of

the rare metals. Kinetic methods have been widely applied to the determination of many trace-level elements. In this study the catalytic effect of Ce (IV) upon the oxidation of Nile blue (NB) by potassium periodates was investigated. A catalytic kinetic spectrophotometric method for the determination of Ce (IV) was developed. The method was applied successfully to the determination of Ce (IV) in water samples.

1-Reagents and solutions

Cerium stock standard solution $1000 \mu\text{g ml}^{-1}$, prepared by dissolving 0.3913 gr of Cerium ammonium nitrate $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, in 100 ml water. Used solutions were subsequently prepared before use by appropriate dilution of the stock solution. Nile blue concentration, $2 \times 10^{-4} \text{ mol L}^{-1}$, was prepared by dissolving 0.0083 gr Nile blue solution in 100 ml water. Potassium periodate 0.03 mol L^{-1} , solution prepared by dissolving 0.6900 gr Potassium periodate, in 100 ml water. Buffer solution was made by addition sodium acetate 0.1 mol L^{-1} solution to solution trichloroacetic acid 0.1 mol L^{-1} and adjusted to obtain the desired pH by appropriate volume of its. Ionic buffer 3.0 mol L^{-1} solutions were made by dissolving appropriate sodium nitrate in doubly deionized water. All chemicals were of analytical-reagent grade (Merck) and doubly deionized water was used throughout.

2- Apparatus

Absorption spectra were recorded with a PERKIN ELMER UV/Vis Spectrometer Lambda 2 with a 1-cm glass cell. A model JENWAY 6305 UV/Vis Spectrophotometer with a 1-cm glass cell was used for absorbance measurements at a fixed wavelength. A Jenway 3510 pH – meter which calibrated against two standard buffer solutions at pH 4.0 and 10.0 was used to measure the pH of the solutions. A thermostat water bath (FATER RIZ PARDAZ) was used to keep the reaction to obtain the desired temperature. A stopwatch was used for recording the reaction time.

3- Recommended procedure

The redox reaction was monitored spectrophotometrically by measuring the change of absorbance of the reaction mixture at λ_{\max} Nile blue (636 nm). The fixed time method (3.0 min from initiation of the reaction) was used for obtained signal. A sample solution was prepared by pouring 1 ml of buffer solution pH = 1.0 into a 1 cm glass cell, after addition of 0.5 ml of periodate 3.0×10^{-2} M, and 0.5 ml of 2.0×10^{-4} M NB, respectively, then the mixture was diluted with suitable amount of water. The solution was transferred to the spectrophotometer and finally added 0.3 ml of cerium with various concentrations. Total volume of solution in cell was 3 ml. Immediate after addition of different amounts of cerium the initial absorbance (A_i) at λ_{\max} was recorded, after 3 min final absorbance (A_f) was measured. The net values (signal) obtained from standard cerium solutions ($\Delta A = A_i - A_f$). A calibration graph was plotted with absorbance change at a fixed time versus cerium (IV) concentration.

Results and Discussion

The absorption spectra of the catalytic and noncatalytic systems, was measured against water over the range of 400–800 nm, has been showed in Fig. 1. The results showed an absorbance maximum at 636 nm, and the oxidation of NB by periodate in acidic buffer was very slow. In the presence of small amounts of cerium, the oxidation rate of NB increased. Cerium catalyzes the decolorizing oxidation. The absorbance after three minutes was proportional to the cerium concentration, in a certain range.

As can be seen in Fig. 2, the variation of absorbance has a large value within a range of uppermost of reaction to 180 second at different concentration of Ce (IV). The 3 minute of the initiation of reaction started was selected of signal measurement.

1-Effect of acidity

The experimental variables were optimized to apply the univariate method. pH depended to the system was studied over the range of 0.5-5.0 in the presence of 3.3×10^{-5} M NB, 5×10^{-3} M IO_4^- , and $10.0 \mu\text{g ml}^{-1}$ Ce (IV) at 25°C. The experimental results In Fig. 3 showed that the maximum different between sample and blank signal

was at pH=1. Therefore pH=1 was selected for further study.

