

Spectrofluorometric Determination of Hydrogen Peroxide

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A spectrofluorometric method for microdetermination of H₂O₂ has been developed. The method is based on the oxidation of hydrogen peroxide with ceric ion in acid solution and measurement of the fluorescence during titration of the Ce(III) ions produced. The fluorescent species have excitation and emission maxima at 260 and 360 nm, respectively. The detection limit of measurement by this method was 0.1 ppm hydrogen peroxide.

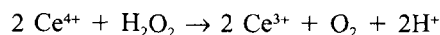
KEY WORDS: Hydrogen peroxide; ceric ion; spectrofluorometric titration.

INTRODUCTION

Hydrogen peroxide is an important chemical in environmental and biological studies and it is also used as a chemical in many industries, such as epoxidation, hydroxylation, oxidation, and reduction. Therefore a rapid and simple method for its microlevel determination is needed. Determination of hydrogen peroxide is usually based on the production of colored peroxy compounds or on its oxidizing and reducing properties. For the sensitive determination of hydrogen peroxide chemiluminescence [1,2], spectrophotometric [3–6], and spectrofluorimetric [7–10], continuous-flow analysis [11], flow injection [12], and kinetic methods [13] have also been reported.

In the present study a sensitive and simple spectrofluorometric method for the determination of hydrogen peroxide was developed. This method is based on the oxidation of hydrogen peroxide with ceric ion in acid solution and determination of Ce(III) ions produced by

a fluorimetric method. The reaction between H₂O₂ and Ce(IV) ions is as follows:



Ce(IV) is nonfluorescent and a strong oxidizing agent. Thus determination of hydrogen peroxide is possible by measurement of the fluorescence of the Ce(III) produced. The fluorescent species have excitation and emission maxima at 260 and 360 nm, respectively.

EXPERIMENTAL

Apparatus

All fluorescence measurements were made with a Perkin Elmer LS 50 luminescence spectrometer and all the spectrophotometric measurements were made with a Philips-3700 spectrophotometer.

Reagents

All chemicals were of analytical reagent grade. Aqueous stock solutions were prepared using double-distilled (over KMnO₄) water as follows.

Ce(IV) Solution (0.01 mol dm⁻³). For this solution 4.043 g of AnalaR (Merck 2274) ceric sulfate was dissolved in 50 ml of water containing 10 ml of concen-

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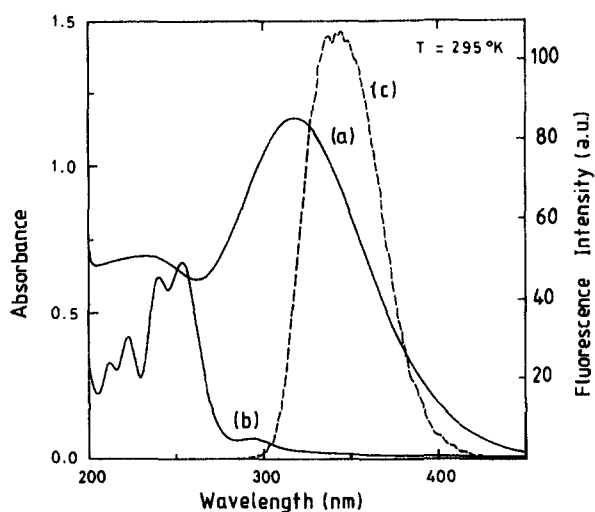


Fig. 1. (a) Absorption spectrum of 5 μmol of Ce(IV) in 10 ml. (b) Absorption spectrum of 5 μmol of Ce(III) in 10 ml. (c) Emission spectrum of a 1×10^{-4} mol dm^{-3} Ce(III) solution.

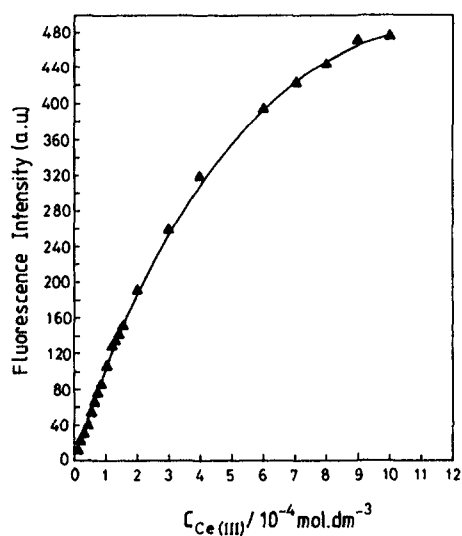


Fig. 2. Change of fluorescence with the concentration of Ce(III).

trated sulfuric acid. Then this solution was diluted to 500 ml with water. This was standardized by the iodometric method. A calculated quantity of this solution was diluted to 1 L for the preparation of the 0.01 mol dm^{-3} Ce(IV) solution.