2- Effects of reagent concentration

The effect of periodate on the reaction rate was studied in the range 2×10^{-3} – 7×10^{-3} M in the presence of 3.33×10^{-5} M NB, and $50.0 \mu\text{g ml}^{-1}$ Ce (IV), pH=1 at 25°C. The absorbance difference (ΔA) reached a maximum at 5×10^{-3} M of periodate (Fig. 4). Hence, 5×10^{-3} ml of periodate solution was chosen for the remaining study. In contrast, there was a remarkable increase of the absorbance difference ΔA with an increase in NB in the presence of $50.0 \mu\text{g ml}^{-1}$ Ce (IV). As it shows in Fig. 5 the sensitivity of the reaction was improved with increasing NB concentration until 3.5×10^{-5} M and after that remain constant therefore 3.5×10^{-5} M was chosen.

3- Effects of reaction temperature

The influence of temperature on the decolorizing reaction was examined over a range of 5–50°C when the concentration of Ce(IV) was $10.0 \mu\text{g ml}^{-1}$. The experimental results in Fig. 6 showed an approximately linear relationship between increase ΔA and increase temperature. But for simplisity subsequent determinations were carried out at room temperature 25°C.

4-Calibration graph, precision and detection limit

The calibration graph was obtained at a fixed time under optimum conditions. A linear calibration graph was obtained over a concentration range for cerium (IV) of 0.3 – $50 \mu\text{g ml}^{-1}$ with a correlation coefficient of 0.9998 and the regression equation was: $\Delta A = 0.007 C_{\text{Ce(IV)}} + 0.1$, where ΔA is the difference in absorbance between 3 min of the initiation of reaction and $C_{\text{Ce(IV)}}$ is the concentration of Ce (IV) $\mu\text{g ml}^{-1}$. The relative standard deviation of eleven replicate measurements were 1.47 and 0.22% for a solution of 0.5 and $20 \mu\text{g ml}^{-1}$ Ce(IV) respectively. The detection limit ($\text{DL} = 3S_b/m$) for Ce was $0.15 \mu\text{g ml}^{-1}$.

5-Influence of external substances

Interference tests for foreign ions during the determination of $1 \mu\text{g ml}^{-1}$ Ce (IV) were carried out. The proposed method was performed in the presence of several ions. A relative error of $\pm 5\%$ was considered permissible. The presence of the following ions caused no interference, at least up to the specified amounts (Wion/W):

Cr^{3+} , Ba^{2+} , Ni^{2+} , NO_3^- , NO_2^- , Mg^{2+} , CrO_4^{2-} , Mn^{2+} , $\text{Cr}_2\text{O}_7^{2-}$, Ca^{2+} , Fe^{3+} , Ag^+ , Zn^{2+} (>700 , the maximum tolerated concentration of these ions was not tested), Al^{3+} , Pb^{2+} , MnO_4^- , SCN^- (500) and CN^- , Cd^{2+} (400).

6- Analytical application of the proposed method

In order to validate the analytical capability, i.e. to establish the reliability and applicability of the developed method, it was applied to the determination of Ce (IV) in sea, tap and hat spring water samples. The results shown in Table 1 indicate that the Ce (IV) recoveries from the

samples are quantitative. Thus, cerium can be determined in the specified concentration range in real samples.

A simple accurate kinetic spectrophotometric determination of traces of Cerium (IV) based on the catalytic effect of Cerium (IV) on the oxidation of NB by periodate was studied. The proposed method was applied to the determination of trace Cerium in sea, tap, hat spring water samples. The results are in good agreement with certified values. This is a suitable method for simple and accurate determination of Ce (IV) in a variety of water samples with satisfactory results.

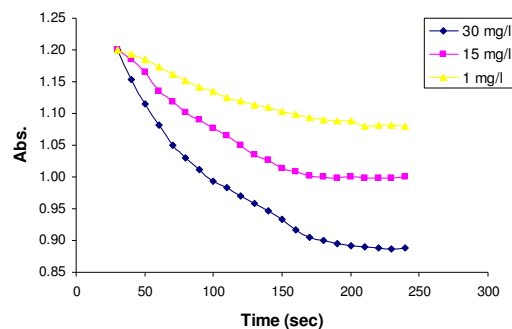


Fig. 2. Variation of absorbance with different concentration)