Ce(III) Solution (0.001 mol dm^{-3}). One hundred milliliters of 0.01 mol dm^{-3} Ce(IV) was reduced with hydrogen peroxide in acidic medium and the unreacted hydrogen peroxide was boiled away. This solution was diluted to 1 L with water.

Hydrogen Peroxide (0.001 mol dm^{-3}). Hydrogen peroxide solution was prepared daily and standardized with permanganate solution and used after the desired dilution.

Recommended Analytical Procedure

Three and one-half milliliter of 1.2×10^{-4} mol dm^{-3} Ce(IV), pH 1–2, was transferred into a Cuvars cell placed in the spectrofluorometer cell compartment and it was immediately titrated with $10 \mu\text{l}$ of a 10^{-3} -mol dm^{-3} H_2O_2 solution. Changes in the fluorescence intensity of the solution were measured at an excitation of 260 nm and an emission of 360 nm. The titration end point was obtained from the plot.

RESULTS AND DISCUSSION

Absorption and Fluorescence Spectra

The absorption spectrum of the ceric sulfate solution in 1.0 mol dm^{-3} sulfuric acid is shown in Fig. 1a. It can be seen that $5 \mu\text{mol}$ of ceric sulfate in 10 ml of solution gives a maximum absorbance at 320 nm against water. An excess amount of hydrogen peroxide was added to $5 \mu\text{mol}$ of Ce(IV) solution in 1.0 mol dm^{-3} sulfuric acid and the mixture was diluted to 10 ml with water. After the mixture was shaken for a few minutes at room temperature the absorption spectra of the solution were plotted against a water blank (Fig. 1b).

The emission spectrum of Ce(III) is shown in Fig. 1c was measured by fixing the excitation wavelength at 260 nm. It can be seen that the fluorescent species of the 1×10^{-4} mol dm^{-3} Ce(III) solution has an emission maximum at 360 nm. No fluorescence was observed from the solution containing Ce(IV) only.

Change in Fluorescence with the Concentration of Ce(III)

The fluorescence of 1×10^{-5} – 1×10^{-3} mol dm^{-3} Ce(III) solutions was measured at an excitation of 260 nm and an emission of 360 nm. A calibration graph for Ce(III) was constructed. Good linearity was obtained for the concentration range 1×10^{-5} – 2×10^{-4} mol dm^{-3} Ce(III). The curve obtained is shown in Fig. 2.

Effect of the Addition of Ce(IV) to Ce(III) Solutions

Two milliliters of a 1.2×10^{-3} mol dm^{-3} Ce(III) solution was added to each of 15 volumetric 10-ml

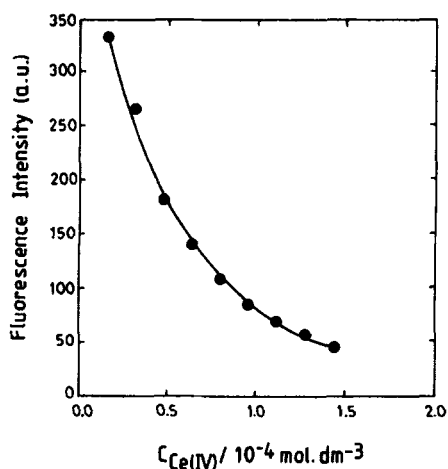


Fig. 3. Effect of Ce(IV) ions on Ce(III) solution: Ce(III) concentration constant ($2.4 \times 10^{-4} \text{ mol dm}^{-3}$); Ce(IV) concentration variable.

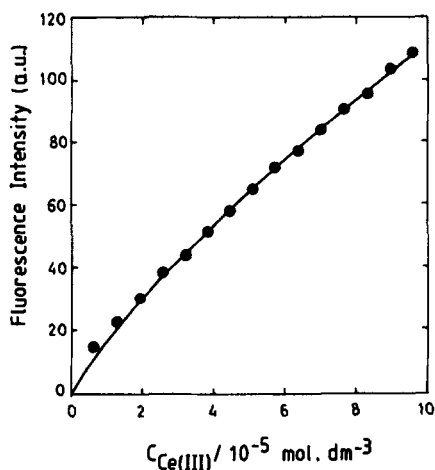


Fig. 4. Effect of Ce(IV) on Ce(III) solution: Ce(IV) concentration constant ($8 \times 10^{-5} \text{ mol dm}^{-3}$); Ce(III) concentration variable.

flasks. After the addition of Ce(IV) solution the mixture was diluted to 10 ml with water. If it was necessary, before dilution the pH of the solution was brought to 1.0 with concentrated H_2SO_4 . Final Ce(IV) concentrations of the solutions were maintained at 0.16, 0.32, 0.48, 0.64, 0.80, 0.96, 1.12, 1.28, and $1.44 \times 10^{-4} \text{ mol dm}^{-3}$ by the addition of sufficient amounts of Ce(IV) solution. The intensity of fluorescence of the solutions was measured at 260/360 nm. The graph of fluorescence intensity versus Ce(IV) concentration is an exponential curve (Fig. 3). Figure 3 shows that Ce(IV) has a strong quenching action on Ce(III) ion fluorescence.

The experiments were repeated with a constant concentration of Ce(IV) ($8 \times 10^{-5} \text{ mol dm}^{-3}$) and a variable

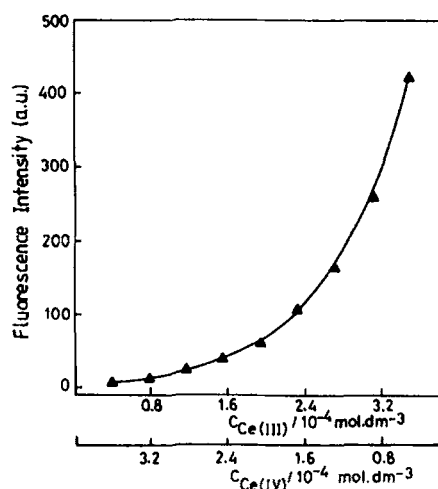


Fig. 5. Effect of Ce(IV) ions on Ce(III) solution: Ce(III) and Ce(IV) concentrations variable.

Ce(III) concentration, in the range of 0.64×10^{-5} to $9.6 \times 10^{-5} \text{ mol dm}^{-3}$. The fluorescence of the solutions was measured at 260/360 nm (Fig. 4). Figure 4 shows that the change in fluorescence intensity versus Ce(III) concentration is linear.

The experiments were repeated with a variable Ce(III) concentration in the range of 4×10^{-5} – $4 \times 10^{-4} \text{ mol dm}^{-3}$ and a variable Ce(IV) concentration in the range of 4×10^{-4} – $4 \times 10^{-5} \text{ mol dm}^{-3}$. The fluorescence of the solutions were measured at 260/360 nm (Fig. 5). Figure 5 shows that fluorescence intensity versus Ce(III) concentration is an exponential curve.

Determination of Hydrogen Peroxide

Hydrogen peroxide was determined according to the recommended analytical procedure by the titration technique. Three sample titration curves are shown in Fig. 6. The standard deviation obtained in the replicated analysis of solutions containing hydrogen peroxide (0.1 ppm) was 3.5%.

Hydrogen peroxide could also be determined by the spectrofluorometric method. Therefore, between 0.2 and 1.4 ml of standard hydrogen peroxide solution ($1.17 \times 10^{-3} \text{ mol dm}^{-3}$) was added to 0.5 ml of Ce(IV) solution ($1 \times 10^{-2} \text{ mol dm}^{-3}$) in a 10-ml volumetric flask and solutions were diluted to volume with water. The fluorescence intensity of the final solutions was measured at 260/360 nm. The change in fluorescence intensity against concentration of hydrogen peroxide was exponential, due to the energy transfer from Ce(III) to Ce(IV) (Fig. 7). But the graph obtained between the common