Table 1
Application of the proposed method for the determination of cerium (IV) in water samples^a

Samples	Cerium(IV) Added (mg/L)	Cerium(IV) Found (mg/L)	Recovery (%)
Sea \ Cerium(IV) added 0.3	0.3	0.304	101.33
Tap \ Cerium(IV) added 0.3	0.3	0.299	99.66
Hat spring \ Cerium(IV) added 0.3	0.3	0.299	99.66

^a Every test were done 3 times

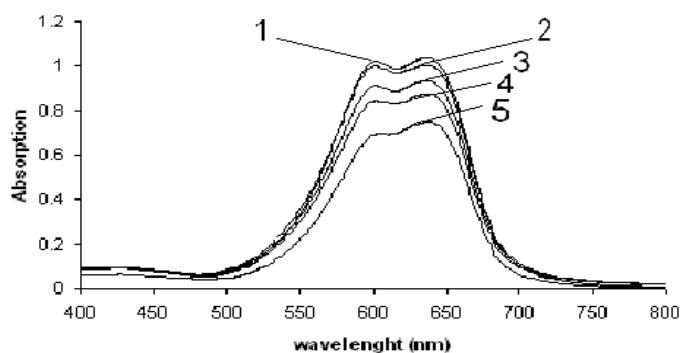


Fig. 1 Absorption spectra: 3.33×10^{-5} M NB; pH 1; temperature 25°C.
1. NB; 2. NB+ IO_4^- ; 3. NB+ IO_4^- + $0.3(\mu\text{g}.\text{ml}^{-1})\text{Ce(IV)}$;
4. NB+ IO_4^- + $0.7(\mu\text{g}.\text{ml}^{-1})\text{Ce(IV)}$; 5. NB+ IO_4^- + $30(\mu\text{g}.\text{ml}^{-1})\text{Ce(IV)}$

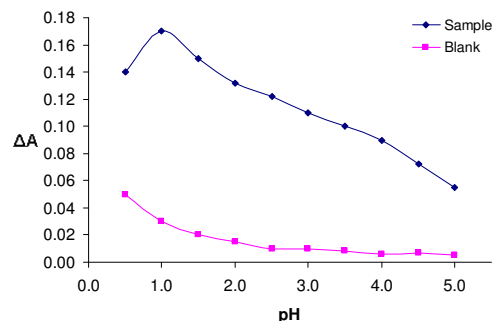


Fig. 3. Influence of pH

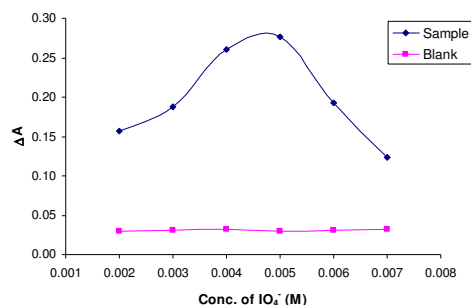


Fig. 4. Effect of concentration of preiodate

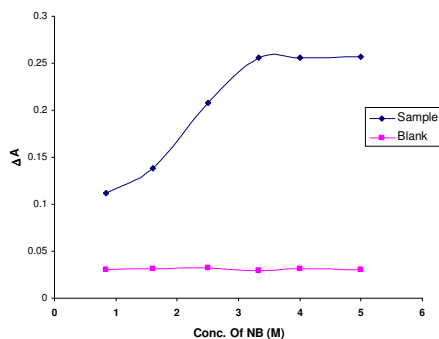


Fig. 5. Effect of nile blue concentration

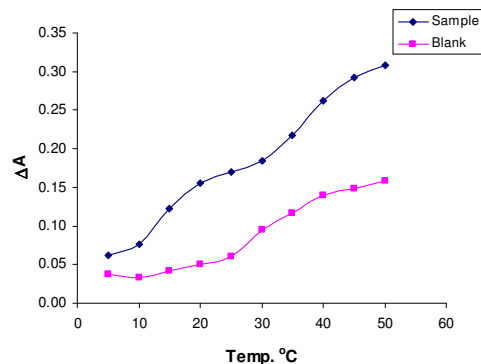


Fig. 6. Effect of Temperature on reaction rate

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