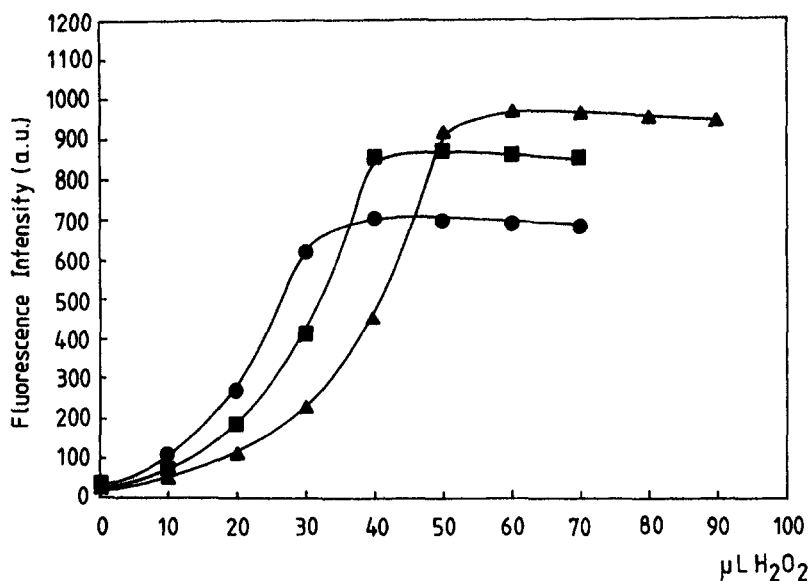


Fig. 6. Spectrofluorometric titration of H_2O_2 ($8.3 \times 10^{-3} \text{ mol dm}^{-3}$). (●) $C_{\text{Ce(IV)}} = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$; concn of $\text{H}_2\text{O}_2 = 32.5 \mu\text{l}$. (■) $C_{\text{Ce(IV)}} = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$; concn of $\text{H}_2\text{O}_2 = 40.0 \mu\text{l}$. (▲) $C_{\text{Ce(IV)}} = 2.4 \times 10^{-4} \text{ mol dm}^{-3}$; concn of $\text{H}_2\text{O}_2 = 51.0 \mu\text{l}$.

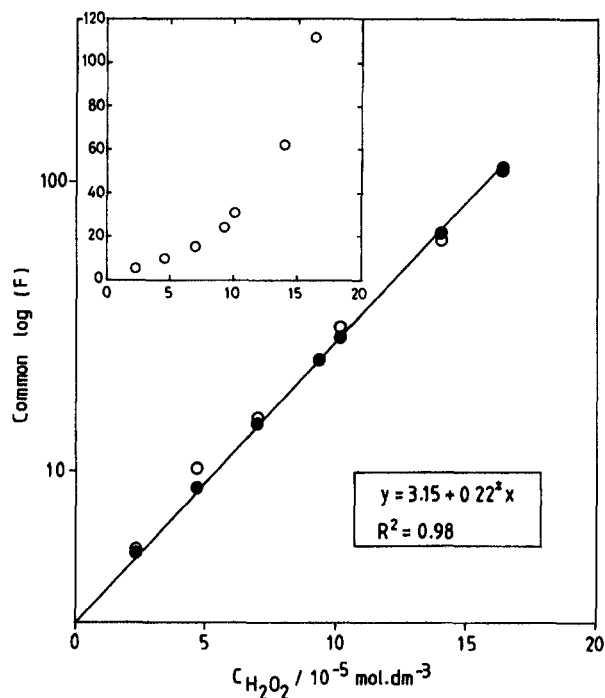


Fig. 7. Change in fluorescence intensity with the concentration of hydrogen peroxide: Ce(IV) concentration constant ($5 \times 10^{-4} \text{ mol dm}^{-3}$).

log of the fluorescence value and the concentration of hydrogen peroxide was linear. Thus hydrogen peroxide

could be determined by the use of this graph as the calibration curve.

CONCLUSION

- The pectrofluorimetric method has the basic advantage of considerably greater sensitivity than absorption spectrophotometry.
- No fluorescence was observed from the solution containing Ce(IV) only.
- The solution contain Ce(III) showed an emission band centered at 360 nm.
- The reaction between hydrogen peroxide and ceric ion proceeds at a sufficient rate in acidic medium and at room temperature.
- For the elimination of some metal ions such as copper(I), lead, tin(II), and thallium(I), H_2SO_4 is useful for acidification [14].
- Since hydrogen peroxide has a high oxidation potential, many of the reducing ions are not present and they do not interfere with the analysis of hydrogen peroxide.
- But substances having a standard potential between those of hydrogen peroxide and Ce(IV) interfere with the analysis.
- In-addition, the proposed method is simple and rapid. It has been calculated that the minimum determination limit of the method is 0.1 ppm hydrogen peroxide.

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